Planar contraction/expansion multiple-stream flow instability and mixing of viscoelastic fluids in microchannels

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**PLANAR CONTRACTION/EXPANSION
MULTIPLE-STREAM FLOW INSTABILITY
AND MIXING OF VISCOELASTIC FLUIDS
IN MICROCHANNELS**

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SUMMARY

Small lengthscale inherent to microfluidic devices have key implications on the flow behavior of fluids containing a very low concentration of high molecular weight polymer. However, there is much less attention on the multiple-stream flow of viscoelastic fluids than that on single homogeneous viscoelastic fluid flow, particularly in planar contraction/expansion geometry.

This dissertation examines viscoelastic multiple-stream fluid flow, including flow instability, in planar contraction/expansion microchannels. The mixing performance of two dissimilar polyethylene-oxide (PEO) fluid streams was investigated. Rigorous investigations and characterizations of flow dynamics of these PEO streams were conducted in high precision micromachined silicon/glass microdevices with three different contraction ratios ($CR = 8:1$, $5:1$ and $4:1$). Fluorescent dye and microspheres were used with mercury lamp (for dye concentration measurement) and Nd-YAG twin lasers (for micro particle imaging velocimetry (μ PIV) measurement) to characterize the dynamical flow field and mixing efficiency.

The necessity of fluid viscoelasticity for multiple stream flow instability and resultant mixing enhancement was first addressed. We investigated the dynamics of multiple-stream flow based on the competition of the dominant forces in the flow field, namely viscous/elastic, viscous/viscous and viscous/inertial. The experimental observation and evaluated mixing performance showed that fluid viscosity and low fluid inertia were insufficient to induce multiple-stream flow instability. The viscoelasticity of the fluids is essential for chaotic flow instability and for mixing enhancement, which can be typified by Deborah number (De , a ratio of elastic forces to viscous forces).

The complex interplay that arises between the elasticity and viscosity of the fluids, and the contraction effects were studied. The viscoelasticity effects of both the mainstream

and side streams fluids and the effects of geometry were investigated in order to reveal the underlying mechanism of multiple-stream flow kinematics.

Chaotic flow instability was generated at very high values of Elasticity number (El, a ratio of elastic to inertial forces of the flow system), which are approximately 932 (Polymethylmethacrylate device) and 7998 (silicon-glass device). Flow regime at such an enormous El has not been explored extensively and Reynolds number (Re, a ratio of inertial forces to viscous forces) is no longer relevant in describing the flow behaviors. Experimental observations showed that the viscoelastically induced chaotic flow instability depended strongly on the ratio of viscoelasticity of the mainstream to side-stream fluids and the viscoelastic energies of the flow streams. A new governing parameter, $De_{ratio} = De_{main} / De_{side}$ was proposed, where De_{main} and De_{side} are Deborah number associated with the mainstream and side streams respectively. De_{ratio} was subsequently employed to characterize the dynamical flow behaviors. Furthermore, a De_{ratio} - De_{main} operating space was employed to provide a guide for the prediction of multiple-stream flow instability and mixing performance.

All the flow experiments and findings were finally summarized in the De_{ratio} - De_{main} operating space. With the De_{ratio} - De_{main} operating space, the evolution in dynamical flow behavior of multiple-stream flow was well characterized. The operating space illustrated the development of four specific flow regimes. They were steady Newtonian-like flow regime, onset elastic instability flow regime, symmetric vortex growth flow regime and chaotic flow instability flow regime. Slanted regime boundaries were identified in the space to categorize these four flow regimes. These slanted boundaries imply that De_{ratio} and De_{main} are important parameters governing the development of these flow regimes. The performance of mixing enhancement through viscoelastic instability was similarly characterized in the De_{ratio} - De_{main} operating space. The effects of De_{ratio} and De_{main} associated with mixing enhancement were projected in the operating space. It shows that mixing performance was greatly improved with increasing De_{ratio} and/or De_{main} . However, as illustrated in the operating space, De_{ratio} was found to be a more significant parameter for mixing performance. Our analysis suggests that these mixing

enchancements were attributed to the direct correlation between De_{ratio} and the viscoelastic energies of the two streams and the energy discontinuity at the stream-stream interfaces at downstream of contraction. This correlation has a direct bearing on the chaotic inter-penetration of the streams at downstream of contraction.

Efficient and effective mixing of fluid streams was achieved through viscoelastically induced flow instability with negligible diffusion and inertial effects (i.e. at enormous Peclet $> 8 \times 10^6$ and very small $Re < 0.1$), which could potentially be implemented in a micro-total-analysis-system (μ TAS) platform with minimum requirements for design and fabrication. Such viscoelastic mixing was achieved over a short effective mixing length (< 5 mm) and relatively fast flow velocities ($\sim 10^1$ mm/s). In addition, this study lays the foundation for investigating further the behavior of polymer fluids in this new flow regime.

This work was conducted in Nanyang Technological University, School of Mechanical and Aerospace Engineering during the period from year 2004 to 2007. It is part of the “Transportation and Mixing of Liquids in Microchannels” project supported by Agency of Science, Technology and Research, Singapore (A*STAR) (SERC grant no. 052 101 0013). This research is protected by a US provisional patent – “Viscoelastic Mixers for Microfluidics Application” (application no. 67/701,078).

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*To my mother, Giok Hong KERK
my sister and brother, Valerie and Jolvin
and my wife, Kitty*

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List of Symbols

$\dot{\gamma}_{char}$	average characteristic shear rate
$\dot{\gamma}_{ave}$	average shear rate
$\dot{\gamma}$	shear rate
Γ_{rel}	dimensionless instantaneous stress magnitude
Γ_{Ret}	relaxation retardation (dimensionless)
Π	total stress tensor
$\dot{\Phi}$	rate of strain tensor
$\dot{\epsilon}$	strain rate
ρ	density
ϕ	diffusion flux
ν	kinematic viscosity
ω	oscillation frequency
$\boldsymbol{\tau}$	stress tensor
τ	shear stress
$\boldsymbol{\tau}_p$	elastic stress tensor
$\boldsymbol{\tau}_s$	viscous stress tensor
$\tau_{xx}, \tau_{yy}, \tau_{zz}$	normal stresses
ϵ	strain
ϵ_{eff}	mixing efficiency
σ	stress
σ_s	surface tension
ϑ_{∞}	characteristic ratio of polymer
κ	characteristic strain rate
η	viscosity
η^*	complex viscosity

η_{∞}	limiting viscosity at high shear rate
η_{app}	apparent extensional viscosity
η_e	elongational viscosity
η_o	zero shear viscosity
η_s	viscosity of solvent
$[\eta]$	intrinsic viscosity
λ	relaxation time
λ_e	elongational relaxation time
λ_M	Maxwell relaxation time
λ_Z	Zimm relaxation time
χ_L	dimensionless vortex length
A_s	interfacial area
c	concentration of solute
C_{∞}	normalized concentration for perfect mixing
c^*	critical overlap concentration
C_i	normalized observed concentration
CR	contraction ratio
∇c	specie concentration gradient
d	characteristic dimension
D	diffusion coefficient
D_0	maximum diffusion coefficient
d_c	channel depth
De	Deborah number
De_{main}	mainstream fluid's De
De_{ratio}	ratio of De_{main} / De_{side}
De_{side}	sidestream fluid's De
D_{mid}	mid-diameter of filament
E	elastic modulus
E_A	activation energy for diffusion
El	elasticity number
F	body force
f_d	disturbance frequency
G'	storage modulus
G''	loss modulus
G_o	instantaneous shear modulus
h_0	initial gap of CaBER stage
k_b	Boltzmann constant

l_b	length of carbon-carbon bond
L_c	length of contraction channel
L_{char}	characteristic length
l_d	diffusion length
L_m	mixing length
L_v	vortex length
M_0	molecular weight of a monomer
M_n	number average molecular weight
M_w	weight average molecular weight
M_{wt}	molecular weight
N_1, N_2	normal stress differences
N_A	avogadro's number
n_m	number of carbon-carbon bond
p	pressure field
Pe	Peclet number
PEO	poly(ethylene-oxide)
$\dot{Q}$	total flowrate
$\langle R^2 \rangle$	mean square radius of gyration of polymer chain
R	universal gas constant
R_0	radius of CaBER stage
Re	Reynolds number
St	Strouhal number
T	temperature
t	time
t_c	capillary break up time
t_{diff}	diffusion time
Tr	Trouton ratio
t_{res}	fluid residence time
V	velocity
$\bar{V}$	average velocity
$\vec{V}$	velocity vector
Vol	sample volume
W	upstream channel width
w_c	contraction channel width
Wi	Weissenberg number

CHAPTER 1

INTRODUCTION

1.1 “Turbulence” Flow at Small Reynolds Number

The notion of turbulence is widely used in scientific and technical literature, however, hitherto there is no unique commonly accepted definition of it. Generally, the main features identifying turbulent flow are (i) the fluid motion is in a broad range of temporal and spatial scales, thus many degrees of freedom are excited in the flow system, (ii) no characteristic scales of time and space in the flow, and (iii) the flow is usually accompanied by a significant increase in momentum and mass transfer. The flow resistance and rate of mixing in a turbulent flow would become very much higher than in a laminar flow.

For constant density (ρ) and viscosity (η), motion of a Newtonian fluid is governed by the Navier–Stokes equation, which was first developed from molecular arguments by Navier and from continuum arguments by Stokes [Potter and Wiggert 1997, Bird *et al.* 2002]. The general dynamical equation for an isotropic, incompressible Newtonian fluid in vector notation can be expressed as

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \nabla) \vec{V} = -\nabla p + \eta \nabla^2 \vec{V} + \vec{F} \quad (1.1)$$

where $\vec{V}$ is the velocity vector, p is the pressure field, $\vec{F}$ is the body force applied to the fluid.

The first term at the left side of equation (1.1), $\rho \partial \vec{V} / \partial t$, is the transient term or commonly known as the inertial term. The equation has a non-linear term, $(\vec{V} \nabla) \vec{V}$, known as the convective (flow developing) term which is also inertial in nature. In a fully-developed region, a region where the velocity profile does not change in the flow direction, this convective term would vanish as the partial derivative of the velocity field with respect to the flow direction is zero. However, steady-state flow is not necessarily fully-developed and vice versa. A steady flow can be developing because the flow velocity profile changes in the flow direction but does not change with time. The second term at the right side of equation (1.1), $\eta \nabla^2 \vec{V}$, is the viscous dissipative term. Generally, this term has to be overcome in order to maintain a flow.

It is known that the flow of a simple Newtonian fluid is likely to be turbulent, when the velocity V is high, the kinematic viscosity of the fluid, $\nu = \eta/\rho$ is low, and the characteristic length L_{char} is large. This basically means that the Reynolds number (ratio of inertia force to viscous force) is large, e.g. $Re > 2300$ in an ideal round pipe for turbulent flows. Reynolds number can be defined as $Re = VL_{char}/\nu = \rho VL_{char}/\eta$. (1.2)

When Re is high, the non-linear inertia effects are strong and the flow is likely to be turbulent. Therefore, turbulence in fluids at high Re is a paradigm for a strongly non-linear phenomenon in spatially extended systems [Potter and Wiggert 1997, Ottino 1989].

Viscoelastic fluids, e.g. solutions with flexible high molecular-weight polymers, are very different from Newtonian fluids in many aspects [Bird *et al.* 1987]. These fluids are non-Newtonian fluids in nature and have a complex internal microstructure which can lead to counterintuitive flow and stress response. The most notable elastic property of these polymer solutions is its dependence of flow stresses on the history of the flow. The properties of these complex fluids can be varied through the lengthscales and timescales of the associated flows

[Bird *et al.* 1987]. Typically the elastic stress, by shear and/or elongational strains, experienced by these fluids will not immediately become zero with the cessation of fluid motion and driving forces, but decays with a characteristic time, λ , due to its elasticity.

Assuming incompressibility and negligible gravitational effects, the total stress tensor of a dilute viscoelastic fluid can be expressed as the sum of the isotropic pressure and the deviatoric stress [Bird *et al.* 1987],

$$\Pi = Ip - \nabla \tau \quad (1.3)$$

where I is the identity tensor.

Thus, the equation of motion for a dilute polymer solution can be expressed as,

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \nabla) \vec{V} = -\nabla p + \nabla \tau \quad (1.4)$$

When a polymer solution is sufficiently dilute, its deviatoric stress tensor, τ , can be written as the sum of stresses from the solvent and the polymer components of the fluid yielding the expression

$$\tau = \tau_s + \tau_p \quad (1.5)$$

The first part of the viscous stress tensor, τ_s , is defined by the viscosity of the Newtonian solvent, η_s , and the rate of strain tensor in the flow,

$$\tau_s = -\eta_s \left[\nabla \vec{V} + (\nabla \vec{V})^T \right] = -\eta_s \dot{\Phi} \quad (1.6)$$

The rate of strain tensor $\dot{\Phi} = \nabla \vec{V} + (\nabla \vec{V})^T$, is also known as the rate of deformation tensor.

Hence, the equation of motion reduces to

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \nabla) \vec{V} = -\nabla p + \eta_s \nabla^2 \vec{V} - \nabla \tau_p \quad (1.7)$$

Here the elastic stress tensor, $\boldsymbol{\tau}_p$, due to the polymer molecules which are stretched in the flow, is strongly dependent on the history of the flow.

The simplest model incorporating the elastic nature of the polymer stress tensor, $\boldsymbol{\tau}_p$, is a Maxwell-type constitutive equation [Bird *et al.* 1987] with a single relaxation time, λ ,

$$\boldsymbol{\tau}_p + \lambda \frac{D}{Dt} \boldsymbol{\tau}_p = -\eta_0 \dot{\boldsymbol{\Phi}} \quad (1.8)$$

Here η_0 is the zero shear rate viscosity and $D\boldsymbol{\tau}_p/Dt$ is the substantial time derivative of the polymer stress [Bird *et al.* 2002]. Using this materials derivative implies that we observe changes as we follow a fluid volume instead of considering a volume fixed in the initial frame.

An appropriate expression for the time derivative $D\boldsymbol{\tau}_p/Dt$ has to take into account that the stress is carried by the fluid elements, which move, rotate and deform in the flow [Bird *et al.* 1987]. A simple model equation for $D\boldsymbol{\tau}_p/Dt$, which is commonly used for the description of dilute polymer solutions, is the upper convected time derivative [Bird *et al.* 1987],

$$\frac{D\boldsymbol{\tau}_p}{Dt} = \frac{\partial \boldsymbol{\tau}_p}{\partial t} + (\vec{V}\nabla) \cdot \boldsymbol{\tau}_p - (\nabla \vec{V})^T \cdot \boldsymbol{\tau}_p - \boldsymbol{\tau}_p (\nabla \vec{V}) \eta_p \quad (1.9)$$

Those non-linear terms in the constitutive equations (1.8) and (1.9) are all of the order $\lambda(V/L_{char})\boldsymbol{\tau}_p$. The ratio of these non-linear terms to the linear relaxation term, $\boldsymbol{\tau}_p$, is given by a dimensionless expression $\lambda(V/L_{char})$, which is usually called the Weissenberg number, Wi.

The mechanical property of a viscoelastic fluid can be notably nonlinear at sufficiently large Weissenberg numbers. Indeed, quite a few effects originating from the non-linear polymer stresses have been known for a long time [Bird *et al.* 1987]. Two examples of interesting flow behavior resulting from these elastic stresses are rod climbing (or Weissenberg effects [Weissenberg 1947]) and the tubeless siphon, see Figure 1-1. For more comprehensive illustration of non-Newtonian fluids behaviors, readers are referred to the reference text “Rheological Phenomena in Focus” by Boger and Walters [Boger and Walters 1993].

Furthermore, in a uni-axial extensional flow (purely extensional flow), flow resistance of a viscoelastic fluid is strongly, and non-linearly, dependent on the rate of extension. There is a significant growth in the elastic stresses, when the rate of extension exceeds $1/(2\lambda)$, that is at $Wi > 1/2$. As a result, apparent viscosity of a dilute polymer solution can increase by up to three orders of magnitude [Tirtaatmadja and Sridhar 1993].

Figure 1-1. (a) An example of rod climbing. The elastic hoop stresses generated by a rotating rod immersed in a viscoelastic fluid will cause the fluid to climb up the rod. (b) An example of the open siphon or Weissenberg effects. A viscoelastic fluid can be drawn out of the beaker without physically in contact with a siphon or nozzle [Boger and Walters 1993].

There is this possibility of generating turbulent flows produced by the non-linear polymer stresses with little inertial effects at low Re . Indeed, in the fifties, such irregular flow instabilities was referred as elastic turbulence by Tordella [Tordella 1969]. An important step in this direction was made about two decades ago when purely elastic instabilities were experimentally identified in a rotational flow between two plates [Magda and Larson 1988] and in the Couette–Taylor (CT) flow between two cylinders [Muller *et al.* 1989]. The experiments were carried out with a viscoelastic fluid of high-molecular-weight polymers in a viscous Newtonian solvent which was named as a Boger fluid [Boger 1977/78]. The Boger fluids are custom-made viscoelastic fluid which have large relaxation times (seconds or even

minutes) and constant viscosity in nature. The purely elastic instabilities were observed at Wi of order unity and very small Re . In addition, as a result of these chaotic instabilities, secondary vortex flows were developed [Muller *et al.* 1989], and flow resistance was increased [Magda and Larson 1988] in the flow system. The purely elastic instabilities were also found in other shear flows with curvilinear streamlines, for examples the flow between a rotating cone and a plate and the Taylor–Dean flow. However, no quantitative data on either flow velocity field or spatial and temporal velocity spectra in those irregular flow patterns were presented in these studies. Therefore, turbulence was yet to be properly defined.

In more recent study, Groisman and Steinberg [Groisman and Steinberg 2000] have demonstrated the key features of turbulence flow with quantitative analysis in the flow of a highly elastic polymeric liquid at very small Re . Their experiments were conducted in a swirling flow between two plates with a wide gap. Elastic turbulence were observed and quantified. In the following year, they presented the elasticity-driven turbulence flow in a curvilinear channel (Dean flow) [Groisman and Steinberg 2001]. In this work, mixing enhancement through the elastically induced irregular flow instability was first reported.

1.2 Contraction Flow (Entry Flow) of Viscoelastic Fluids

Indeed, to exploit effectively the viscoelasticity of fluids for chaotic flow instability, sharper (abrupt contraction geometry) and smaller geometries should be employed. Stress singularities developed at sharp corners have been the source of elastic instabilities in many macroscale experiments [Bird *et al.* 1987], while rounded corners tend to suppress elastic behavior.

Abrupt contraction, axis-symmetry or planar contraction geometry, in which the viscoelastic fluid flows from one conduit into another smaller conduit, may appear to be relatively simple

and well-characterized. In reality, a complex flow is induced as the fluid approaches and passes through the contraction, exhibiting regions of strong shearing near the walls and uniaxial extension along the centerline. In addition, due to its simplicity in geometry and industrial applications relevance (in polymer processing such as extrusion process, injection molding process), this contraction flow dynamics has been the subject of many experimental and numerical simulation studies involving viscoelastic fluids.

As a consequence of the shear and extensional deformation, these viscoelastic fluids manifest significantly different flow behavior to Newtonian fluids in flowing through a contraction. Typically, under creeping flow conditions, Newtonian fluids will flow radially through the entry region into the contraction sweeping out the corners in the upstream channel. However, many non-Newtonian fluids, particularly viscoelastic fluids, will form vortices in the corners of the upstream channel, see Figure 1-2. It is this latter behavior which is being used as a benchmark problem for the computation of viscoelastic flows, and detailed discussions is presented in Chapter 3. A comprehensive review of the literature on the contraction problem can be found in the book by Tanner and Walters [Tanner and Walters 1998] and Chapter 8 of the book by Owens and Phillips [Owens and Philips 2002]. The presence of secondary flow in non-Newtonian fluids results in different pressure drops and stress fields than those found in Newtonian fluids.

Figure 1-2. Streak-line photographs illustrating the changing vortex shape and growth as a function of $\lambda\dot{\gamma}$ for a constant-viscosity elastic liquid flowing in a 4:1 circular contraction. [Boger 1987]. $\dot{\gamma}$ is the average shear rate.

1.3 Microfluidic Planar Contraction Flow of Viscoelastic Fluids

On a macroscale, particularly for dilute aqueous (low viscosity) viscoelastic fluids, it is almost impossible to generate large deformation rates and correspondingly a high Deborah number ($O(2)$) whilst also maintaining a small Reynolds number. As a result, it is difficult to induce an elastic response in which the effects of viscoelasticity are not dampened off, partially or completely, by the competing effects of flow inertia. A dilute viscoelastic fluid would then behave essentially as Newtonian fluids in the equivalent macroscale flows. However, the recent advancement of microfluidic technology offers a solution to this limitation by allowing high deformation rates and low Re for flows in microchannels. As such, through the high deformation rates achievable in microdevices, strong viscoelastic effects can be generated even in dilute aqueous viscoelastic fluids.

Microfluidics is a term that is used to describe fluid flow in devices with lengthscales less than a millimeter and capable of handling volumes of fluid in the range of micro- to nano-litres. Hitherto little attention has been given to microfluidic flow involving viscoelastic fluids with

the notable exception of inkjet printing. Inkjet printing applications, whose typical dimensions are on the order of 50 μm or less, utilizes aqueous fluids containing low concentrations of high molecular weight polymers. A prototypical geometry that captures a number of features in an inkjet print head is a converging flow through abrupt contraction–expansion geometry. This geometry, as aforementioned, has been used extensively to study the nonlinear flow phenomenon associated with non-Newtonian fluid elasticity in converging flows at macro lengthscale. Albeit the abrupt contraction-expansion geometrical configuration is simple, it contains the key features of complex viscoelastic flows, which involved a combination of shear deformation and extensional distortion.

Several recent studies have shown that the reduced lengthscales associated with microdevices can enhance the magnitude of viscoelastic effects in dilute polymer solutions. Distinct similarities of these early works on macroscale were demonstrated qualitatively on microscale in micro-fabricated planar contraction geometries by Groisman *et al.* [Groisman *et al.* 2003, Groisman and Quake 2004], and in more recent works of Rodd *et al.* [Rodd *et al.* 2005]. Indeed, the same phenomena were also observed in the much earlier work of James and Saringer [James and Saringer 1982] at similar lengthscales and using similar aqueous solutions of flexible polymers.

In addition to the unique flow conditions attainable by scaling down the geometry, microfluidic devices also offer the advantage of allowing access to a greater range of Wi with very small Re . This has been shown in Rodd *et al.* [Rodd *et al.* 2005], in which elasticity numbers spanning almost two orders of magnitude could be achieved. Accessibility to wide regions of Wi – Re space provides an avenue for generating suitable experimental data to test the performance of constitutive models over a wide range of flow conditions (with and without inertia). Furthermore, the ability of achieving high Wi at low Re offers the possibility of developing microfluidic rheometers suitable for probing the rheological properties of weakly

elastic fluids such as inks or dilute polymer solutions that appear Newtonian under the conditions that can be attained in conventional rheometers [Kang *et al.* 2005, Oliveira *et al.* 2007]. Rodd *et al.* [Rodd *et al.* 2005] has carried out an experimental study which attempts to provide an insight on the elasticity effects on the non-linear dynamics of planar entry viscoelastic fluid flows in microdevices.

Majority of the works reviewed so far, either on macroscale or microscale devices were solely focused on studying single homogeneous viscoelastic fluid flow. A possible reason for this bias could be that the key interests of the Rheological community are mainly on polymer processing (e.g. injection molding, fibre spinning, film blowing), spraying, coating, adhesive and extrusion. Hitherto, there are no works reporting on the elastic instability in multiple-stream flow of dissimilar viscoelastic fluids through microfluidic planar contraction/expansion devices.

1.4 Microfluidic Technology

In the last decade, microfluidic technology has received enormous attention because of several developments. A notable development is the confluence of technologies, which involves (i) advancement of machining technology in fabricating geometrical configurations with lengthscales of the order of microns or smaller, e.g. silicon micro-machining for micro-electro-mechanical systems (MEMS), soft lithography, micro-molding and laser ablation, (ii) rapid development in manipulating flow at micro lengthscale and for very small volumes and (iii) notable improvement in the detection capability for micro- to nano-liter samples. In addition, microfluidics has developed into a multi-disciplinary research area where various fields share a common interest towards portability and ‘lab-on-a-chip’ (LOC) concepts, for instance in analytical chemistry, high-throughput synthesis, drug discovery and microbiological analysis systems. The quest for low-cost portable devices and the potential use of microfluidics systems

to perform fundamental studies continuously push for greater progression and development of microfluidic technology. There have been two general approaches to microfluidics LOC design: the micro-total analysis systems (μ TAS) approach and single-purpose LOC approach. The LOC is defined as microfabricated devices or chips with dedicated task or functionality. While, the μ TAS design combines all laboratory functions (enable them to perform sample addition, pretreatment, sample transportation, chemical reactions, separation, and detection) on a single chip or connected series of LOCs with integrated electronics, sensors, and other components.

Prior to the materialization of fully functional μ TAS devices, sufficient development of all the necessary components and fundamental science are critically needed. Out of this vast scope of microfluidic research, mixing (or lack thereof) is often one of the crucial tasks to the effective functioning of microfluidic devices [Knight 2002, Ottino and Wiggins 2004]. A key attribute of flow dynamic in microdevices is their laminar character, which is in sharp contrast to the easily achievable turbulent flow in macroscopic process equipment. The reason for predominantly laminar flow in microdevices is their microscale dimensions, which lead to a small Reynolds number (ratio of inertia to viscous effects). The dominance of viscous effects suppresses viscous-inertial flow instabilities on microscale. Mixing of multiple streams in microchannels often relies on molecular-diffusion mechanism, and not on the effective mechanism of chaotic/turbulent flow instability.

The term ‘mixing’ is defined here as the reduction of inhomogeneities concerning the reagents composition or concentration. The desired homogenization requires both a decrease in the lengthscales on which these variations are present as well as a reduction of their amplitudes. Very often, the objective of mixing in general applications is rapid and complete mixing between two initially segregated streams: rapid interspersions in minimum time and a minimal amount of space, particularly in chemical or biological processes. As a result to avoid the

adverse effects of imperfect mixing on conversion and selectivity, total mixing should be achieved well below the time-scale of the reaction. However, mixing by molecular diffusion of macromolecular solutions may take considerable time, of the order of tens of minutes [Stone *et al.* 2004]. In addition, the typical residence times in microchannels are significantly smaller than in macroscopic systems; therefore the contact area between the species has to be increased considerably in order to enhance diffusive dissipation of concentration gradients. An increase of contact area can either be achieved mechanically or hydrodynamically. Further details are discussed in Chapter 3.

Therefore a better and efficient way to mix fluid streams in small-scale geometries in acceptable time-scales is required. A large variety of mixing methodology has been reported in the literature. However, many designs suffer from one or more disadvantages. Active-type micromixers require external actuators. Passive-type micromixers, which include lamination and chaotic advection micro-mixers, require long or complicated channel geometry. Both mixing methods lead to complex and expensive fabrication processes. In addition, most of the designs are efficient in the $1 < Re < 100$ range but their mixing efficacy below $Re < 1$ is low. A superior solution is to adopt a different approach that bypasses the limitation of the low Reynolds number, yet provides efficient mixing, will be a significant improvement not only for mixing problem and also for microfluidic system design.

1.5 Thesis Objective and Planning

It has been recently shown that the small lengthscale inherent to microfluidic devices have key implications on the flow behavior of fluids containing a very low concentration of high molecular weight polymer. Elastically induced flow instability was observed in a planar entry flow of dilute viscoelastic fluids in microchannels at low Re but high Weissenberg (Wi) or Deborah (De) number. The majority of the works were focused solely on studying single

homogeneous viscoelastic fluid flow. There is much less attention on the multiple-stream flow instability of viscoelastic fluids through planar contraction/expansion microdevices and its application for mixing enhancement via this viscoelastically induced flow instability.

The focus of this dissertation is to examine the flow instability in multiple-stream flows of dilute viscoelastic fluids through a planar abrupt contraction/expansion microchannel. This little explored viscoelastic flow regime, with negligible inertial effects, can be typified by the Deborah number alone. Purely viscoelastic instability can be expected, which is not possible with macroscale experiments.

One of the main motivations for this work, on planar contraction/expansion flow instability of viscoelastic fluids in microchannels, was to carry out detailed quantitative study of mixing, and the promotion mixing by elastically induced chaotic flow instability. From a practical standpoint, it is necessary to understand the rheological nature of such flow in order to optimize the use of viscoelastic effects in microfluidic mixing applications. The complex interplay that arises between the elasticity and viscosity of the fluids, and the contraction ratio of the channel are the keys for efficient mixing of fluid streams in microfluidic channels. The present study employs experimental observation and analysis as the first step for a better understanding of this flow regime – the viscoelastically induced flow instability with a negligible Reynolds number and large Peclet number, which could potentially be implemented in a μ TAS platform with minimum requirements for design and fabrication.

CHAPTER 2

VISCOELASTICITY

2.1 Viscoelasticity

When an elastic solid is subjected to an applied force, it deforms instantaneously. However, the induced deformation will be fully recovered with the removal of the applied force. Conversely, the deformation of a viscous fluid increases with time when a force is applied. With the removal of the force, a viscous fluid ceases to deform further, but any prior deformation remains. A viscoelastic material exhibits both elasticity and viscosity. When it is subjected to an applied force, it deforms and its deformation increases with time, i.e. it creeps. When the force is removed, only partial deformation is recovered instantaneously. It recovers more, but not all of its deformation recovers as time progresses. Depending on the time scale of interest, a viscoelastic material could behave solid-like or fluid-like or a combination of both.

2.2 Physical Principles

Sir Isaac Newton proposed the law of viscosity in 1687 [Malkin and Isayev 2006]. Subsequently, the analogous supposition, giving the modern form to the Newton hypothesis, was formulated by Navier and then by Stokes. Liquid with flow properties obeying the Newton hypothesis is called a Newton-Stokes liquid, or a Newtonian liquid. In a simple Newtonian shear flow, the shear stress is linearly proportional to the deformation rate,

$$\tau = \eta \dot{\gamma} \quad (2.1)$$

where τ is the shear stress and $\dot{\gamma} = d\gamma/dt$ is the shear rate or rate of shear deformation. The Newtonian viscosity, η , is constant for a given temperature and is independent of shear rate or stress. Thus, a plot of shear stress versus shear rate at a given temperature is a straight line with a constant slope.

Another model describing the mechanical properties of materials originated in the seventeen century is Hooke's law for a linear elastic solid [Malkin and Isayev 2006].

$$\sigma = E\varepsilon \quad (2.2)$$

where ε , σ and E are the strain, the stress and the elastic modulus, respectively.

Newton's law is satisfactory for describing the flow of simple liquids and gases with molecular weights less than $M_{wt} \leq 1000$ g/mol [Bird *et al.* 1987]. However, it is not adequate to describe the behaviors of polymer melts and simple liquids with the addition of high molecular weight macromolecules (polymers). For a given temperature, η is no longer constant but depends on the flow conditions such as the shear rate, $\dot{\gamma}(t)$, or the shear stress, $\tau(t)$. Any fluid that does not obey the Newtonian relationship is termed as a non-Newtonian fluid.

The first person who paid attention to the effect of viscoelasticity was *C.A. Coulomb* in 1784 [Malkin and Isayev 2006]. He showed that the damping in torsional oscillations of wires is caused by the viscoelasticity of the materials. Subsequently, it has been shown that fluids can

also exhibit viscoelastic behavior, which has now been comprehensively documented over the last three decades. Some excellent references are “*Viscoelastic Properties of Polymers*” by Ferry (1980) [Ferry 1980], “*The Dynamics of Polymeric Liquids*” by Bird *et al.* (1987) [Bird *et al.* 1987] and “*Rheological Phenomenon in Focus*” by Boger and Walter (1993) [Boger and Walters 1993].

2.2.1 Viscoelastic Behavior

Creep-and-recovery and stress relaxation experiments are the simple methods to illustrate the viscoelasticity of a material.

A) CREEP AND RECOVERY TESTS

When a Newtonian fluid is stretched by a stress at $t = t_0$, as shown in Figure 2-1A(a), the strain, $\epsilon(t)$, will increase linearly with time, see Figure 2-1A(b). If the stress is removed at $t = t_s$, the strain $\epsilon(t)$ will remain at the level reached at $t = t_s$, i.e. $\epsilon(t_s)$.

When a Hookean solid is stretched, the strain $\epsilon(t)$ will instantly increase proportionally to the stress to $\epsilon(t_0)$, see Figure 2-1A(c). $\epsilon(t)$ will remain constant until the stress is removed at $t = t_s$, at which time all the strain is recovered and $\epsilon(t_s)=0$.

For a viscoelastic material under a constant applied stress, the strain $\epsilon(t)$ shows a delay in response to the applied stress, see Figure 2-1A(d). When the load is removed at $t = t_s$, a viscoelastic liquid will recover partially its deformation at $t = t_s$ over a period of time. Some deformation remains permanently. In contrast, for a viscoelastic solid, on load removal, the deformation recovery over time is relatively faster, and almost all the deformation may be recovered over a sufficiently long period of time.

Figure 2-1. (A) Creep and recovery tests: (a) stress step (b) response of an ideal viscous liquid (c) response of an ideal elastic solid (d) response of two different viscoelastic materials, both are showing delayed recovery of deformation. (B) Stress relaxation tests: (a) strain step (b) ideal viscous liquid relaxation curve (c) ideal elastic solid relaxation curve (d) Stress relaxation curves of two viscoelastic materials, both are showing delayed relaxation. (C)(a) Schematic of Maxwell liquid model and its response to (b) creep and recovery test and (c) stress relaxation test.

B) STRESS RELAXATION TEST

Figure 2-1B(a) shows at time $t = t_0$, a material is subjected to a strain step, and with the strain remains at this value for a prolong period of time. For a Newtonian fluid, the stress, $\tau(t)$, will increase suddenly with the sudden and step increase in strain. However, $\tau(t)$ will instantly drops to zero, see Figure 2-1B(b). Thus, an immediate and complete stress relaxation occurs. For a Hookean solid, the stress $\tau(t)$ remains constant after strain step at $t = t_0$, i.e. no stress relaxation occurs.

After the application of a strain step at $t = t_0$, both viscoelastic liquid and solid show a non-linear delay in stress relaxation as a function of their viscoelastic properties, see Figure 2-1B(d). For a viscoelastic liquid, a delayed but complete stress relaxation takes place if the period of observation is sufficiently long. However, for a viscoelastic solid, a delayed and partial stress relaxation takes place even after a long period of observation.

C) MATHEMATICAL MODEL FOR VISCOELASTIC FLUID BEHAVIOR

It is rather complex to describe viscoelastic behaviors mathematically. We will only focus here the simple, but representative Maxwell model for viscoelastic liquids. A mechanical analogue of a Maxwell liquid model is obtained by a serial combination of a spring and a dashpot, see Figure 2-1C(a). If the individual strain rates of the spring and the dashpot respectively are $\dot{\epsilon}_{solid}$ and $\dot{\epsilon}_{liquid}$, then the total strain rate $\dot{\epsilon}$ is given by the sum of these two components:

$$\begin{aligned}\dot{\epsilon} &= \dot{\epsilon}_{fluid} + \dot{\epsilon}_{solid} \\ \Rightarrow \dot{\epsilon} &= \frac{\tau}{\eta} + \frac{\dot{\tau}}{G}\end{aligned}\tag{2.3}$$

where G is the shear modulus.

Incorporating Hooke's law of elasticity and Newton's law of viscosity with equation (2.3), the stress-strain relationship can be expressed as

$$\eta \dot{\epsilon} = \tau + \lambda \dot{\tau} \quad (2.4)$$

where $\dot{\tau}$ is the time derivative of τ and $\lambda = \eta/G$ is the relaxation time.

From equation (2.4), if a constant stress is applied to a Maxwell-model fluid, the strain rate will be constant and the strain will increase indefinitely, the so-called creep phenomenon, see Figure 2-1(b). If instead, a constant strain is applied to the fluid, the stress will decay as $\exp(-t/\lambda)$, the so-called stress relaxation, see Figure 2-1(c). An important feature of the Maxwell model is its predominantly fluid-like response, see Figure 2-1C. However, comparing Figures 2-1C(b) and C(c) to Figures 2-1A(b) and A(d) respectively, it can be observed that the Maxwell model is only an approximation to a viscoelastic liquid.

There are other models based on springs and dashpots such as the simple Kelvin-Voigt model for viscoelastic solid and the Burgers model. Readers are referred to [Malkin and Isayev 2006, Mezger 2006] for details. Other elementary models are the dumbbell, bead-spring representations, network and kinetic theories. However, the most notable limitation of all these models is their restriction to small strain and strain rates [Bird *et al.* 1987, Ferry 1980].

2.2.2 Viscoelastic Fluid Behavior

Polymeric solutions are inherently viscoelastic due to their long molecular chains. Dilute polymeric solutions will be of interests for microfluidic and nanofluidic applications, due to their ease of implementation. Since the polymer coils in a dilute solution are isolated and independent in their molecular movements, their viscoelastic behavior can be explained by the deformation of the individual coil or molecule in the stream [Bird *et al.* 1987, Ferry 1980]. As a result, the viscoelasticity of polymer solutions is generally attributed to the deformation of polymer chains and the consequent generation of unequal normal stresses.

A) STEADY SHEAR FLOWS

For a one-dimensional steady shear flow of a fluid between two planes, the velocities of an infinitesimal element of fluid in the y- and z-directions are zero. The velocity in the x-direction is a function of y only. Note that in addition to the shear stress, τ_{yx} , (refer to τ subsequently), there are three normal stresses denoted by τ_{xx} , τ_{yy} , τ_{zz} within the sheared fluid. Weissenberg in 1947 [Weissenberg 1947] was the first to observe that the shearing motion of a viscoelastic fluid gives rise to unequal normal stresses, known as Weissenberg effects. Since the pressure in a non-Newtonian fluid cannot be defined, and as the normal stress differences [Bird *et al.* 1987, Ferry 1980], $\tau_{xx} - \tau_{yy} = N_1$ and $\tau_{yy} - \tau_{zz} = N_2$, are more readily measured than the individual stresses, it is therefore customary to express N_1 and N_2 together with the shear stress τ as functions of the shear rate $\dot{\gamma}_{yx}$ to describe the viscoelastic behavior of a material in a simple shear flow.

The first and second normal stress differences N_1 and N_2 can be expressed in terms of two coefficients, ψ_1 and ψ_2 , defined as follows:

$$\psi_1 = \frac{N_1}{\dot{\gamma}_{yx}^2} \quad \text{and} \quad \psi_2 = \frac{N_2}{\dot{\gamma}_{yx}^2} \quad (2.5)$$

It is common that the first normal stress difference N_1 is higher than the shear stress τ . The ratio of N_1 to τ is often taken as a measure of how elastic a liquid is; specifically (N_1/τ) is referred as the recoverable shear.

B) ELONGATIONAL FLOW

Three main types of elongational flow are uniaxial, biaxial and planar. Although resistance to flow can be referred to loosely as an elongational or extensional viscosity (which further depends upon the type of elongational flow), this parameter generally is not constant.

For simplicity, we consider the behavior of an incompressible fluid element which is being elongated at a constant strain rate $\dot{\epsilon}$ in the x-direction (uniaxial extensional flow). For an incompressible fluid, the volume of the element must remain constant and therefore it must contract in both the y- and z-directions at the rate of $(\dot{\epsilon}/2)$ for a system symmetrical in these directions. The three components of the velocity vector $\vec{V}_i$ are given by:

$$\vec{V}_x = \dot{\epsilon}x, \quad \vec{V}_y = -\frac{\dot{\epsilon}}{2}y, \quad \vec{V}_z = -\frac{\dot{\epsilon}}{2}z \quad (2.6)$$

The rate of elongation in the x-direction can be written as:

$$\dot{\epsilon} = \frac{\partial \vec{V}_x}{\partial x} \quad (2.7)$$

In uniaxial extension, the elongational viscosity η_e can then be defined as:

$$\eta_e = \frac{\tau_{xx} - \tau_{yy}}{\dot{\epsilon}} \text{ or } \frac{\tau_{xx} - \tau_{zz}}{\dot{\epsilon}} \quad (2.8)$$

The earliest determinations of elongational viscosity were for the simplest case of uniaxial extension or stretching of a fiber or filament of liquid. Trouton [Trouton 1906], and subsequently many other investigators, found that at low strain (or elongation) rates, the elongational viscosity η_e was three times the shear viscosity η . The ratio η_e/η is referred to as the Trouton ratio, T_r :

$$T_r = \frac{\eta_e}{\eta} = 3 \quad (2.9)$$

The value of 3 for Trouton ratio refers specifically to the viscosities in shear and elongation for an incompressible Newtonian fluid.

By analogy, the Trouton ratio for a non-Newtonian fluid, for which T_r is not necessary equal to three, can be defined as:

$$T_r = \frac{\eta_e(\dot{\epsilon})}{\eta(\dot{\gamma})} \quad (2.10)$$

Since the Trouton ratio depends on both $\dot{\epsilon}$ and $\dot{\gamma}$, in eq.(2.10), there is some ambiguity in choosing their values. To provide a convenient estimate without this ambiguity, Jones *et al.* [Jones *et al.* 1987] proposed the following definition:

$$T_r = \frac{\eta_e(\dot{\epsilon})}{\eta(\sqrt{3}\dot{\epsilon})} \quad (2.11)$$

i.e. in the denominator, the shear viscosity is evaluated at $\dot{\gamma} = \sqrt{3}\dot{\epsilon}$. They also suggested that for inelastic isotropic fluids, the Trouton ratio is equal to 3 for all values of $\dot{\epsilon}$ and $\dot{\gamma}$, and any departure from the value of 3 can be ascribed unambiguously to viscoelasticity.

A common behavior of polymeric solutions [McKinley and Sridhar 2002, Li *et al.* 2000, Gupta *et al.* 2000] and polymer melts [Cogswell 1972] is that the Trouton ratio is greater than three at moderate and higher deformation rate. Their typical behaviors are illustrated in Figure 2-2, which show that the Trouton ratio can be a function of both strain and strain rate.

Figure 2-2. Extensional viscosity curve of polymeric solution and polymer melt. (a) Comparison between steady shear and elongation response (b) Trouton ratio as a function of total Hencky strain $\epsilon = \dot{\epsilon}t$ for polymeric solution.

2.3 Dimensionless Parameters

The relaxation time (λ), which describes the time required for the polymer coil to relax from a deformed state back to its equilibrium configuration, is a key parameter for characterizing a viscoelastic fluid. For a fluid with large λ , the stresses relax slowly and the elastic effects can be observed even at low deformation rates. A fluid with small λ can also exhibit significant elastic effects provided that the deformation rate is high. Clearly, both the fluid characteristic time (the relaxation time) and the flow characteristic time (e.g. the inverse of the deformation rate) are crucial in determining the viscoelastic response of a viscoelastic liquid. For many polymeric liquids, λ lies between 10^{-3} s for dilute solutions and 10^3 s for concentrated solutions.

The relative importance of elasticity in a flow is often described by the Deborah number, De introduced by Reiner [Reiner 1964]. This number may be interpreted as the ratio of the magnitudes of the elastic forces to that of the viscous forces. It is defined as the ratio of a characteristic time (time scale) of the fluid, λ , to a characteristic time of the flow system, t_{flow} , [Bird *et al.* 1987]

$$De = \frac{\lambda}{t_{flow}} \quad (2.12)$$

The characteristic time of the fluid is often taken to be the largest time constant describing the slowest molecular motions, or else some mean time constant determined by linear viscoelasticity. The characteristic time may also be chosen as a time constant in a constitutive equation. The characteristic time for the flow is usually taken to be the time interval during which a typical fluid element experiences a significant sequence of kinematic events, for example the duration of a characteristic experimental observation. If the flow following a material particle is steady, the characteristic time can be the reciprocal of a characteristic strain rate.

For the flow cases investigated (to be discussed in the next chapters), Deborah number may be expressed based on the characteristic shear rate,

$$De = \lambda \dot{\gamma}_{char} = \lambda(2\bar{V} / d) = 2\lambda\bar{V} / d \quad (2.13)$$

The characteristic shear rate may be expressed as $\dot{\gamma}_{char} = (\bar{V})/(d/2) = 2\bar{V}/d$, where λ is the relaxation time of the viscoelastic fluid measured in shear, $\bar{V}$ is the average velocity, d is the characteristic dimension of the contraction channel

Generally, smaller dimension results in a higher characteristic deformation rate for the same flowrate, resulting in higher elastic effects and a higher De. It should be noted that for some problems there is more than one characteristic time for the flow that can be identified [Bird *et al.* 1987]. Thus, a second dimensionless group, the Weissenberg number, Wi, is sometimes used in polymeric fluid dynamics, which can be defined as,

$$Wi = \lambda \kappa \quad (2.14)$$

where κ is a characteristic strain rate in the flow. For problems where there is only one identifiable characteristic time, the Deborah number should be preferred. Indeed, in a steady channel flow, De and Wi are interchangeable. However, there are debates for the most appropriate terminology for more complex flows that are associated with the unsteadiness of the process, see Bird *et al.* [Bird *et al.* 1987] and Metzner *et al.* [Metzner *et al.* 1966] for further discussion.

A smaller channel possesses smaller flow characteristic length and time. Thus, Re is smaller and it is difficult to generate inertia/viscous flow instability. Conversely, De becomes larger and it is easier to have elastic/viscous instability. The relative dominance of elastic to inertial effects is typified by the elasticity number, El, i.e. the ratio of fluid elasticity to fluid inertia. El is expressed as

$$El = De/Re = \frac{2\lambda\eta_0}{\rho d^2} \quad (2.15)$$

El is a function of the given fluid and geometry. It is dependent on the fluid properties and the inverse of the characteristic cross-sectional area.

The contraction ratio (CR) is another key parameter in determining the entry flow behavior.

The contraction ratio is defined as

$$CR = \frac{W}{w_c} \quad (2.16)$$

where W is the upstream channel dimension and w_c is the contraction dimension.

However, in general the rheological properties of a viscoelastic fluid are shear rate ($\dot{\gamma}$) dependent. Thus the various dimensionless parameters are also shear rate dependent. For example, the elasticity number El is now dependent on the change in shear rate $\dot{\gamma}$, which could be written as

$$El(\dot{\gamma}) = De/Re = \frac{2\lambda(\dot{\gamma})\eta(\dot{\gamma})}{\rho d^2} \quad (2.17)$$

However, as $\dot{\gamma}$ is a function of flowrate, it implies that both λ and η are functions of flowrate.

Thus, in contrast to equation (2.15), equation (2.17) indicates that El is also a function of flowrate.

2.4 Rheological Measurements

Rheological properties of the same polymeric solution measured in shear and elongational flows can be very different as discussed in the earlier section. However, a cursory examination of current textbooks on rheology (e.g. Bird *et al.* 1987 [Bird *et al.* 1987], Ferry 1980 [Ferry 1980], Tanner 2000 [Tanner 2000]) shows that shear rheology dominates and research in extensional rheology is comparatively much more recent. The measurements of the shear

properties of polymeric fluids are well established and a number of rheometers are available for both melts and dilute polymeric solutions. Lately, more efforts have been directed in measuring the extensional properties of fluids [Jones *et al.* 1987, McKinley and Sridhar 2002, Tirtaatmadja and Sridhar 1993, Sridhar *et al.* 1991, Entov and Hinch 1997, Bazilevsky *et al.* 1990, McKinley and Tripathi 2000].

In practice, the steady shear and oscillatory tests are commonly conducted via rotational rheometers, and the extensional test is widely performed in “liquid filament rheometers” or “capillary breakup extensional rheometers (CaBER)”.

2.4.1 Rotational Shear Measurement

A) STEADY SHEAR FLOW CURVES

Steady shear flow generally is a viscosity measurement on materials undergoing steady and continuous shear. A flow curve, viscosity (η) versus shear rate ($\dot{\gamma}$), across a wide range of shear rate is often used to design pumps and mixing devices. This method is also used to provide flow behavior which indicates the relationship of shear rate to shear stress between suitable limits. A commonly observed feature of polymeric solutions is the shear thinning characteristic, i.e. the decrease of viscosity with increasing shear rate, which can be determined from this technique. This typical flow curve exhibits two Newtonian plateaus – one at low shear and another at high shear regimes. The shear thinning region lies between the two limiting conditions and may extend over a few decades of shear rate.

However, dynamic measurements, such as the oscillatory tests, are preferred in practice over the steady shear measurements for determining the viscoelastic properties of fluids. This is not only because of the difficulty in determining the first normal stress coefficient accurately, the

determination of a fluid's viscosity by steady shear measurement is only a partial characterization of a viscoelastic fluid's properties.

B) DYNAMIC OSCILLATORY EXPERIMENTS

The dynamic rheological properties of a polymeric solution can be determined by small-amplitude oscillation tests [Bird *et al.* 1987]. In small amplitude oscillatory measurements, a sinusoidally varying shear stress field is imposed on a fluid and the amplitude of the resulting shear strain and phase angle between the imposed stress and the strain is measured. The test is said to be in the "linear viscoelastic" regime if the strain is linearly proportional to the imposed stress and the response is sinusoidal [Malkin and Isayev 2006, Mezger 2006].

In practice, dynamic oscillatory measurements are sensitive probes of molecular structure and interactions, for examples in emulsions and dispersions. Oscillatory measurements probe emulsion structure without destroying it. This is accomplished by applying very small sinusoidal displacements or strains to the emulsion at controlled amplitude and frequency. In general, there are two mechanisms for a material to respond to a deformation:

- Elastic energy storage (typified by G' , known as storage modulus), and
- Viscous dissipation (typified by G'' , known as loss modulus)

G' , which is proportional to the strain in-phase with the stress, provides information about the elasticity of a material. G'' , the loss modulus, is proportional to the stress out-of-phase with the displacement. These parameters are termed the elastic and viscous loss moduli, G' & G'' respectively. The values of the respective stresses measured are divided by the appropriate strains, resulting in the respective moduli. The shapes of the curves for G' and G'' versus the test frequency ω for polymeric solutions are described by Ferry [Ferry 1980]. At low

frequency, G' and G'' are proportional to ω^2 and ω respectively. As frequency increases, the slope of these curves decreases, as illustrated in Figure 2-3.

Qualitatively, the stress created by imposing oscillatory strains will be a function of (a) the amplitude of strain, (b) its frequency, and (c) the properties of the polymeric solution. By applying sufficiently small strains, we can minimize the strain dependency from the material response. Thus, the amplitude of strain is no longer an important consideration, resulting in a "linear viscoelastic" response. Small strain measurements can be important for certain application as they do not adversely affect the structure of the fluid.

These linear viscoelastic dynamic moduli are functions of frequency. For a suspension or an emulsion material at low frequency, elastic stresses relax and viscous stresses dominate with the result that the loss modulus, G'' , is higher than the storage modulus, G' . For a dilute solution, G'' is larger than G' over the entire frequency range but they approach each other at higher frequencies as shown in Figure 2-3.

Figure 2-3. Dynamic test: frequency oscillation sweep. For viscoelastic fluid of 1 wt% poly (ethylene-oxide) (PEO) in 55 wt% glycerol water. Molecular weight of PEO is 2×10^6 g/mol.

The Maxwell relaxation time is commonly evaluated from the first normal stress difference measurement,

$$\lambda_M = \frac{N_1}{2\dot{\gamma}^2 \eta_o} \quad (2.18)$$

However, at zero deformation rate, where the simple fluid theory applies, λ_M^0 can be evaluated from the oscillatory data by

$$\lambda_M^0 = \lim_{\dot{\gamma} \rightarrow 0} \frac{N_1}{2\dot{\gamma}^2 \eta_o} = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2 \eta_o} \quad (2.19)$$

It was shown that for water soluble polymeric solution such as Separan AP30, NP10 and Keltrol with polymer concentration less than approximately 1500, 5000, and 500 ppm, respectively, λ_M^0 is independent of polymer concentration [Tam and Tiu 1996]. These observations were consistent with the molecular theories such as the Zimm theory, which

states that at infinite dilution, the relaxation time is independent of polymer concentration and is given by

$$\lambda_z = 0.423 \frac{[\eta] \eta_s M_{wt}}{RT} \quad (2.20)$$

where $[\eta]$ is the intrinsic viscosity [Bird *et al.* 1987, Ferry 1980], and η_s is the solvent viscosity.

By Cox-Mertz rule, for polymeric solutions at low frequency and shear rate in accordance with the simple fluid theory, the zero shear viscosity can be estimated by [Bird *et al.* 1987, Tam and Tiu 1996]

$$\eta_0 = \lim_{\dot{\gamma} \rightarrow 0} \eta = \lim_{\omega \rightarrow 0} |\eta^*| = \lim_{\omega \rightarrow 0} \left(\frac{G''}{\omega} \right) \quad (2.21)$$

2.4.2 Extensional Strain Measurement

Elongational or extensional flow of polymeric fluids are experienced in important industry processes, such as food dispersion, paints, adhesives, coating, inkjet printing, enhanced oil recovery, and lubrication. However, extensional properties cannot be determined from shear rheometry experiments.

Filament-stretching has been studied for obtaining extensional properties of polymeric solutions and melts. A comprehensive review of the flow dynamics of filament-stretching is provided by McKinley and Sridhar [McKinley and Sridhar 2002]. Subsequently, ‘liquid filament rheometers’ or ‘capillary breakup extensional rheometers (CaBER)’ has been developed for the characterization of the dynamics of complex fluids undergoing extensional flows.

A) TECHNICAL ASPECT OF CABER MEASUREMENTS

Recently, rheometer for measuring extensional properties is commercially available. It is called the CaBER 1 (the Capillary Breakup Extensional Rheometer). It was designed by the Cambridge Polymer Group and is manufactured by Thermo Haake. The measuring procedure involves the placing of a small quantity of sample fluid between two parallel plates. A fluid filament is formed when the sample fluid is subjected to a rapid extensional step strain, see Figure 2-4. The filament evolution as a function of time is dictated by the surface tension and the viscoelastic stresses of the fluid. The surface tension is trying to “pinch off” the filament and the extensional properties of the sample are trying to prevent it. A laser micrometer measures the midpoint diameter of the gradually thinning fluid filament when the upper plate extends to its final position. From the measured data, several elongational rheological properties can be determined such as the extensional viscosity, evolution of the filament diameter as a function of time, the extensional deformation and deformation rate, and the filament break-up time.

Figure 2-4. Sequence of a CaBER 1 experiment snapshots.

In general, the changes of a fluid filament are governed by a balance of forces on the filament, assuming that a fluid sample is at rest initially, and is subjected to a constant strain rate subsequently. With reference to the mid-diameter (D_{mid}) of the filament and ignoring the very small inertial effects [Li *et al.* 2000], the governing equation can be expressed as,

$$\eta_e \dot{\epsilon}_0 = \langle \tau_{zz} - \tau_{yy} \rangle = \frac{4F_z}{\pi D_{mid}^2} - \frac{2\rho g(Vol)}{\pi D_{mid}^2} - \frac{2\sigma_s}{D_{mid}} \quad (2.22)$$

where ρ and Vol is the density of the sample fluid, and the sample volume respectively. σ_s is the surface tension of the fluid, which has to be measured separately. g is the gravitational constant. F_z is the tensile force acting on the column ends, and $\langle \tau_{zz} - \tau_{rr} \rangle$ represents the non-Newtonian contribution to the average total normal stress difference over the filament cross section.

Equation (2.22) is model-dependent and the resulting solution to the differential equation depends on how the polymeric contribution to the stress varies with the rate of deformation. Solutions to this evolution equation have been found for a number of models [Entov and Hinch 1997, Bazilevsky *et al.* 1990, McKinley and Tripathi 2000] and are summarized in Table 2-1.

Table 2-1. Evolution of the mid-filament diameter in a fluid filament undergoing capillary-driven breakup. Note: λ_c is the characteristic relaxation time of the sample, t_c is the filament break-up time and μ_s is the Newtonian viscosity of the solvent.

Constitutive Model	Growth of Filament	Inferred Parameters
Newtonian Fluid, $\tau = \mu \dot{\gamma}$	$D_{mid}(t) = 0.142(\sigma_s / \eta_s)(t_c - t)$	$t_c, \sigma_s / \mu_s$
Power Law Fluid, $\tau = K \dot{\gamma}^n$	$D_{mid}(t) = 2^{1-n} (0.142)(\sigma_s / K)(t_c - t)^n$	$t_c, \sigma_s / K, n$
Upper Convected Maxwell	$D_{mid}(t) = D_0 (GD_0 / \sigma_s)^{1/3} \exp(-t / 3\lambda_c)$	$\lambda_c, G / \sigma_s$

B) THE APPARENT EXTENSIONAL VISCOSITY

The evolution of filament diameter is driven by the capillary pressure and resisted by the extensional stress in the fluid. Thus, measurements can also be represented in terms of an apparent extensional viscosity, define as

$$\eta_{app}(\epsilon) = \langle \tau_{zz} - \tau_{yy} \rangle / \dot{\epsilon}(t) \quad (2.23)$$

where under steady elongation flow, the natural-strain or Hencky strain [McKinley and Sridhar 2002] is given by

$$\varepsilon(0, t) = \dot{\varepsilon}_0 t = -2 \ln(D(t)/D_0) \quad (2.24)$$

Hence, the apparent viscosity can be written as,

$$\eta_{app}(\varepsilon) = \frac{\frac{2\sigma_s}{D_{mid}(t)}}{-\frac{2}{D_{mid}(t)} \frac{dD_{mid}}{dt}} = \frac{\sigma_s}{\frac{dD_{mid}}{dt}} \quad (2.25)$$

2.5 Basic Viscoelastic Contraction-Expansion Flow Phenomena

In the last few decades, understanding and controlling contraction flow (or entry flow) behavior of single homogeneous viscoelastic fluids has been one of the classical fluid mechanics problems in the Rheology fraternity. Reviews of investigations published prior to 1987 can be found in Boger [Boger 1987] and White *et al.* [White *et al.* 1987], and a brief summary of more recent works is given by Rodd *et al.* [Rodd *et al.* 2005]. In this section a brief review of the flow structures observed in contraction and expansion flows of single homogeneous viscoelastic fluid will be presented.

The flow phenomena of viscoelastic contraction flow for macrochannels have been explored more comprehensively for axisymmetric geometries as compared to planar geometries. Details of the complex interplay between elasticity and inertia of viscoelastic fluids for macrochannels with axisymmetric geometries can be found in Cable and Boger [Cable and Boger 1978, Cable and Boger 1979], who employed a number of shear thinning viscoelastic fluids in axisymmetric contractions, spanning a wide range of the De-Re operating space.

However, planar geometrical configurations will be the main focus here, as they are commonly found in microfluidic devices due to their ease of fabrication. Recently, Rodd *et al.* [Rodd *et al.* 2005] had summarized the non-linear flow phenomena in microfluidic channels in the De-Re

space, see Figure 2-5. Care should be taken when relating various phenomena from axisymmetric to planar geometries at similar De-Re regimes. For example, the formation and changes of the vortical flow pattern can be qualitatively different as a result of the difference in total strains and strain-rate histories experienced by the fluid elements in the two geometries [Nigen and Walters 2002, Rodd *et al.* 2005].

2.5.1 Contraction Flow Behavior

Contraction flow is commonly known as converging entry flow. Interesting flow phenomena have been observed with increasing Deborah number in an entry flow. Flow structures observed in a converging entry flows, for viscoelastic fluids, can be categorized into three distinct regimes: vortex growth, diverging flow and unstable flow.

A) VORTEX GROWTH

Formation and growth of the vortex upstream of the contraction is proportional to De, which increases with an increase in flowrate, see equation (2.13). This implies that the elastic forces become more dominant as the flowrate increases. When the elastic effects are great enough to suppress the inertial effects, a viscoelastic fluid undergoes transitions from the Newtonian like behavior (low flowrate structure) to regimes with vortex formation and enhanced vortex size. This competition between elastic and inertial forces within the flow becomes violent with further increment in flowrate. At a high enough flowrate, the large vortex observed in many viscoelastic entry flows ultimately becomes unstable, resulting in large fluctuations in the flow field and gross distortion of the viscoelastic fluid downstream of contraction.

According to convention in macroscale entry flow study, vortex length was used widely to characterize the vortical flow pattern observed in viscoelastic converging entry flow, see equation (2.26). The dimensionless vortex length is defined as the axial distance from the

upstream contraction plane at which the primary flow first detaches from the wall to the upstream channel width. It can be expressed as,

$$\chi_L = L_v/W \quad (2.26)$$

where L_v is the vortex length and W is the upstream channel width

For similar geometrical dimensions and flow conditions, a difference in the observations between planar and axisymmetric entry flows is the smaller size of the salient corner vortex. This difference was believed to be caused by the difference in the total Hencky strain imposed on the macro-molecules during the converging entry flow, which is less for planar than axisymmetric entry flows [Rodd *et al.* 2005].

B) DIVERGING FLOWS

Diverging streamlines at upstream of the contraction are a feature of contraction flows, which are mainly controlled by both elasticity and inertia. When the flow system reaches a critical Re , inertial effects cause a reduction in size of the vortex and often accompanied by diverging flow patterns at the interface region between the main stream flow and the secondary stream flow (corner vortices), which is indicated in Figure 2-5 by the dashed line at $De \approx 240$. A comprehensive illustration of this flow regime can be found in Cable and Boger [Cable and Boger 1978]. These flow structures have also been predicted numerically in the presence of both elasticity and inertia, for shear-thinning fluids, by the PTT or FENE-P models [Rodd *et al.* 2005]. However, the precise dynamical mechanisms that lead to the development of the diverging streamlines upstream of the contraction are yet to be fully elucidated.

C) UNSTABLE FLOW

Steady viscoelastic converging entry flows could become unstable at moderate Deborah and Reynolds numbers in both axisymmetric and planar geometries [Rodd *et al.* 2005]. It has been

found that viscoelastic fluids experience regimes consisting of diverging flow with unstable salient vortices, and regimes with Goertler-like and lip vortices [Chiba and Nakamura 1990].

Figure 2-5. Flow regimes in De - Re space for dilute aqueous PEO solutions through micro length scale contraction geometries [Rodd *et al.* 2005].

2.5.2 Expansion Flow Behavior

Lesser research was reported in observing the exit behavior of fluids from the contraction. Generally, the elasticity of a viscoelastic fluid has the opposite effects to fluid inertia. As a result, the large viscoelastic forces that generate vortex behavior upstream work in an opposite fashion at downstream of the contraction, and thus suppress downstream vortex growth. These flow behaviors were reported by Townsend and Walters [Townsend and Walters 1994]. They investigated the expansion of viscoelastic and Newtonian fluids in an identical channel. They found that at high Reynolds number, Newtonian fluids generated large circulation zones or

corner vortices downstream of contraction, which are a feature of expansion flow behavior for Newtonian flow [Hawa and Ruzak 2001]. However, for a viscoelastic fluid with the same Reynolds number and a low Deborah number, the exit vortex behavior was completely suppressed.

2.6 Brief Review of Numerical Modeling and Simulation

Modeling and numerical approaches applied to complex flows of viscoelastic liquids have expanded significantly in scope since its inception thirty years ago. The simulations of viscoelastic fluid in planar converging/diverging flow behavior, however, show a limited success. Viscoelastic fluids, which have a complex internal microstructure, are highly non-Newtonian. They often lead to counterintuitive flow and stress responses, and result in intricate flow phenomena whose prediction requires sophisticated modeling approaches and numerical tools. This field hitherto remains challenging due to numerous unresolved difficulties such as the sharp corner singularity, the mixed type of the governing equations and the constraint arising from the exorbitant unknown parameters [Keunings 2000, 2001, 2003, Kim *et al.* 2005].

Certainly, numerical simulation of viscoelastic flow dynamics requires considerable background on continuum physics, statistical mechanics, polymer chemistry, fluid dynamics, and experimental strategies [Bird and Wiest 1995]. A considerable gap remains between those who use constitutive equations to solve realistic boundary value problems and those who are concerned with the experimental observation of the dynamic kinematics of these flows [Crochet and Walters 1993, Keunings 2000]. As commented by Boger, the causes inherent to this gap are “*the constitutive is simple enough for solution of the boundary value problem, no*

material of ideal enough properties is available for experimental verification of the predicted kinematics” [Boger 1977/78].

2.6.1 Background

Albeit the contraction geometrical configuration (planar or axisymmetry) is simple, it contains the key features of complex viscoelastic flows, which are often involved in polymer processing applications, such as a hybrid deformation of shear and extensional distortions. The flow through abrupt contraction also gives rise to a singularity at the re-entry corner, where the stress tends to infinity thus causing many difficulties associated with the numerical simulations of viscoelastic flows [Bird *et al.* 1987]. These issues make it an ideal benchmark problem for both experimental and computational studies for complex viscoelastic flows of polymeric fluids.

The progress of modeling and numerical simulation over the last few decades, particularly in the aspect of differential equations, has been well summarized and reviewed [Crochet and Walters 1983, Crochet *et al.* 1984, White *et al.* 1987, Crochet and Walters 1993, Baaijens 1998, Keunings 2000, 2001, 2003]. Since its pioneering days (~ 1975), the majority of publications in the numerical simulation of viscoelastic fluid flow dynamic has adopted the macroscopic approach, wherein the rheological behavior of the fluid is described by a differential constitutive equation. The governing equations are solved numerically by means of a suitable finite element method [Baaijens 1998]. Recently, advancement in computer processing capacity has made feasible the complementary simulation approach, particularly in micro-macro approach, which involves the use of a microscopic model of kinetic theory in the numerical simulation of viscoelastic flows, in combination with the macroscopic conservation laws. This hitherto is an emerging methodology, wherein they allow the direct use of kinetic theory models in flow simulations and thus avoiding potentially inaccurate closure

approximations. One should take note that micro-macro techniques are much more demanding in terms of computer resources than conventional continuum computations. The micro-macro numerical techniques for predicting complex flows of viscoelastic fluids is notably reviewed by Keunings [Keunings 2004].

2.6.2 Flow Simulation Method

Polymer constitutive models for viscoelastic flows lead to highly nonlinear problems because of the elliptical and hyperbolic parts of the equations. This causes difficulties for computational fluid dynamics techniques especially at high Deborah (De) or Weissenberg number (Wi), which characterizes the combined effects of the fluid elasticity and viscosity. The challenges of simulating viscoelastic flows at high flowrates has been described as the ‘High Weissenberg Number Problem’ (HWNP) in the literature [Keunings 1989, 2000, Owens and Philips 2002]. The limiting value of De in numerical simulation strongly depends on the constitutive equation used and the mesh size [White *et al.* 1987]. Several algorithms such as Explicitly Elliptic Momentum Equation (EEME) and Elastic Viscous Stress Split (EVSS) were developed to strengthen the ellipticity in the momentum equation. EVSS and Discrete Elastic Viscous Stress Split (DEVSS) based algorithms have gained popularity due to their simplicity and can be applied to a variety of constitutive equations more easily, while maintaining stability. Readers can refer to “*Computational Rheology*” for comprehensive discussions [Owens and Philips 2002].

As aforementioned the formulated constitutive equations cannot be solved analytically and require the use of approximation methods, such as the finite element (FEM), finite difference, finite volume (FVM), semi Lagrangian and hybrid FEM/FVM techniques. The most commonly used method based on mixed finite element formulations was introduced by Crochet *et al.* [Crochet *et al.* 1984] for viscoelastic flow simulation. In their later studies, they

used mixed finite element method for the simulation of Oldroyd B fluid through a 4:1 planar contraction [Marchal and Crochet 1986, Marchal and Crochet 1987]. Hermitian finite elements were first employed for interpolating the velocity field [Marchal and Crochet 1986], thus the stress shape functions were able to represent every derivative of the velocity field. The highest De simulated was 6.57 before the loss of convergence. Subsequently, they proposed a new mixed finite element method [Marchal and Crochet 1987] which used Streamline Upwind (SU) methods with 4×4 linear stress sub-elements. Limiting De number was not reported in this case but the simulations were stopped at $De = 20$. A small lip vortex along with the salient corner vortex was observed at $De = 7.6$, but this disappeared at higher values of De . Recently, Kim *et al.* [Kim *et al.* 2005] used high resolution FEM for simulating Oldroyd B fluid flow through planar contraction at high $Wi \approx 5$ using coarse mesh and $Wi = 2.5$ with the finest mesh.

Lower computational cost compared to FEM, FVM gains its attention to viscoelastic flows simulation by computing stress components at center point or edges of the cell. Alves *et al.* [Alves *et al.* 2003] used a high resolution FVM for simulating the inertialess flow through a 4:1 planar contraction of viscoelastic fluids, i.e. constant viscosity Oldroyd-B, and the shear thinning PPT with linear or exponential stress function. No upper limit on De was reported for the exponential form of the PPT constitutive model, while a $De \approx 20$ was found for the linear form, in contrast to maximum $De = 9$ for the linear PPT, and 35 for the exponential PPT reported by Aboubacar *et al.* [Aboubacar *et al.* 2002]. Furthermore, FVM was also extended to study three dimensional viscoelastic flows by Xue *et al.* [Xue *et al.* 1998] and for transient analysis by Mompean and Deville [Mompean and Deville 1997].

Indeed, many numerical studies have used EVSS/SUPG techniques for FEM [Kim *et al.* 2005] and FVM [Xue *et al.* 1998, Alves *et al.* 2003] to overcome the challenges of HWNP to a reasonable extent. However, the mesh dependency on the limiting De is not completely eliminated. Other schemes such as hybrid FVM/FEM and semi Lagrangian techniques were

also reported for Oldroyd-B constitutive model. Sato and Richardson [Sato and Richardson 1994] have employed a combined finite volume / finite element method for simulating the flow of an Oldroyd-B fluid. The momentum equation is solved explicitly with respect to time by FEM, while the constitutive equation for an upper-convected Maxwell (UCM) is solved implicitly by FVM. In a planar 4:1 contraction flow, the critical value was evaluated at $Wi = 2$ because of the transient behavior of viscoelastic flow. The hybrid FVM/FEM was also reported by Aboubacar and Webster [Aboubacar and Webster 2001], with momentum and continuity equations solved by a Taylor–Galerkin /pressure correction finite element method and the stress constitutive equation discretized with a cell-vertex FVM algorithm. This combination resulted in a time-stepping process, with fractional-staged formulation based upon each time step. However, the critical Wi reached was ~ 4 approximately. Philips and Williams [19] have presented a semi-Lagrangian FVM technique applied to planar contraction using Oldroyd-B model. The momentum and mass conservation equations were solved in FV framework and the extra-stress tensor was calculated using FEM.

In spite of the high computational cost imposes to the semi-Lagrangian FVM, hybrid FEM/FVM and high resolution methods, these numerical simulation techniques have yet to overcome the challenge of HWNP completely. Further details of some numerical simulation works carried out in the last decade for planar and axisymmetry geometries are presented in Table 2-2.

2.6.3 Remarks on Numerical Simulation Research

In most studies, numerical methods have failed at Deborah numbers on the order of 1 for sharp corner planar contraction entry flow problems. The Deborah number represents the ratio of a characteristic relaxation time of the fluid to the time scale of the flow. Therefore, inaccuracy and loss of convergence are occurring at the point where the viscoelastic character is becoming

more apparent. As such the viscoelastic flow computations have not yet provided reliable solutions at high De or Wi for a variety of HWNP flow problems. As a result their success, particularly the accuracy of simulation, was not guaranteed. In fact, some have been generated with numerical schemes that either explicitly or implicitly smoothes out the difficulties. However, as stated by Keunings [2000], *“Getting high- Wi (smooth) solutions using risky, “false diffusion” numerical schemes often essentially means that the numeric have computed an approximate solution to a different problem than the one under investigation”* [Keunings 2000].

Hence, difficult issues mentioned at the beginning of this section do remain, especially for the flow problems characterized by stress singularities or boundary layers which are essentially without satisfactory mathematical descriptions. Thus there is a need for the careful evaluation of numerical techniques in benchmark flow problems. One could argue that mesh refinement experiments would readily settle the matter of numerical accuracy. However unfortunately, these are not always successful in that the range of Weissenberg number that can be covered in the simulations may decrease as the grid is further refined. This problem often occurs in the presence of a stress singularity, thus preventing the safe interpretation of the rheological results obtained in the vicinity of the singular point [Keunings 2000].

Table 2-2. Summary of numerical simulation on entry flow studies in axisymmetric (A) and planar (P) geometries.

Author	Year	Geometry	CR	Fluid Model	Wi/De range	Re range	Comments
Kim <i>et al.</i>	2005 [Kim <i>et al.</i> 2005]	P	4	Oldroyd-B	$Wi < 2.5$	$Re = 0$	Lip vortices did not show in simulation which is in contradiction to the experimental observations [Evans and Walters 1989, Nigen and Walter 2002]. The max. attainable Wi decreased with increasing mesh resolution.
Edussuriya <i>et al.</i>	2004 [Edussuriya <i>et al.</i> 2004]	P	4	Oldroyd-B	$0.1 Wi < 3$	$Re = 0$	2D constitutive equations for the Oldroyd-B model were implemented. A sharp decrease in vortex length is observed for increasing Wi .
Alves <i>et al.</i>	2004 [Alves <i>et al.</i> 2004]	P	4, 10, 20, 40, 100	PTT	$0 < Wi < 250$	$Re = 0$	For $\beta > 4$, vortex length increased with a lip-vortex mechanism. For $\beta > 10$, the lip vortex was dependent on the downstream length scales, while the corner vortex was scaled with upstream length scales.
Alves <i>et al.</i>	2003 [Alves <i>et al.</i> 2003]	P	4	Oldroyd-B and PTT	(Oldroyd-B) $0 < Wi < 2.5$; (linear PTT) $1 < Wi < 100$	$Re = 0$	The corner vortex decreased with increasing elasticity or Wi . Model unable to predict lip vortices and pressure drop (predicted negative Couette correction coefficient).
Kwon <i>et al.</i>	2003 [Kwon <i>et al.</i> 2003]	P	4	Leonov	$De \approx 200$	$Re = 0$	The rational interpolation of both elastic strain and velocity results in severe distortion of solution, implying only applicable for applications with negligible strain effects.

Philips and Williams	2002 [Philips and Williams 2002]	P and A	4	Oldroyd-B	$0 < Wi < 1.5$	$0 < Re < 1$	Corner vortices were suppressed by inertial effects in both configurations. The size and intensity of the vortex growth occurred in axisymmetric geometry while opposite occurs in planar contraction.
Aboubacar and Webster	2002 [Aboubacar <i>et al.</i> 2002]	P and A (Sharp and rounded corner)	4	Oldroyd-B and PT (linear and exponential with $\varepsilon=0.02$ & 0.25)	$0.1 Wi < 50$	$Re = 0$	For oldroyd –B model, vortex enhancement observed in axisymmetric flows, and vortex reduction in planar flow. For PT, both vortex enhancement and inhibition were observed.
Aboubacar and Webster	2001 [Aboubacar and Webster 2001]	P	4	Oldroyd-B	$0 < Wi < 3.7$	$Re = 0$	The corner vortex decreased with increasing elasticity or Wi , while Lip vortex occurred in opposite for $Wi > 1$. Lip vortex reduction with mesh refinement was observed.
Alves <i>et al.</i>	2000 [Alves <i>et al.</i> 2000]	P	4	UCM	$De \approx 5$	$Re \approx 0$	As De increased, the size and strength of corner vortex were found to decrease, and lip vortex to increase. When $De = 5$, the tow vortices merged together, with the lip vortex still being dominant and then start growing as a single remaining vortex.
Philips and Williams	1999 [Philips and Williams 1999]	P	4	Oldroyd-B	$0 \leq Wi \leq 2.5$	$0 < Re < 1$	For $Re = 0$, the corner vortex decreased slightly with Wi increase for $0 \leq Wi \leq 1.5$ before increasing when $Wi > 1.5$. Lip vortex is formed at $Wi \geq 2$. For $Re = 1$, Corner vortex decreased with increasing Wi . Size of vortex was reduced approx. 20% in $Re = 0$ case. Weak lip vortex was detected at $Wi = 2.5$.

Xue <i>et al.</i>	1998 [Xue <i>et al.</i> 1998]	P	4	UCM and PTT	$0.4 < Wi < 2.9$	$0.08 < Re < 0.56$	3D FVM for the simulation of time-dependent incompressible viscoelastic flow is reported.
Mompean and Deville	1997 [Mompean and Deville 1997]	P	4	Oldroyd-B	$0.15 < De < 27.3$	$Re = 0.1$	The size of the corner vortex in the 3D case was always smaller than the 2D. No lip vortex was observed in the range of De investigated.
Purnode and Crochet	1996 [Purnode and Crochet 1996]	P	4, 16, 80	PENE-P	$0.033 < Wi < 145$	$3 \times 10^{-5} < Re < 6.37$	Reducing the concentration of polyacrylamide (from 1% to 0.5%) led to a strengthening of the salient corner vortex with no lip vortex. However, further reduction (0.25%) led to a convex lip vortex appears at the re-entrant corner.
Baloch <i>et al.</i>	1996 [Baloch <i>et al.</i> 1996]	P (expansion and contraction)	4, 13.3, 40, 80	PTT	(Expansion) $1 < Wi < 2$; (Contraction) $1 < Wi < 25$	(Expansion) $1 < Re < 4$ (Contraction) $Re = 1$	For planar contraction, $Re = 1$, lip vortex was observed at $Wi = 5$. Increasing the density of melt was observed to delay the onset of the lip vortex to $Wi = 20$.
Sato and Richardson	1994 [Sato and Richardson 1994]	P	4	UCM and Oldroyd-B	$0 < Wi < 2$	$Re = 1$	Vorticity separation from a re-entrant corner and a temporary lip vortex in transient flow induced by an instantaneous increase of Wi . This finding is due to numerical artifacts.

CHAPTER 3

MIXING OF MISCIBLE LIQUIDS

Efficient and effective mixing is often important to the effective functioning of microfluidic devices in real-world applications [Ottino and Wiggins 2004]. A brief review on microfluidic mixers and their mixing principles, particularly miscible liquids, is presented in this chapter. Typical mixing element designs, methods for mixing characterization, and fields of application are also covered. Readers are also referred to the two recent review articles by Nguyen *et al.* [Nguyen and Wu 2005] and Hessel *et al.* [Hessel *et al.* 2005] for more comprehensive discussions of the current stage of microfluidic mixers. In brief, the basic design principles of micromixers are to increase the concentration gradient or the interfacial contact area between the two mixing liquids, resulting in the reduction of mixing length and mixing time. The two mixing techniques commonly employed at microscale are: (i) Active-mixing methods in which mixing enhancement is achieved by flow disturbance generated from external energy sources (e.g. oscillatory forcing mechanically or electrically). (ii) Passive-mixing methods in which mixing enhancement results from the interaction of the externally driven flow (e.g. pressure-driven or electroosmosis-driven) with specific designed channel geometry. The mixer designs based on these two methods are commonly termed as active and passive micromixers, respectively. In this thesis more attentions are given to passive micromixers.

3.1 Types of Microfluidic Mixers and its Application Fields

Microfluidic mixing technology has received enormous attention and rapid development in the past few years. Typically, based on fields of application, microfluidic mixers can be classified into two main groups. (i) Micromixing element – commonly found in micro total analysis system (μ TAS) applications as a part of an integrated system. μ TAS requires integrated mixing units capable of mixing small sample volumes in a short time and mixing length, particularly for specialized applications such as sample preparation for initiation in pharmaceutical, chemical and biological analyze. (ii) Microreactors – commonly employed in chemical processing as a reacting unit (single purpose LOCs) for either laboratory-scale applications (appear as chip-like components, for brevity termed as micromixers) or production-scale applications (appear in much larger components which comprise microstructured units in large housings). Generally, microreactors possess slightly different requirements because the typical flowrates and fluid volumes involved are usually much larger than those in μ TAS. Hitherto microreactors were widely used for prevalent mixing tasks like chemical reaction, synthesis, gas-absorption, foaming, emulsification and blending [Hessel *et al.* 2005].

Micromixing elements, micromixers and microstructured mixers typically have flowrates in the sub ml/h, ml/h – l/h and 10-10,000 l/h ranges, respectively, which covered the whole flow range up to the conventional static mixers. Furthermore, being amenable to analysis and production, the field of microfluidic mixers is currently evolving from a scientific craze to a key enabling technology for applications in life sciences and chemical engineering.

3.2 Motivations for Mixing in Small Space

Mixing has been carried out in a stirred vessel over many decades and most of the mixing problems were avoided by using pre-mixing operation as a starting condition. In addition, the

general perception towards mixing is easy and simple and all the necessary knowledge is available in text book. As such the myth continues to plague the development of microfluidic technology towards a true μ TAS device.

Indeed, mixing of miscible liquids in micro-lengthscale is one challenging aspect of microfluidic science. In most circumstances, μ TAS and microreactor applications are subjected to small Reynolds number (Re) due to small channel dimensions. Typically, Re is of the order of 100 for microreactor and in the order of 10 for μ TAS. Laminar flow is expected as generally transition turbulent in a pipe occurs at $Re > 2300$, and fully developed turbulence is often found at much higher Re. Therefore, to induce turbulence to achieve mixing in μ TAS is perceived to be impractical. As a result microfluidic mixing is generally achieved by diffusion mechanism. Diffusive mixing in laminar flows is notoriously slow. A different approach that bypasses the limitation of a low Reynolds number, yet provides efficient mixing, will be a significant improvement for microfluidic mixing, with immense implications for the development of μ TAS and LOC.

Microfluidic mixers have obvious benefit that only small sample volumes are involved. They are particularly useful in handling hazardous chemical reaction [Hass-Santo 2001, Veser 2001, Hessel *et al.* 2004] as well as rare, precious samples or numerous samples on a small format in chemical and biological analyze which will benefit from the mixing of small volumes.

3.3 Mixing Principles

Basically, mixing comprises three mass transfer mechanisms – molecular diffusion, eddy diffusion and bulk diffusion. On a macro lengthscale, large eddies and bulk diffusion dominate in an induced turbulent flow while molecular diffusion is insignificant. However, on a micro lengthscale, molecular diffusion becomes dominant while eddy diffusion and bulk diffusion

components are impeded. Time inefficiency is one of the major problems with molecular diffusion; the speed of mixing is notoriously limited. Hence, by shrinking existing macroscale devices to microscale and expecting them to function properly is often counterproductive, one must first understand the peculiar physical phenomena that dominate at micro lengthscale while working with micromixers.

3.3.1 Dimensionless Parameters

Reynolds number (Re), Peclet number (Pe) and Strouhal number (St) are commonly used as dimensionless parameters to characterize convective-diffusive mixing process.

(i) Reynolds number describes the relative importance of inertial and viscous effects in a fluid flow, which is commonly used to characterize the onset of flow instability for Newtonian solution. It is named after Osborne Reynolds (1842 - 1912), who proposed it in 1883, typically it is expressed as,

$$Re = \frac{\rho \bar{V} d}{\eta_0} \quad (3.1)$$

where ρ , $\bar{V}$, d , and η_0 are the fluid density, the average velocity, the characteristic length (e.g. hydraulic diameter), and the viscosity, respectively.

(ii) Peclet number indicates the relative importance of convection (advection) to diffusion. Convection is dominant at higher Peclet number. Peclet number can be expressed as,

$$Pe = \frac{\bar{V} d}{D} \quad (3.2)$$

where d is the characteristic dimension or the transverse diffusion distance and D is the diffusion coefficient.

For laminar uni-axial flows in a microchannel, the mixing length L_m is directly proportional to the product of Pe and channel width.

(iii) Strouhal number indicates the relative importance of the residence time of a species to the time period of its disturbance, particularly in active mixing. Often it is given by

$$St = \frac{f_d d}{\bar{V}} \quad (3.3)$$

where f_d is the disturbance frequency.

3.3.2 Laminar Flow

In fluid mechanics, Reynolds number, particularly for Newtonian fluids, is generally used to characterize the different flow regimes, such as laminar ($Re < 2100$), laminar to turbulent transition ($2100 < Re < 3000$) or turbulent flow ($Re > 3000$). In μ TAS or LOCs fluid dynamic, microscale dimensions lead to a small Reynolds number ($Re < O(1)$), where viscous effects become dominant and suppress chaotic or turbulent flow instabilities. Typical flow of a Newtonian fluid in microchannels is then confined within the laminar flow regime where the flow velocity is not a random function of time. Moreover, for small volume of liquids flows in a microchannel, the interaction between a fluid and the channel wall increases enormously, the surface to volume (SAV) ratio increases tremendously compared to that at macroscopic level. In the absence of turbulence, it is difficult to increase the interfacial area of contact for segregate-streams to mix on microscale efficiently. Consequently, mixing of multiple streams in microchannels is generally achieved by diffusion, convection or a combination of the two. However, small spatial scale and short mixing time requirements render it ineffective.

3.3.3 Diffusion Mechanism

Diffusion is a process by which a concentrated group of species in a confined volume, by Brownian motion, spread out over time so that the average concentration of specie throughout the whole sample space is constant.

According to Fick's law, diffusion flux can be modeled as

$$\phi = -D \cdot A_s \cdot \nabla c \quad (3.4)$$

where D is the diffusion coefficient [m^2/s], A_s is the interfacial area [m^2] and ∇c is the specie concentration gradient [kg/m^3].

For simplicity, diffusion can be modeled in one-dimension by

$$l_d^2 = 2Dt_{diff} \quad (3.5)$$

where l_d is the diffusion distance (or particle displacement by diffusion) over time t_{diff} .

As described by equation (3.5), diffusion across laminar streams is slow because the mixing time, t_{diff} , is proportional to the square of the initial striation length, l_c , the distance over which mixing occurs by diffusion with a diffusion coefficient, D [Song *et al.* 2003]. Thus, in order to mix two protein solutions with a diffusion coefficient $D = 2 \times 10^{-11} \text{ m}^2/\text{s}$ at a constant flowrate of 1 mm/s in a 100 μm characteristic dimension microchannel, a channel length ($= 0.5vl_c^2/D$) of 25 cm is required [Chen and Meiners 2004].

In addition, when solute molecules diffuse through liquid medium, solvent molecules must be displaced out of the way. As such, liquid-phase inter-diffusion coefficients are inversely proportional to both the viscosity of the solvent and the effective radius of the solute molecules [Einstein 1956].

Clearly, diffusive mixing can be enhanced by optimizing its constituting factors, such as increased diffusion coefficient, decreased characteristic distance or striation thickness, i.e. reducing the diffusive time scales and increasing the interfacial areas. For example, by invoking an external energy source, i.e. employing an active mixing method, to increase the system temperature, it will increase the diffusion coefficient and thus the diffusion mixing can

be enhanced [Crank 1956]. The diffusion coefficient as a function of temperature can be expressed as

$$D = D_0 e^{-\frac{E_A}{RT}} \quad (3.6)$$

where D is the diffusion coefficient, D_0 is the maximum diffusion coefficient (at infinite temperature), E_A is the activation energy for diffusion, T is the temperature, R is the gas constant.

3.3.4 Convective Diffusion Mechanism

Diffusion on microscale is faster compared to that on macroscale. However, the flows are inherently viscous-dominated with large surface to volume effects. In steady and stable laminar flows, it is difficult to increase the interfacial contact area of separate streams through molecular diffusion. Consequently, molecular diffusion is inefficient and ineffective for continuous mixing on microscale, especially for short mixing length and time requirements.

Convection mechanism – another mechanism which can increase the interfacial area of two segregated streams, co-exists with diffusion in a mixing process. However, skillful combinations of convection and diffusion are required, and complex geometrical configurations are necessary, in order to reduce the mixing time to a desired level. Typically convective-diffusion mixing was achieved through secondary-flow patterns superposed to the main flow or recirculation patterns within liquids plugs of segmented liquid/liquid flows [Ottino 1989]. By distorting the lamellae arrangements into whorl-, tendril-, or striation-like shapes, the interfacial areas and the concentration gradient are thereby improved due to the reduction of the striation thickness. In fact, transverse flow is generated from the physical distortion of lamellae streams (convective diffusion effects) with the characteristic mixing length reduces accordingly, thus mixing time can be shorten to an acceptable level.

3.4 Mixing Methods and Exemplary Devices

Micromixers require a hybrid mixing mechanism of convection and diffusion because of low Reynolds number inherent to a micro-lengthscale and the absence of turbulence or chaotic instability. Numerous ingenious micromixer designs have been developed and attempted to bypass the limitations imposed by the laminarity of microfluidic flows.

3.4.1 Mixing Methodology

Certain nomenclature nuances have to be clarified, particularly on the definition of mixing processes and mixing devices, to avoid any confusion because they have very different meanings at different contexts.

(a) Mixing processes: Active mixing refers to the flow processes in which the interaction between the axial-flow and the stream contact interfaces eventually modifies the axial-flow streamlines, while passive mixing refers to the flow processes in which the segregate streams interfaces follow the flow without changing the axial-flow streamlines [Ottino 1989].

(b) Mixing devices (micromixers): (i) Active micromixers are those with additional external energy source to the basic flow energy to generate flow disturbance for the enhancement of mixing. The energy sources are either from externally applied forcing functions or from the propulsion of mechanical moving parts, such as acoustics [Yang *et al.* 2000, Yang *et al.* 2001, Sritharan *et al.* 2006], electrohydrodynamics [Tsouris *et al.* 2003], electrokinetics [Jacobson *et al.* 1999, Oddy *et al.* 2001, Stroock *et al.* 2002, Shin *et al.* 2005, Sasaki *et al.* 2006], bubble-burst perturbation [Liu *et al.* 2002, Liu *et al.* 2003], integrated microvalves/pumps [Voldman *et al.* 2000], micro-impellers [Lu *et al.* 2002], magneto-hydrodynamics [West *et al.* 2002, Yi *et al.* 2002, Bau *et al.* 2001], periodical injections [Nguyen and Huang 2005] and thermal actuations.

(ii) Passive micromixers are those with solely the basic flow energy (e.g. mechanical-, electrokinetic- or hydrostatic potential- driven) with its specific designed channel geometry. These types of mixers do not have moving parts and mixing is achieved by virtue of their topology alone. Mixing relies entirely on diffusion or chaotic advection (convection). Examples are (i) Serial lamination or Split-and-Recombine (SAR) flow guidance for creating multi-lamellae along the flow [Schwesinger *et al.* 1996, Liu *et al.* 2000, Chen and Meiners 2004, Schönfeld *et al.* 2004]. (ii) Lamellae injection of streams, which is different from the previous examples in that the lamellae stream is formed at the inlet section [Bessoth *et al.* 1999, Hessel *et al.* 2003, Löb *et al.* 2004, Drese 2003]. (iii) Splitting and folding of flow streams through delicate 3D micro-geometry configurations [Chen and Meiners 2004]. (iv) Chaotic mixing creating eddy-based flow patterns which provide larger contact interfaces, albeit bearing the danger of being spatially inhomogeneous, by means of redirecting or diverting of flows through number of specialty micro-geometries [Liu *et al.* 2000, He *et al.* 2001, Ottino and Wiggins 2004, Chen and Meiners 2004, Simonnet and Groisman 2005, Sudarsan and Ugaz 2006, Stroock *et al.* 2002, Stroock *et al.* 2002, Niu and Lee 2003, Jen *et al.* 2003, Solomon and Mezic 2003, Jiang *et al.* 2004]. (v) Droplet mixing by forming droplets of to-be-mixed fluids, which reduce the mixing path [Song *et al.* 2003] and (vi) Turbulent mixing by collision of jets [Hessel *et al.* 2005].

In principle, one can have passive mixing in active mixer or vice versa. For conciseness, in the following chapters we will use the terms active and passive, only for the context of mixing devices. Classification of micromixers based on its mixing technique is summarized in Figure 3-1. Selected categories will be presented in the subsequent section.

Figure 3-1. Classification of micromixers based on its mixing techniques.

3.4.2 Active Micromixers

In spite of the setup cost and their complex fabrication and control, which are often needed, the advantage of controllability makes the active micromixers a candidate to be considered in microfluidic technology. Active micromixers can be controlled externally which makes them favorable components of reconfigurable μ TAS and LOCs, where the system can perform several different functions by programming different states of control.

Laminar chaos has been exploited in active-mixer designs that utilize local forcing within the fluid carrying system. These mixers can further be categorized according to the source of the additional energy, i.e. either from mechanical moving parts or from an externally applied forcing function.

A) MECHANICAL STIRRING

Stirring in vessel mechanically, e.g. by mean of rotating impellers, is one of the simplest and prevalent mixing methods. A 3×3 array of magnetic rotary microimpellers developed by Lu *et al.* [Lu *et al.* 2002] were powered by an external, rotating magnetic field, see Figure 3-2. These microimpellers of several tens microns in diameter were made by electroplating from the ferromagnetic material Permalloy. They consisted of a cap, hub, and two rotary blades. The micromachined impeller was inserted at the interface between the two segregated streams in a T-mixer. For a rotational speed of 600 rpm, complete mixing (defined as mixing index < 0.2) of a $0.2 \mu\text{L}$ sample volume (mixing chamber volume) was achieved within a minute from onset of stirring.

Figure 3-2. Schematic diagram of a single microstirrer in the fluidic device. The rotating bar is prevented from leaving the substrate by a hub [Lu *et al.* 2002].

B) ACOUSTIC DISTURBANCE

A micromixer using direct ultrasonic vibration for mixing enhancement was demonstrated by Zhu and Kim [Zhu and Kim 1998], see Figure 3-3. High intensity of bursts of acoustic waves generated by piezoelectric transducer (PZT), produces strong fluid movement resulting in mixing was reported. The PZT was fixed at the solid-liquid interface at the bottom of the mixing chamber. As the waves propagated through the chamber, they generated vertical and lateral motions throughout the fluid. Effective mixing was observed with resonance frequencies of the thickness-mode vibration of the piezoelectric film (e.g. 240 MHz and 480

MHz). The mixer operated with negligible energy consumption and temperature rise, thus it could be used for temperature-sensitive fluids. Another similar device was developed with an oscillating, silicon diaphragm driven by a PZT transducer [Yang *et al.* 2000]. The diaphragm was bonded to a mixing chamber etched out of glass. When the transducer was operated at a frequency of 48 kHz, it generated ultrasonic vibrations which caused strong disturbance in the fluid and promoted effective mixing within 2 seconds. There are other similar ultrasonic micromixers developed based on piezoelectrical actuation [Yang *et al.* 2000, Yang *et al.* 2001]. Another approach to acoustical micromixing is by means of acoustic disturbance to induce bubble actuation within the mixing space [Liu *et al.* 2002, Liu *et al.* 2003]. An air bubble or droplet can act as an actuator when it is energized by an acoustic field. Bubble vibration due to acoustic waves induces frictional forces at the air/liquid interface which cause a bulk fluid to flow around it. This phenomenon was termed as acoustic microstreaming or cavitation microstreaming. In this design, an array of small air bubbles was resting at the bottom of the mixing chamber. When the bubbles were made to vibrate, they created steady circular flows around them. When PZT vibrated at 5 kHz, mixing in a 50 μl chamber was achieved within a few seconds [Liu *et al.* 2003]. The performance of this micromixer was also validated by applying it for polymerase chain reaction (PCR) and the results showed that it was five times faster than that of a conventional large-scale device. In more recent study, pronounced microstreaming effects induced by the interaction between surface acoustic waves (SAWs) and two segregated streams confined to a Y-micromixer was reported [Sritharan *et al.* 2006]. Internal stirring to the flow system generated by SAWs and good mixing were achieved. Acoustical agitation was generated by the interdigital transducers (IDTs) which was attached to the glass substrate and positioned at the junction of two inlets. Complete mixing was achieved at a distance of 2 mm downstream of the junction with acoustic waves at 146 Hz and a steady flow velocity of 250 $\mu\text{m/s}$.

Figure 3-3. Cross-section view (along with typical liquid-flow direction) of the liquid mixer. The electrode pattern of the transducer to form the acoustic-wave sources for constructive wave interference in the liquid is shown [Zhu and Kim 1998].

C) MAGNETO HYDRODYNAMIC (MHD) DISTURBANCE

An active micromixer has been developed by coupling the electric and magnetic fields to create Lorentz forces which in turn induced MHD flows in an electrolyte [Bau *et al.* 2001], see Figure 3-4. The device was fabricated by mean of low-temperature co-fired ceramic (LTCC) method. The Lorentz forces were induced parallel to the axis of the mixing chamber to roll and fold the liquids in the chamber. Liquids were mixed within several seconds. However, it only works with ionic solutions. A similar device was demonstrated by West *et al.* 2002 [West *et al.* 2002]. Mixing chamber wall was deposited with arrays of electrodes. With an arrangement of alternate potential differences across pairs of electrodes, electrical current in various directions (alternately in this case) of the mixing sample was generated. Hence, a cellular motion was initiated to enlarge the fluid interfaces for effective mixing.

et al. 2003] proposed another method solely based on EHD flows to efficiently mix segregated streams in microchannels. This device used a direct electrical current for the development of EHD flows. Electrostatic forces were identified to be the main cause of this motion because the polarization forces (dielectrophoretic) was negligible, if any, unless alternating currents (AC) were applied.

El Moutar *et al.* [El Moutar *et al.* 2003] induced EHD instability in a T-channel by generating a transversal secondary flow, see Figure 3-5. Four pairs of electrodes were placed along the mixing channel so that the electric field was perpendicular to the interface of two segregated streams. With AC field at sufficiently high frequency (35 Hz) and differential voltage strength of 300 V / 250 μm , good mixing was achieved at $\text{Re} < 0.02$ within 0.1 s without electrolysis taking place.

Figure 3-5. Configuration of the flow: the microchannel, the electrodes, and the two fluids used [El Moutar *et al.* 2003].

E) ELECTROKINETIC (EK) DISTURBANCE

EK disturbance micromixer employs electroosmotic flow, either by DC or AC, to create flow instabilities resulting in rapid stretching and folding of the fluid and mixing enhancement. Jacobson *et al.* [Jacobson *et al.* 1999] proposed two designs based on T-intersections microfluidic manifold with the desired voltage division, i.e. series and parallel mixing schemes,

to promote mixing electrokinetically. Only one DC voltage source was required to transport and mix the fluidic streams.

In a different approach [Oddy *et al.* 2001], mixing was accomplished by the action of oscillatory electroosmotic flow in a mixing chamber which was induced by an AC-voltage supplied. Rapid stretching and folding of streamlines were generated. Two micromixers were developed, one generated electrokinetic instability throughout the entire channel and the other confined the instability to a small mixing chamber. Effective mixing was attained within 3 s for a volumetric flow of 0.5 $\mu\text{L}/\text{min}$.

More recently, a time-periodic electric field was introduced to excite the electrokinetic instability in a cross channel (or T channel) [Shin *et al.* 2005]. A function generator coupled with a dc-power supply was connected to the main reservoir corresponding to the outlet reservoir to produce the time-periodic electric field. Only static potential (dc-power supply) was applied to both side-reservoirs corresponding to the outlet reservoir. It was found that instability was most agitated when the period of the applied electric field was approaching to half of the period of instability in the form of a sinusoidal wave generated.

F) THERMAL DISTURBANCE

From equation (3.6), diffusive mixing can be enhanced by invoking thermal energy to alter the diffusion coefficient of a fluid to a higher value [Mao *et al.* 2002], see Figure 3-6. For example, the viscosity of water is about a factor of 4 greater at 8 $^{\circ}\text{C}$ than it is at 80 $^{\circ}\text{C}$.

An active microfluidic mixing system based on thermal energy disturbance was proposed by Tsai and Lin [Tsai and Lin 2002]. The oscillatory flow motion was generated, by mean of the thermal bubble agitation mechanism, in the direction perpendicular to the interface between the two laminar streams. These transverse flows increased the contact area between the fluids and thus promoted effective mixing. At a flow of 6.5 $\mu\text{L}/\text{min}$ and at a pulse frequency of ~ 200 Hz, the system achieved effective mixing through a channel length of 10 mm.

Figure 3-6. Illustration of the concept of a linear temperature gradient microfluidic system. The array of microfluidic channels sits between a hot source on the left and a cold sink on the right. q_x designates the direction of heat flow. The temperature varies linearly between the parallel heat source and sink where the portion of the device containing the linear array of microchannels is situated. Inside the heat source and sink the temperature gradient is nonlinear as heat is added and carried away, respectively [Mao *et al.* 2002].

G) ALTERNATING FLOW DISTURBANCE

One of the most direct and simple methods to achieve active mixing in microchannels is by alternating or periodical injection of sample fluids. Glasgow *et al.* [Glasgow and Aubry 2003] demonstrated a simple T-mixer and its simulation with a pulsed side flow at a small Reynolds number of 0.3. Time pulsing of one inlet flowrate distorts the interface of the flow streams, and transverse dispersion was generated. This increased the contact area between the fluids and thus promoted effective mixing. Best mixing was observed for two pulsed inlet flows with 180 ° phase shift. This mixing approach could be extended to multiple, pulsing flow injections [Niu and Lee 2003] and chaotic advection could be generated. However, it required a sophisticated control system.

3.4.3 Passive Micromixers

Passive mixers employ channel geometry to either laminate the segregated fluids in plane or out-of-plane to promote chaotic advection in the flowing streams. Both approaches lead to an increase in the interfacial contact areas and resulting in better mixing. The ease of integration (to μ TAS or LOCs) due to the lack of moving parts, free of additional friction and wear-and-tear effects, however, is somewhat offset by their intricate channel topologies which are often costly and hard to fabricate. Passive can be broadly sub-classified into designs based on lamination and chaotic advection (folding and stretching) techniques.

Lamination based mixers rely on the concept of repeated inter-layering of multiple parallel flow streams in order to increase the interfacial contact areas between streams and accelerate the diffusive transport process. Numerous parallel and serial lamination-based mixers have been proposed and investigated. Chaotic advection based mixers rely on special channel geometry to generate transverse flows across the channel cross-section. For example, 3D serpentine-, spiral -shaped flow geometry or patterning the channel walls with oblique grooves or ridges to generate lateral flows to repeatedly stretch and fold fluid segments across the channel cross-section.

A) PARALLEL LAMINATION MIXING

The configuration of the micromixers is based on the principle of distributive mixing. Referring to equation (3.5), the diffusion time is proportional to the square of the diffusion distance. Thus, by sub-dividing the flows of segregated fluids to be mixed, and rearranging them in alternating thin lamella, will significantly decrease the mixing times. Indeed, the mixing path in the transversal direction (i.e. the characteristic width in Pe) is then shortened. Theoretically, a subdivision of each stream into n lamella leads to n^2 -times faster mixing [Bessoth *et al.* 1999]. There are several methods to shorten the transversal mixing path, such as narrowing the mixing channel, hydrodynamic focusing, and lamellae flow injections. In these micromixers,

although chaotic flow for effective mixing could be generated for very high velocity on order of m/s [Nguyen and Wu 2005], the required high pressure becomes a challenging issue for bonding and inter-connection to the peripheral instruments. Figure 3-7 shows some of the typical parallel lamination micromixer designs. More details will be discussed in the following sections.

Figure 3-7. Parallel lamination micromixer: (a) the basic T-mixer and (b) Y-mixer, (c) concept of parallel lamination, (d) concept of hydraulic focusing [Nguyen and Wu 2005].

i. T- and Y- Type Lamination Mixing

The basic design of parallel lamination –based mixers is a long microchannel with two inlets ($n = 2$). Consider a simple laminar flow case, the mixing length by molecular diffusion can be estimated by the product of Peclet number and the channel width ($Pe \times W$). As a result, long channel and slow flowrate are generally required to improve diffusive mixing in these types of mixers. Based on the inlet channels orientation, these $n = 2$ designs are generally named as T-mixer or Y-mixer, see Figures 3-7(a) and (b).

Details of the Y-type configurations have been studied by Gobby *et al.* [Gobby *et al.* 2001] numerically for the mixing process of oxygen and methanol. The Y-intersection configuration (arrangement and orientation) showed a significant impact on the mixing performance. The venturi-type (throttling the channel entrance) Y-mixer with a throttle of 100 μm diameters was

estimated to have a 500 μm mixing length which was four times faster than conventional orientations. In this design, somewhat converging/diverging flow was induced and, consequently, enhances transverse dispersion in the flow streams. Throttling channel in fact is another method to improve T-mixer performance. This concept has been demonstrated by narrowing the channel at mixing chamber which results in a reduction in the mixing path for segregated streams [Veenstra *et al.* 1999].

There are some other designs which can further enhance T-mixer performance, such as roughening the channel wall, patterning the channel walls with oblique grooves, ridges or obstacles to generate chaotic advection. All these designs are classified under other types of passive mixers which will be discussed in the following sections.

ii. Multi-Lamination Mixing

Multi-laminating mixing can be achieved by employing different types of sample injection arrangements, see Figure 3-7(c). For example bifurcation-type of injection, which was demonstrated by Bessoth *et al.* [Bessoth *et al.* 1999], created an alternated arrangement of injection lamellae. Both sample liquids to be mixed, i.e. liquid A and liquid B, were split into 16 partial flows by repeatedly bifurcating the channels. Both 16 partial flows of liquids A and B then sequentially combined two neighboring channels into one and this combination was repeated until all partial flows were united in one broad outlet channel. The mixing path was then shortened in the transversal direction by narrowing the mixing channel. The outlet channel was very long, so as to give enough time for further diffusion. 95% of mixing level was achieved within 15 ms.

In fact, one of the simplest method to obtain rapid mixing in microchannels is to have a narrow mixing channel [Veenstra *et al.* 1999] to reduce the mixing path. However, the advantage is somewhat offset by the cost of microfabrication. An alternative method to achieve a short mixing path is by hydraulic focusing [Knight *et al.* 1998, Weigl and Yager 1999, Wu and Nguyen 2005], see Figure 3-7(d). This idea has been demonstrated to reduce the effective

mixing time to the order of few microseconds [Knight *et al.* 1998]. However, the major drawbacks of this method are that the sample fluid would diffuse into the sheath flows and the focusing ratio is constrained by the applied flowrate or pressure. These drawbacks limit the implementation of hydraulic focusing to actual μ TAS.

SuperFocus -- a special liquid focusing interdigital mixer with parallel injection of streams, is another approach of multi-lamination mixing which is commonly found in chemical reaction applications [Hessel *et al.* 2003]. These types of mixer significantly enhance diffusive mixing by coupling the parallel-flow interdigital injection arrangement with the hydro-focusing flow mechanisms. Typically, the sample fluids were primed into the mixers in an alternating lamellae arrangement by means of special design injection conduits. Subsequently, hydro-focusing concept was employed for accelerating lamellae mixing. The multi-laminated flows were focused by posing geometric constraints (typically a triangular focusing chamber). This compresses the lamellae streams into a relatively small channel. As such the diffusion distance was reduced to a few μm and, consequently achieved complete mixing in the milliseconds range. Some similar mixers, e.g. Counter-flow interdigital mixers, Cyclone mixers, StarLamiators, have been demonstrated; more comprehensive discussions can be found in the review article of Hessel *et al.* [Hessel *et al.* 2005].

B) SERIAL LAMINATION MIXING

Serial lamination micromixers, or known as Split-and-Recombine (SAR) mixers, create multi-laminating patterns sequentially along the flow path, see Figure 3-8. This is different from the parallel lamination approach which imposes lamellae injection at the entrance of the mixing chamber. The idea of serial lamination mixing was suggested by Schwesinger *et al.* [Schwesinger *et al.* 1996] and Branebjerg *et al.* [Branebjerg *et al.* 1996]. Basically, it can be divided into three steps: flow splitting, flow recombination and flow arrangement [Hessel *et al.* 2005].

Usually, the streams are first primed into a common horizontal channel. Subsequently one or both of the streams are twisted vertically to initiate separation, followed by a sequence of turns (*m*-splitting) to finally re-joining the fluids and creating alternating lamellae streams. This process leads to 4times improvement in mixing time. Schonfeld *et al.* [Schönfeld *et al.* 2004] designed a split-and-recombine mixer incorporating minimal channel curvature capable of generating nearly ideal lamellae profiles. However, in addition to the complex and costly fabrication steps involved, the footprints occupied by these channels do not make them conducive for integration into μ TAS. Recently, the same approach was realized on lamination of multiple polymer layers [Munson and Yager 2004]. Figure 3-8 shows some of the typical designs for serial lamination micromixers mentioned previously.

Figure 3-8. Serial lamination mixer. (a) join-split-join, (b) split-join, (c) split-split-join, (d) multiple intersecting microchannel [Nguyen and Wu 2005].

C) CHAOTIC ADVECTION MIXING

Micromixers based on chaotic advection is similar to their macroscopic counterparts, which are well documented in the reference text “The Kinematics of Mixing: Stretching, Chaos, and Transport” [Ottino 1989]. The basic idea is to generate chaos advection along the flow path by

stretching, folding and breaking of the flow through specially designed channel geometrical configuration. In the following discussions, we categorized the mixers into three different ranges of Re : (i) high Re ranges, $Re > 100$, (ii) intermediate Re ranges, $10 < Re < 100$, and (iii) low Re ranges, $Re < 10$. More comprehensive discussions can be found in the review article by Nguyen and Wu [Nguyen and Wu 2005].

i. Chaotic Advection at High Reynolds Number ($Re > 100$)

An easier method to generate chaotic advection in microchannels is by employing zigzag geometry configuration to produce recirculation flow patterns, i.e. hydrodynamic flow eddies, at the channel recesses (i.e. at the turning corner) at high Reynolds numbers [Mengeaud *et al.* 2002], see Figure 3-9(a). Mixing in different zigzag microchannels has been studied based on finite element simulation. For higher Reynolds numbers (e.g. $Re \sim 267$) mixing performance is enhanced by the effects of laminar recirculation along the channel, while $Re < Re_{crit} \approx 80$, the flow profile remains parabolic and mixing is only ensured by molecular diffusion. These recirculations induce a transversal component of the velocity and greatly improve the mixing efficiency as compared to an equivalent straight channel. Moreover, for a large angle of turning, the geometry would induce a larger effective width and result in poor mixing efficiency.

Another approach to generate chaotic advection is by physical obstructions to the flow streams, particularly by inserting obstacles along the mixing channel, see Figure 3-9(b). Lin *et al.* [Lin *et al.* 2003] coupled the effects of physical obstruction and narrow channel (5:1 contraction ratio) to generate chaotic advection for effective mixing. Seven cylindrical pillars ($\sim 10 \mu m$ in diameter) were placed at the upstream mixing channel with dimension of $50 \mu m \times 100 \mu m \times 100 \mu m$. The flow was distorted and the fluids forced to interact and hence created transversal mass transport. The chaotic mixed fluids from the mixing chamber were subsequently compressed into a contraction channel ($10 \mu m$ in width) to further enhance the mixing quality.

This investigations showed that at low Reynolds numbers the obstacles in mixing chamber were not able to generate chaotic eddies or recirculations. However, at a constant flowrate of 20 m/s the mixing results were significantly improved due to the high Reynolds numbers generated. This micromixer worked with Reynolds numbers ranging from 200 to 2000, with a mixing time of 50 μ s.

Figure 3-9. Planar design for mixing with chaotic advection at high Re; (a) zig-zag shaped channel, and (b) obstacles in the channel [Nguyen and Wu 2005].

ii. Chaotic Advection at Intermediate Reynolds Number ($10 < Re < 100$)

A passive micromixer with recycling side-channels to re-direct the mixed streams (out from the mixing unit) back to the inlet flow was proposed by Jeon *et al.* [Jeon *et al.* 2005], see Figure 3-10(c). The proposed geometry required to repeatedly recycle the flow and achieve effective mixing was studied by CFD simulations. As a result of recycling the mixed streams back into the inlet flow, internal flow circulation was generated within each mixing unit. For complete mixing, five mixing units were required and connected in series. For a channel depth of 150 μ m, mixing efficiency was increased from 98.4 % to 98.6 % with an increase of Re from 28 to 42.

Indeed chaotic advection can be generated through three-dimensionally (3D) twisted conducts which stretch and fold the flow stream repeatedly [Liu *et al.* 2000, Vijayendran *et al.* 2003, Chen and Meiners 2004, Park *et al.* 2004], see Figures 3-10 (d,e,f,g). Liu *et al.* reported a 3D serpentine mixer design with a series of C-shaped units, see Figure 3-10(a). Basically, the micromixer can be divided into three section T-shaped inlet channel for two sample fluids, a straight channel of 7.5 mm in length, and six repeated mixing segments. The effective mixing length was 20 mm approximately. Mixing performance increased significantly with Re, the occurrence of chaotic advection was initiated at relatively high Reynolds numbers ($Re \sim 25$ to 70). The mixing performance of serpentine mixer mainly relied on the flow field being sufficiently ‘3-D’ to generate the secondary flows, and thus stretching and folding the fluid to greatly increase the interfacial areas.

Stretching and folding, diffusion, and breakup are three basic processes that occur while mixing fluids in 3D serpentine micromixers. Although stretching and folding the interface of two fluids by twisting enables mixing at microscale level in both low and high Re, twisting is not as effective at low Re as at high Re. Therefore, developing a rapid micromixer for microfluidic systems that can be used at low Re remains a challenging task.

Figure 3-10. 2-dimensional designs for mixing with chaotic advection at intermediate Re. (a) C-shape, (b) L-shape, (c) connected out of plane L-shape, (d,e,f,g) several designs of twisted microchannel [Nguyen and Wu 2005].

iii. Chaotic Advection at Low Reynolds Number ($Re < 10$)

Chaotic advection can also be generated by micromixers that pattern oblique grooves or ridges within the flow path on one side of the microchannel. By these obstructions, flow circulations can be generated and lead to an exponential increase of interfacial areas and hence to effective mixing.

Johnson *et al.* [Johnson *et al.* 2002] were believed to be the first reporting this phenomena. In their mixer design, a series of slanted grooves were laser ablated on the channel platform (bottom wall) at the junction of T-shaped micro-geometry. The presence of the grooves led to a high degree of lateral transport within the channel and rapid mixing of two confluent streams. High mixing efficiency (~80%) was achieved within 443 μm of the T-junction at a flowrate of 0.81 cm/s. Without the presence of the mixer and at the same flowrate, a channel length of 2.3 cm would be required to achieve the same mixing performance. While solely relying upon molecular diffusion, channel length of 6.9 cm would be required for 99% mixing.

Stroock *et al.* [Stroock *et al.* 2002] suggested staggered herringbone mixer (SHM), see Figure 3-11(c). High resolution cross-sectional flow images were presented, showing the onset folding of flow streams. The basic T mixer required a mixing length of 10 m for a Peclet number of 10^5 , while, using SHM the mixing length was shortened to 1.5 cm. The major effect of the herringbone structures was to deflect the flow in such a way that the interface area between the fluids increased and therefore mixing was enhanced. This flow pattern resulted in convective rolls in the cross section of the microchannel.

Figure 3-11. A microchannel with square grooves in the bottom wall. Below the channel to the right, the average flow profile in the cross section is drawn schematically. The ribbon indicates schematically a typical helical streamline in the channel [Stroock and Whitesides 2003].

Recently, Kim *et al.* [Kim *et al.* 2004] further extended the work of Stroock *et al.* to a new design known as embedded barriers micromixer (BEM). Chaotic flow was induced by periodic perturbation of the velocity field due to periodically inserted barriers along the top surface of the channel while a helical type of flow was obtained by slanted grooves on the bottom surface for a pressure driven flow. Imposing of barriers perturbation, the original elliptic mixing profile (using SHM) was transformed to a hyperbolic profile (using BEM).

Figure 3-12. Barrier embedded micromixer: (a) schematic view, (b) and (c) cross-sectional velocity fields at two typical locations. Slanted grooves patterned on the bottom wall cause helical flow the cross-sectional velocity field of which is schematically represented by (b) while the cross-sectional velocity field of (c) is obtained due to the existence of a barrier inserted on the top wall [Kim *et al.* 2004].

D) DROPLET MICROMIXERS

Another alternative method to reduce the mixing path is to encapsulate the liquids to be mixed into droplet-form. As the droplet is carried along with the carrier fluid, the movement of each droplet causes an internal flow field and allows mixing inside each droplet. Hosokawa *et al.* [Hosokawa *et al.* 1999] demonstrated the ability to form droplets using a hydrophobic microcapillary valve device and later transported, merged and actively mixed the droplets with the help of air pressure.

A few passive droplet mixers based on electro-wetting effects were also proposed. Pamula *et al.* [Pamula *et al.* 2001] employed an array of electrodes to actuate the droplets through electrowetting to coalesce. Subsequently, they [Paik *et al.* 2003] demonstrated an active droplet mixer using the same system, where coalesced droplets were oscillated among a linear array of electrodes, see Figure 3-13. Fowler *et al.* [Fowler *et al.* 2002] also developed a fast droplet mixer using similar electrowetting actuation to roll coalesced droplets in order to double the number of interfacial layers.

Figure 3-13. Side and top view of the electrowetting-based droplet mixer [Paik *et al.* 2003].

In addition, droplets can be generated due to the large difference of surface forces in a small channel with multiple immiscible phases such as oil/water or water/gas. Flow instability

between two immiscible liquids was also employed for micromixer design [Song *et al.* 2003, Tice *et al.* 2004]. Using a carrier liquid such as oil, droplets of the samples-to-be-mixed were formed. While moving through the microchannel, the shear force between the carrier liquid and the sample accelerated the mixing process within the droplet. See Figure 3-14 for the micromixer developed by Tice *et al.* (2004).

Figure 3-14. Mixing behavior in plug behaviors (a) when all three aqueous streams were non viscous and (b) when one of the aqueous stream was viscous [Tice *et al.* 2004].

3.5 Chaotic Mixing Based on Viscoelasticity

3.5.1 Overview of Viscoelasticity

It is known that a viscoelastic fluid, e.g. a liquid with a trace amount of highly deformable polymers, can lead to elastic flow instability at Reynolds number well below the transition number ($Re \approx 2000$) for turbulence flow. Such chaotic flow behavior was referred as elastic turbulence by Tordella [Tordella 1969]. Indeed, the proper characterization of viscoelastic flows requires an additional non-dimensional parameter, namely the Deborah number, De , which is the ratio of elastic to viscous forces. Viscoelastic fluids, which are non-Newtonian fluids, have a complex internal microstructure which can lead to counterintuitive flow and stress response. The properties of these complex fluids can be varied through the lengthscales and timescales of the associated flows [Bird *et al.* 1987]. Typically the elastic stress, by shear and/or elongational strains, experienced by these fluids will not immediately become zero with the cessation of fluid motion and driving forces, but decays with a characteristic time due to its

elasticity. Therefore, through the high deformation rates achievable in micro length-scale devices, strong viscoelastic effects can be generated even in dilute aqueous polymeric solutions.

Hitherto little attention has been given to microfluidic flow involving viscoelastic fluids with the notable exception of inkjet printing. Inkjet printing applications, whose typical dimensions are on the order of 50 μm or less, utilizes aqueous fluids containing low concentrations of high molecular weight polymers. A prototypical geometry that captures a number of features in an inkjet print head is a converging flow through abrupt contraction–expansion geometry. This geometry has been used extensively to study the nonlinear flow phenomenon associated with non-Newtonian fluid elasticity in converging flows at macro lengthscale. The re-circulating flow vortices have been comprehensively documented for large number of polymeric solutions and polymer melts [Rodd *et al.* 2005]. Lately, distinct similarities of these early works at macro lengthscale were demonstrated qualitatively in a micro-length scale planar contraction by Rodd *et al.* [Rodd *et al.* 2005], and in a flip-flop memory devices by Groisman *et al.* [Groisman *et al.* 2003].

Limited research has been conducted on the enhancement of mixing through viscoelastically induced flow instability in microfluidic devices. Groisman and Steinberg [Groisman and Steinberg 2001] presented the use of a polymeric liquid for the purpose of enhanced mixing in small geometries of millimeter lengthscale. Moderate shear rates were generated in small channels to induce elastic flow instabilities. Using repeated half ring flow geometry with a uniform cross-section, mixing was achieved with a relatively long mixing path at a moderate flowrate.

Indeed, to exploit effectively the viscoelasticity of fluids for chaotic flow instability, sharper and smaller geometries should be employed. Stress singularities developed at such corners

have been the source of elastic instabilities in many macroscale experiments [Bird *et al.* 1987], while rounded corners tend to suppress elastic behavior. It is crucial to understand the rheological nature of such flow in order to optimize the use of viscoelastic effects in microfluidic mixing applications.

3.5.2 Recent Development on Viscoelastic Mixing in Microchannels

Lately, the work of Groisman and Steinberg had been extended to micrometer lengthscale [Burghilea *et al.* 2004]. By utilizing high molecular weight polyacrylamide, with mean molecular weight (M_{wt}) = 1.8×10^7 g/mol, dissolved in two different Newtonian solvents with different viscosities, Burghilea *et al.* 2004 [Burghilea *et al.* 2004] demonstrated chaotic flow through a flat curvilinear microchannel with uniform square cross section of 100 μm , see Figure 3-15. The characteristic mixing distance was estimated to be 7.3 segments of the curvilinear channel (two half-ring form one segment) or a nominal flow length of 6.88 mm. Characteristic mixing times were approximately 40 s. They showed that the stirring behavior induced in the flow by these viscoelastic dilute polymeric solutions resulted in efficient mixing in the microchannel with characteristic mixing length significantly shorter than the herringbone patterning method for laminar flow of aqueous solutions. The characteristic mixing times for these viscoelastic fluids were reduced by approximately 3 to 4 orders of magnitude compared to mixing mechanism based on molecular diffusion. However, a relatively long mixing length was required.

Figure 3-15. (a) Curvilinear microfluidic device. (b) Zoom-in image of a section of the functional curvilinear channel [Burghlea *et al.* 2004].

3.6 Quantification of Microfluidic Mixing Efficiency

3.6.1 Dye-dilution Technique

The simplest and prevalent technique to quantify the mixing performance of a micromixer is via dye-, or tracer-, dilution experiments. Mixing performance is evaluated based on experimental concentration intensity images, which are captured by a high-resolution CCD (coupled-charge-device) camera. The intensity of the grayscale in the recorded CCD images is proportional to the dye concentration, as a result the uniformity of the concentration profile can be quantified by determining the standard deviation of the pixel intensity values [Liu *et al.* 2000, Stroock *et al.* 2002]. Furthermore, flow-visualization or imaging equipments such as high sensitivity CCD camera, illumination module with specify wave-length filter, and microscope with acquisition control are often required.

Indeed, spatial probability density functions (PDF) of intensities integrated over finite regions are commonly employed to quantify mixing [Oddo *et al.* 2001], which enhance the reliability of results (uniformity or homogeneity of mixed samples) where the standard deviation of single pixel intensity values may not be able to resolve the differences between regions in the

image. For example a PDF plot with two prominent peaks that are far apart (one of the dyed fluid, and the other of the non-dyed fluid) means that the two fluids are not mixed. A single peak at the mid-range of concentration means good mixing.

There are some other cases where the evaluated results were strongly dependent on the orientation of the mixed fluids relative to the imaging direction. The mixer proposed by Hinsmann *et al.* [Hinsmann *et al.* 2001] , if the imaging direction was perpendicular to the fluid layers, even at the channel entrance, mixing would appear to be complete. In such cases, an imaging system with a confocal microscope would be required to resolve the 3D spatial distribution of the concentration field.

3.6.2 Reaction Technique

Another technique of quantifying mixing performance is by measuring the product of a reaction process. One of the reaction-type experiments to quantify micromixer performance, particularly in chemical micro-process engineering, is by *Villermaux-Dushman reaction*. In this simple chemical reaction, iodine is formed via an acid catalyzed redox reaction between iodide and iodate. It was first proposed to quantify the stirred batched reactors performance and then adapted for the needs of micromixers [Ehrfeld *et al.* 1999]. More recently, an optimized protocol was developed for the Dushman reaction giving more accurate and better reproducible results [Loebbecke *et al.* 2004].

Another experiment is by measuring the fluorescent product of a chemical reaction. The intensity of the formed product is a measure of the mixing quality. Typically, this process is an acid-base reaction with a dye having a fluorescence quantum yield that is pH dependent. Recently, Munson and Yager [Munson and Yager 2004] reported a new concept to quantify mixing performance without requiring a full three dimensional mapping of the concentration of the dye. The method relies on the increase of intensity of fluorescein at basic pH. In this

method, two liquids are diluted with fluorescein at different pH values. The solution corresponding to the brighter state (basic for fluorescein) is buffered at a higher buffering capacity so that the final pH after complete mixing is very close to the initial pH of the brighter solution. Mixing quality is directly proportional to the total intensity of the fluorescein. Since the total intensity increases as interdiffusion occurs, interdiffusion along the optical axis can also be quantified, without the use of expensive confocal microscopy.

3.7 Summary

In this chapter, key micromixer designs (active and passive) and existing mixing quantification schemes were briefly reviewed. A variety of passive mixing schemes have been reported in the literature and a number of efficient mixer designs have been demonstrated. However, many designs suffer from one or more disadvantages. Active micromixers require external actuators. Passive micromixers, which include lamination and chaotic advection micro-mixers, require long or complicated channel geometry. Both mixing methods lead to complex and expensive fabrication processes. Although most of the designs are efficient in the $1 < Re < 100$ range, their mixing efficacy below $Re < 1$ is low. Thus, a different approach that bypasses the limitation of the low Reynolds number, yet provides efficient mixing, will be a significant improvement for microfluidic system design.

CHAPTER 4

FABRICATION AND SYSTEM SETUP

The ease of fabrication and the shorter design cycle using direct laser micromachining on polymer substrate offer an economical alternative for researchers to prove their ideas and concepts. As a result, the concepts of viscoelastically induced multiple-stream flow instability and thus mixing enhancement in microchannels were first realized on a polymer-based device with a simple convergent/ divergent channel configuration. The viscoelastically induced multiple-stream flow instabilities are apparent for the convergent/divergent viscoelastic fluids flow. Mixing enhancement was also illustrated qualitatively. However, as the polymer-based device was laser machined resulting in rough surfaces and poor micro-geometrical profile definition, the quantitative characterization of the flow behavior and mixing were difficult.

Thus, high precision micromachined silicon/glass chips were fabricated which offered good surface finish, geometrical definition and optical transmittance for rigorous characterization. In later chapters, results and discussions are analyzed based on the silicon/glass chips. Fluorescent dye and micro-spheres were used with mercury lamp (for dye-concentration

measurement) and Nd-YAG lasers (for μ -PIV measurement) to characterize the dynamical flow field and mixing efficiency.

This chapter consists of two sections: the fabrication technologies and the optical characterization techniques employed in this investigation. Laser ablation on polymethylmethacrylate (PMMA) and Deep-Reactive-Ion-Etching (DRIE) micromachining on silicon were used for the fabrication of the micromixers employed in this work. The micromixers were then characterized by two optical characterization techniques: micro-particle imaging velocimetry (μ PIV) and scalar field (dye-dilution experiment) measurements. These techniques allow the measurements of both temporal velocity field and concentration field in a micromixer.

4.1 Microfabrication

The current techniques used for fabricating microfluidic devices include micromachining, soft lithography, hot-embossing, injection molding, and laser ablation. Each technique has its advantages and disadvantages. The most suitable method of device fabrication often depends on the specific application of the device [Madou 2002, Verpoorte and De Rooij 2003]. Details of techniques and examples can be found in Madou (2002) and Verpoorte and De Rooij (2003). This section only deals with laser ablation (for PMMA-based microdevices) and micromachining (silicon-based microdevices) techniques which were employed for the realization of the microdevices for the present investigation.

4.1.1 Laser Ablation – Microchannels in Poly-Methylmethacrylate (PMMA)

Laser ablation mechanism is a complex combination of photochemical and photothermal processes. This means that some chemical bonds of the substance are broken directly during

the process of photon absorption while others are broken thermally by the released heat of those excited molecules that do not break up photochemically [Madou 2002]. The dimensions of any laser-ablated structure depend on the optical and mechanical set-up of the laser system and the material properties of the specific polymer. With respect to the material properties, the thermal diffusivity in particular should be as low as possible to ensure a finer resolution of ablation.

Laser ablation was first introduced by Roberts *et al.* for the fabrication of polymer microchannels [Roberts *et al.* 1997]. This technique involves directing UV excimer laser pulses at the plastic surface in defined regions, which causes degradation of the plastic at these regions as a consequence of a combination of photochemical and photothermal degradation processes. Later, carbon dioxide (CO₂)-laser machining was used to rapidly write structures in PMMA substrate [Klank *et al.* 2002], and has proven to be an effective tool for rapid prototyping of devices for diagnostic applications [Weigl *et al.* 2001], especially for scientific trials and small-scale production.

CO₂ laser is more affordable than a UV laser and it emits infrared radiation at a wavelength of 10.6 μm . This means that the CO₂-laser beam always ablates the underlying material photothermally. Furthermore PMMA has a relatively low thermal diffusivity. It is a thermoplastic polymer which can be reheated and reshaped for many times. In addition, PMMA also offers 92% light transmittance in the visible spectrum because of its non-crystalline structures.

A) CO₂ LASER ABLATION

The micro-geometrical structures (two dimensional drawing) were designed using CorelDraw 13 (Corel Co., Canada). The 2D structures were then sent to a laser scriber for direct micromachining on PMMA substrate. The commercial CO₂ laser scriber (Universal M-300

Laser Platform, Universal Laser Systems Inc., Arizona, USA) was used to engrave the PMMA substrate. The CO₂ laser employed has a wavelength of 10.6 μm and a maximum power of 25 W. A focused laser beam scanned over a two-dimensional area by means of an automated X and Y stage. The maximal achievable speed of the laser beam motion is 640 mm/s. The depth of microchannels was controlled by varying the laser power and scanning speed of the laser beam.

A microchannel of 200 μm in depth with abrupt contraction of 1600 μm : 200 μm : 1600 μm was employed to introduce convergent/divergent flows, see Figure 4-1. The length of the contraction was 800 μm . The two side channels were 800 μm in width and 3400 μm upstream from the centerline of the contraction. For a ready-to-use microdevice, the machined PMMA substrate was sealed by another blank PMMA substrate through direct thermal bonding technique. The entire fabrication process was fast, the ready-to-use microdevice could be completed within a few hours depending on the complexity of the geometrical structures.

4.1.2 Thermal Bonding of PMMA Substrate

Direct thermal bonding approach is preferred for PMMA bonding because it provides uniform surfaces, which composed entirely by the same polymeric material. The technique was studied by Shadpour *et al.* [Shadpour *et al.* 2006] and Alonso-Amigo and Adams [Alonso-Amigo and Adams 2003]. In their works, the bonding temperatures were kept just above the PMMA glass transition temperature $\approx 107^\circ\text{C}$, and relatively high bonding pressure was applied. However, high bonding pressure may induce global and localized geometric deformation of the substrates or leave an interfacial layer with significant thickness variation. To guarantee the structural integrity of the polymeric substrates, thermal bonding with lower pressure is desired. As such, low pressure thermal bonding of PMMA with a modified temperature profile was employed, which involved a multiple-ramping of temperature. The multiple-ramping of

temperature leads to high bonding strength, while the low bonding pressure assures good structural integrities. High quality bonding was achieved with no signs of deformation.

The experimental implementation of this bonding technique will now be described. A hot plate was used for the temperature control. The PMMA substrates were placed between the hotplate and an upper aluminum plate. Bonding pressure was adjusted by putting weights on top of the upper plate and it was kept at around 20 kPa or less. To achieve a better surface flatness of the PMMA layers, PMMA substrates were placed between two polished silicon wafers before placing on the thermal bonder. Prior to the bonding process, PMMA parts were carefully cleaned and rinsed in ethanol and DI-water.

Figure 4-2 shows the temperature regime of the bonding process. The PMMA substrates were pre-heated at 60 °C for 30 mins, and then they were bonded at 120 °C for 30 mins. Finally, the bonded PMMA device was air cooled to room temperature to relieve the stress imposed during the bonding process. The whole bonding process took about 3 hours. Figure 4-1 shows a ready-to-use PMMA-based microchip.

Figure 4-1. PMMA-based planar contraction/expansion passive micromixer.

Figure 4-2. Multiple ramping of temperature for thermal bonding of PMMA substrates.

4.2 Micromachining – Microchannels in Silicon

Micromachining technique is widely used in micro-electromechanical systems (MEMS) and was first applied to microfluidics on silicon (Si). Generally, the technique includes film deposition, photolithography, etching, access-hole drilling and bonding of microchip. Thereafter, glass (Pyrex glass, soda lime glass, or fused silica) is used as the micromachining substrate. The micromachining methods of these substrates differ, and details can be found in “Fundamental of Microfabrication – The Science of Miniaturization” by Madaou [Madou 2002].

Typically micromachining starts with photolithography, the technique used to transfer a copy of a master pattern onto the surface of a substrate [Madou 2002], such as silicon wafer in this investigation. After photolithography, a number of subtractive or additive processes are performed; materials are either removed from, or added to a substrate, usually in a selective manner. Finally, the micromachined substrate is bonded with another substrate to seal off the micro-geometrical structures.

In the subsequent sections, a brief description of photolithography process, DRIE process and anodic bonding were presented. Detailed procedures and parameters setting are contained in Appendix A1.

4.2.1 Photolithography

Lithography is the technique used to transfer copies of a master pattern on to the surface of a solid material. The term photolithography is used when the copy is transferred with the help of light. In this process, a silicon wafer coated with a thin film of photoresist (PR) is selectively exposed to ultraviolet light through a designed mask. The mask used for the selective exposition was a transparent quartz frame that contains opaque chromium regions representing

the geometry to be transferred to the PR. Photoresists are resins that can be made soluble (positive PR) or insoluble (negative PR) upon exposure to ultraviolet light. Lastly, the PR was developed by dissolving the unwanted parts. After the photolithography process, PR acted as a mask in the subsequent etch process.

There is a big variety of PR in the market place and the choice of PR depends on its role in the next fabrication steps. In this investigation PR AZ9260 (Clariant, Muttens, Switzerland), a positive resist, was used for the photolithography process. For DRIE this resin is preferred because it allows thicker layer deposition (about 10 μm in this investigation).

A) HEXAMETHYLDISILAZANE (HMDS) PRIMING

Generally, prior to the actual photolithography process on silicon (Si) substrate, HDMS priming was conducted in order to enhance the PR adhesion. A common step was first to grow a thin layer of silicon oxide on the surface by heating the wafer at temperatures around 100 °C for 60 s. After oxidization, the substrate was then dehydrated (to remove moisture) in an oven at 100 °C for 60 s with nitrogen (N_2) gas purging. Subsequently, the surface was reacted with HMDS gas which modified the surface with a monolayer of trimethylsilane-groups. The coated layer served as an adhesive layer between Si and PR.

B) PHOTORESIST (PR) COATING

After HDMS priming, PR (a viscous solution of the monomer, solvents and photoinitiator) was then spin-coated (Karl Suss Spin coater) on the substrate surface at high rotational speed (i.e. 1500 rpm) depending on the viscosity and the required thickness.

C) PRE-BAKE

After spin-coating, the resist contained approximately up to 15% of solvent. Therefore the substrate was baked at 110 °C for a few minutes to remove the residual solvents. This pre-bake step further enhanced the adhesion of PR.

D) ULTRA-VIOLET (UV) LIGHT EXPOSURE

After pre-bake, the resist coated substrate was transferred to the mask aligner, the UV exposure system where the mask was inserted. In this system, the mask was placed between the UV light source and the wafer. Selective illumination of the substrate made was soluble the exposed PR. After exposure, the substrate was left in the open air for a few minutes to relax the residual stress imposed on the substrate during the exposure process.

E) DEVELOPING AND POST BAKE

The developing process transformed the latent resist image formed during exposure into a relief image which served as a mask for the later etch steps. Finally, before etching, post-bake at 60 °C was applied to remove residual developer or solvents in the resist, and to improve the hardness and the resistance of the resist to subsequent etching steps.

4.2.2 Deep Reactive Ion Etching (DRIE)

DRIE is a dry etch process that permits the fabrication of high aspect ratio silicon structures with little limitation in geometry. In this investigation, the DRIE process was conducted according to the Advanced Silicon Etch (ASETM) process developed by Surface Technology Systems (STS). The ASETM process consists of a sequence of alternating etch and passivation cycles (see Figure 4-3). The etching and passivation gases are SF₆ and C₄F₈, respectively. The passivation phase deposits a fluorocarbon polymer over all the surfaces of the wafer and trenches. During each etch cycle, the passivation is removed from the bottom of the etched features with the assistance of ion energy. The rest of the etch cycle is a short isotropic etch of

the exposed Si. As the vertical etch rate is much faster than the lateral etch rate, highly anisotropic profiles can be achieved.

More precisely, after the masking material (photoresist or silicon dioxide) had been patterned, a shallow isotropic trench immediately was formed by the first etch cycle, in the subsequent passivation step, a protective film was deposited to all surfaces. During the next etch step, the protective film was removed from all horizontal surfaces by directional ion bombardment, and another shallow trench was formed. The machine alternated between an etch cycle and a passivating cycle in a time-multiplexing scheme, TMDE. Appendix A1 contains the detailed fabrication procedures.

Figure 4-3. An illustration of the ASETM, showing alternating passivating and etch cycles. During the passivating cycle (a), fluorocarbon polymer covers all surfaces. During the initial part of the etch cycle (b), the polymer is removed from the base of the trench with the assistance of ion energy. During the rest of the etch cycle (c), the exposed Si is etched isotropically [McAuley *et al.* 2001].

One should take note that in this investigation, all the microdevice access ports (inlet and outlet holes) were machined, together with the microstructures, on the silicon substrate. As a result, there were two DRIE steps involved in the etch process – (i) Through hole etching, and (ii) Microstructure etching. Backing of wafer process, by attaching another wafer to through-hole etched wafer, was required prior to the microstructure etching process. This process was to ensure proper application of the clamping force (by means of vacuum suction) on the substrate during PR spin coating, and to prevent the wafer from breaking during DRIE process (refer to Appendix A1).

4.2.3 Anodic Bonding

A common technique to join silicon and pyrex glass is by means of anodic bonding. For desired bonding quality, all the bonding surfaces must be clean and dust-free. Thus, prior to the bonding process, both the etched wafer and pyrex glass were cleaned in a solution of sulfuric acid and hydrogen peroxide for about ten minutes, then rinsed in water and dried. Lastly, both substrates were etched by O_2 plasma to ensure cleanliness.

For anodic bonding, the working principle is to apply a large voltage potential across the glass-wafer system in order to generate an electric field that drives Na^+ ions in the glass wafer away from the interface region, see Figure 4-4. Thus a Na^+ depletion zone is formed and leaves oxygen molecules at the interface. Oxygen molecules then diffuse into the silicon to form a layer of amorphous SiO_2 . Two layers, silicon wafer and pyrex glass, are then bonded firmly. In this investigation, Karl Suss wafer bonder was utilized to bond the Si wafer with Pyrex glass. The cleaned substrates were placed, as shown in Figure 4-4, with Pyrex glass on top, on the fixture before loading to the bonder chamber. Appendix A1 contains the details of the chosen pre-set recipe for anodic-bonding-glass-wafer. After bonding the ready substrate (silicon-glass wafer) was then diced into individual chip.

Figure 4-4. Principal sketch of anodic glass-to-Si bonding. Control parameters are temperature, bias voltage, time and materials (glasses, Si, SiO_2) [Madou 2002].

4.2.4 Dicing and Device Assembly

One of the final steps in silicon-glass chip micromachining was sawing the finished Si-glass wafer into individual “dice” (ready-to-use silicon-glass chip). After the wafer was probed, it was mounted onto sticky tape and put on to the dicing saw. The sawing blade was rotating at a speed of few thousands rpm (~ 2000 rpm), the blade encounter the Si-glass wafer at a feed rate on the order of a cm/s, sawing partially (the glass wafer) through the silicon-glass wafer. One should take note that (see Figure A1-2 in Appendix A1) parting line (sawing route) had already been etched on the Si substrate during the DRIE process together with the microstructures. These pre-etch parting lines significantly reduced the possibility of breaking the Si-glass wafer during the dicing process. After the silicon/glass stack was diced into $10\text{ mm} \times 10\text{ mm}$ microdevices, the microdevice was assembled with a polymeric holder (with inlets/outlet tubings) for micro-macro fluidic interface. Figure 4-5 shows the ready-to-use Si-glass micromixers and the polymeric holder, which were employed in the present investigations.

Figure 4-5. Silicon-glass micromixer: (a) Silicon-glass stack with $10\text{ mm} \times 10\text{ mm}$ diced microdevices and (b) Silicon-glass micromixers and the polymeric holder.

4.3 Imaging techniques

The experimental setup, for both measurements of the velocity and the concentration fields is depicted schematically in Figure 4-6. Basically, the setup consisted of four main components: an illumination system, an optical system, image acquisition devices and a control system. Two different illumination sources, a double pulsed Q-switch (quality switched) Nd:YAG laser and a mercury lamp, were used for the measurements of the velocity field and the concentration field. The optical system consisted of an inverted microscope (Model ECLISPE TE2000-S) with a set of epi-fluorescent attachments. The image acquisition devices consisted of an interline transfer CCD camera (HiSense MkII), a FlowMap system hub with last-in-first-out (LIFO) capability and a commercial camcorder (Sony, DCR-DVD803E). The resolution of the CCD camera is 1344×1024 pixels with 12 bits grayscale. The recorded images were digitally transferred to a personal computer for further analysis.

For each flowrate, the flow field images in the same experiment were visualized using the green fluorescent dye (main stream) and the red fluorescent microspheres (side streams). The images of the streams, at the same area of interest, were captured by switching the epi-fluorescent attachments of the microscope. The green fluorescent dye has an excitation wavelength and an emission wavelength of 490 and 520 nm, respectively. The epi-fluorescent attachment of type Nikon B-2A (excitation filter for 450–490 nm, dichroic mirror for 505 nm and an emission filter for 520 nm) was used for the green dye. The red microspheres (Duke Scientific Co.) with an excitation wavelength of 540 nm and a maximum emission wavelength of 610 nm were imaged with the epi-fluorescent attachment of type Nikon G-2E/C (excitation filter for 540 nm, dichroic mirror for 565 nm and an emission filter for 605 nm). The relatively large red-microspheres minimized the diffusive effect in the experiments. Both green and red filters have a bandwidth of 25 nm.

Figure 4-6. Optical setup for fluorescent concentration and PIV measurements.

The basic objective of PIV is to visualize the dynamical flow facilitated by the fluorescent tracer particles that move with the fluid stream. The PIV technique can be divided into two steps: image acquisition and image processing. Firstly, the illumination source (i.e. the double pulsed Nd:YAG laser) illuminates the fluorescent tracing particles. Subsequently the fluoresced tracing particles are recorded digitally using charge couple device (CCD) camera. Secondly, the flow field is then evaluated by correlation algorithms based on recorded pair-image with imaging interval accurately controlled. The schematic μ PIV system is shown in Figure 4-6.

The twin-head laser system (Quantel, Quantel twins Q-switched double pulse Nd: YAG laser) allows the firing of two laser pulses at a very short interval ($O \sim (\mu s)$). As mentioned previously, the mercury lamp (a continuous light source) was used for scalar field measurement such as the characterization of mixing, because no synchronization is required.

However, for the measurement of velocity fields, a laser system (pulse light source) is required due to the requirement of precise synchronization for instantaneous imaging (“freezing” the flowing tracer particles at specific instantaneous time).

In actual experiments, fluorescent microspheres were added only to the side streams (0.1% PW) for investigations, therefore only the flow field of the side streams (lower viscosity fluids e.g. 0.1% PW) would be measured. The microspheres have a maximum excitation wavelength close to the characteristic wavelength of Nd:YAG laser. The measurement was carried out with a 4× objective lens and two 30 mJ laser pulses with a delay time of 4 ms. At least 200 images were collected for every flow condition. The fluorescent microspheres solution was not added to the higher viscosity (e.g. 1% PGW). This would ensure that any velocity measured was related to those particles originated from the side streams. This would allow the evaluation of the penetration of the side streams to the main stream. The μ PIV measurements were post-analyzed (streamlines and velocity vector field) using a commercial software (FlowMap, Dantec Inc, Denmark).

4.4 Summary

In this chapter, the techniques employed for device fabrication and quantification of the dynamical flow field are described.

CHAPTER 5

FLUIDS RHEOLOGY

Characterization of sample fluids (dilute polymeric solutions) was conducted by both theoretical dilution polymeric solution approximation and rheological measurements via rotational and extensional rheometers. All fluid properties were measured with the additives in the fluid samples.

5.1 Poly (ethylene oxide), PEO

Polyethylene oxide (PEO) and polyethylene glycol (PEG) are chemically synonymous, but historically PEO has tended to refer to longer polymers while PEG to shorter polymers. PEO and PEG are both prepared by polymerization of ethylene oxide. Polymers of ethylene oxide are the most studied among water-soluble polymers and is the most commercially important polyethers. While PEO and PEG with different molecular weights find use in different applications and have different physical properties (e.g. viscosity) due to chain length effects, their chemical properties are nearly identical. PEO and PEG are polymers composed of repeating monomers of identical structure, the repeat unit in these polyethers is $(\text{CH}_2\text{--CH}_2\text{--O})$. Both polymers refer to an oligomer or polymer of ethylene oxide. Most PEOs or PEGs include molecules with a distribution of molecular weights, i.e. they are polydisperse. The size

distribution can be characterized statistically by its weight average molecular weight (M_w) and its number average molecular weight (M_n), the ratio of which is called the polydispersity index (M_w/M_n). M_w and M_n can be measured by mass spectroscopy.

In this investigation, PEO was employed for its large molecular weight and water solubility. In addition, with its flexible backbone, highly elastic behavior could be attained even at low concentration [Rodd *et al.* 2005]. PEO powder (at different concentrations of 1 000 ppm (0.1 wt%), 6 000 ppm (0.8 wt%), 8 000 ppm (0.8 wt%) and 10 000 ppm (1% wt%)) was mixed with a low viscosity Newtonian fluid (a mixture of 55 wt% of glycerol in deionized (DI) water). PEO fluids has two immediate advantages for bio-applications, the first is that PEO itself is biocompatibility (any residual should not induce an inflammatory response). The second is that PEO is water soluble, thus avoiding the usage of potentially toxic organic solvents for dissolving it [Cima 1994].

5.1.1 Degradation

It is known that poly(ethylene oxide), PEO, can be easily degraded by oxidative attack. This degradation can be accelerated in the presence of heavy metal ions, oxidizing agents, strong acids, and radiation [McGary 1960, Duval and Sarazin 2003]. If a bottle of PEO solution is left at room temperature for over a month, it will become almost Newtonian. PEO shows limited thermal stability and oxidatively degrades in the presence of oxygen by forming hydroperoxides that decomposes into free radicals in the presence of metallic ions. These free radicals in turn cleave other polymer molecules [McGary 1960]. Metallic ions like Fe^{3+} and Cr^{3+} accelerate this process, as does exposure to ultraviolet light.

However, the normal rate (away from direct light) of degradation at room temperature is slow. Measurements by Dontula *et al.* [Dontula *et al.* 1998] on aqueous PEO liquids stored away

from direct light showed that the degradation of viscosity and elasticity of aqueous PEO liquids is greater the higher the molecular weight. The viscosity, and elastic modulus of a 0.5 wt% aqueous PEO liquid of 7×10^6 g/mol molecular weight decreased by 5% within 15 days, while that of a 4.1 wt% liquid of 4×10^6 g/mol dropped immeasurably even after 28 days. Allyl, ethyl, and isopropyl alcohol compete for peroxides and free radicals in liquid better than PEO and are selectively oxidized, thus stabilizing PEO liquid over longer periods of time [McGary 1960, Duval and Sarazin 2003]. In this investigation, all the sample fluids were stored inside a cabinet and kept not more than 72 hours to avoid any significant degradation of the PEO liquids.

Similar to many other polymers, high-molecular-weight PEO (approximately $M_{wt} > 1 \times 10^6$ g/mol) degrades mechanically when subjected to intense deformation for long period of times. For example the viscosity of a 0.5 wt% aqueous PEO liquid of 7×10^6 g/mol molecular weight dropped by about 10 % after shearing for 120 s at 1000 s^{-1} in a Couette fixture [Dontula *et al.* 1998]. Hence high shear rates should be avoided during stirring and during sample preparation. Only fresh sample fluids (not more than 72 hours) were employed and all samples were used once. All expired samples or tested sample-fluids were disposed of according to the NTU chemical handling procedures. This ensured that fluid quality was well controlled for every experiment.

5.2 Polymer Architecture

The dynamics of polymers in a solution is greatly influenced by their concentration relative to the critical overlap concentration (c^*) [Bird *et al.* 1987, Ferry 1980, Malkin and Isayev 2006]. The overlap concentration is the point at which polymer coils begin interacting. At low concentration ($c < c^*$), these polymer coils have no effective entanglements between individual molecule chains, as such this type of polymeric fluids show ideal-viscous flow

behavior. Their viscosity value is directly proportional to their concentration. As the concentration of polymer increases, the fluid system is getting more congested with polymer coils and eventually when the overlap concentration (c^*) is reached, the whole volume of fluid is packed with polymer coils and they interact with each other.

When $c \ll c^*$, the fluid is called dilute and the coils are separated from each other with no strong interaction between them. These polymer coils interact primarily with the solvent molecules. At $c \gg c^*$, the whole volume of fluid is fully packed with polymer coils, they overlap and are entangled. The behavior of the fluid is strongly influenced by the polymer coil interactions and their mobility is greatly reduced compared to the dilute fluid.

The critical concentration (c^*) for polymer fluid is dependent on the properties of both the polymer and the solvent, see Figure 5-1, and can be approximately estimated based on the properties of the fluid-polymer interaction and statistical probabilities of polymer interacting.

Figure 5-1. Concentration--molecular weight diagram of viscoelastic regimes of flexible polymer solution in a good solvent [Dontula *et al.* 1998].

The c^* for a polymer solution can be expressed as,

$$c^* \approx \frac{M_{wt}}{N_A \langle R^2 \rangle^{3/2}} \quad (5.1)$$

where M_{wt} is the molecular weight, N_A is the Avogadro's number, and $\langle R^2 \rangle$ is the mean square radius of gyration of polymer chain.

Statistical probability suggests that the most likely shape for a polymer solution is in the form of a sphere. This radius is a statistical probability determined from the random walk of the polymer [Ferry 1980]. The radius of the polymer can be related to the number of monomer chains in the polymer and its interaction with the surrounding fluid [Anna *et al.* 2001],

$$\langle R^2 \rangle \approx \vartheta_\infty n_m l_b^2 \quad (5.2)$$

where ϑ_∞ is the characteristic ratio of the polymer, indicating freedom of the monomer to rotate back upon itself, n_m is the number of carbon-carbon bonds in the backbone and $l_b = 1.54$ Å is the length of a carbon-carbon bond [Flory 1953]. One should note that equation (5.2) is only an approximation for determining the critical concentration due to the mean radius involved.

The number of bonds, n_m , per PEO molecule can be calculated by

$$n_m = \frac{3M_{wt}}{M_o} \quad (5.3)$$

where M_o is the molecular weight of a monomer.

Combining equations (5.2) and (5.3),

$$c^* \approx \frac{M_{wt}}{N_A \left(\vartheta_\infty \frac{3M_{wt}}{M_o} l_b^2 \right)^{3/2}} = \frac{1}{N_A \left(\vartheta_\infty \frac{3}{M_o} l_b^2 \right)^{3/2} (M_{wt})^{1/2}} \quad (5.4)$$

As described by equation (6.4) and as shown in Figure 5-1, c^* decreases with increasing molecular weight. Each of these variables is well documented for most polymer solutions in the Polymer Handbook [Brandrup *et al.* 1999].

Water is a good solvent for PEO and the polymer coils are extended beyond the random coil configuration, and equation (5.4) overestimates the coil overlap concentration. Thus, the c^* values would be defined according to the definition of Flory [Flory 1953] for flexible polymer fluids, where

$$c^*[\eta] = 1 \quad (5.5)$$

One should note that Graessley [Graessley 1980] had introduced a proportional factor of 0.77 to equation (5.5), resulting in a lower critical concentration by a factor of 23%. As a result, care has to be taken when comparing the rheological properties of similar sample fluids reported in the literature. In the reminder of this thesis, the overlap concentration of PEO solutions were calculated from equation (5.5).

5.2.1 Intrinsic viscosity and Zimm Relaxation time

The relationship between the intrinsic viscosity and molecular weight is best described by the Mark-Houwink-Sakurada equation [Brandrup *et al.* 1999]

$$[\eta] = KM_{wt}^{\alpha} \quad (5.6)$$

where K and α are constants that can be determined from a double logarithmic plot of intrinsic viscosity and molecular weight, and are well tabulated in the Polymer Handbook by Brandrup *et al.* [Brandrup *et al.* 1999].

Tirtaatmadja *et al.* [Tirtaatmadja *et al.* 2006] have summarized previous reported values of intrinsic viscosity as a function of molecular weights (M_{wt}) of PEO, ranging from 8×10^3 to 5

$\times 10^6$ g/mol, in both water and glycerol-water mixtures. A linear regression analysis was fitted to all data set, given a composite Mark-Houwink-Sakurada (MHS) equation for the intrinsic viscosity of the PEO fluids as,

$$[\eta] = 0.072 M_{wt}^{0.65} \quad (5.7)$$

with $[\eta]$ in units of cm^3/g .

Therefore, combining equations (5.5) and (5.7), the estimated overlap concentration of PEO sample used in this study (with $M_{wt} = 2 \times 10^6$ g/mol) is $c^* = 1/[\eta] = 11.143 \times 10^{-4} \text{ g/cm}^3$ (0.111 wt%).

According to Zimm theory, a dilute liquid of polymer coils in a solvent incorporating hydrodynamic interactions gives the scaling $[\eta] \sim K M_{wt}^{3a-1}$ for long chain molecules [Tirtaatmadja *et al.* 2006]. As a result, the solvent quality parameter can be extracted from the exponent in the MHS relationship by equating the exponent value with $(3a-1)$. The resulting value for a is 0.55, indicating that water and mixtures of glycerol and water are good solvents for PEO [Tirtaatmadja *et al.* 2006].

For a polymeric fluid with a good solvent, the longest relaxation time of a monodisperse homopolymer is described by the Rouse-Zimm theory, which can be expressed as

$$\lambda_z = \frac{1}{\zeta(3a)} \times \frac{[\eta] M_{wt} \eta_s}{N_A k_B T} \quad (5.8)$$

where η_s is the solvent viscosity, k_B is the Boltzmann constant and T is the temperature.

A detailed eigenvalue calculation is required to determine the precise value of the numerical prefactor in equation (5.8) [Tirtaatmadja *et al.* 2006], which is strongly dependent on the

solvent quality and the hydrodynamic interaction of polymer coils. It can be approximately evaluated by

$$\zeta(3a) = \sum_{i=1}^{\infty} \frac{1}{i^{3a}} \quad (5.9)$$

For $a = 0.55$ in this work, the prefactor is thus $1/\zeta(1.65) \cong 0.463$ [Tirtaatmadja *et al.* 2006].

Using this value together with the intrinsic viscosity in equation (5.7), the longest Zimm relaxation time, λ_z , can be calculated for each sample. The pre-factor so determined was different from equation (2.20).

5.3 Sample Fluids Preparations

In this study we focused on dilute and semi-dilute liquids of PEO with mean molecular weight (M_{wt}) (The Dow Chemical Company) of approximately 2×10^6 g/mol. The sample fluids in the dilute concentration regime were prepared by mixing the PEO powder (at concentrations of 0.1 wt% or 0.3 wt% PEO) in deionized (DI) water with 3 μ m red fluorescent microsphere liquid. For brevity, these fluids are denoted as (0.1 or 0.3)% PWS. The sample fluids in the semi-dilute concentration regime have a higher viscosity and elasticity than the dilute regime. The sample fluids are 0.6 wt%, 0.8 wt% and 1.0 wt% of PEO dissolved in a mixture of 55wt% glycerol in DI water with green fluorescent dye. For brevity, sample fluid in the semi-dilute regime, for example 1 wt% PEO, is denoted as 1% PGWF. A fluorescence dye (fluorescein disodium salt $C_{20}H_{10}Na_2O_5$, Sigma Aldrich) was added at a weight ratio of 3×10^{-4} :1. The liquid of dispersed 3- μ m red fluorescent microspheres (Duke Scientific Co.) was added at a volume ratio of 0.1:1. These fluorescence green dye and red microspheres were served as tracers, which were used with mercury lamp and in μ -PIV (with appropriate illumination light sources), to characterize the flow fields of planar contraction-expansion multiple-stream flows.

5.4 Steady and Dynamic Shearing Flows

Brief descriptions of the principle of shear flow measurements have been given in Chapter 2, with more detailed explanations and illustrations contained in Bird *et al.* [Bird *et al.* 1987] and, Malkin and Isayev [Malkin and Isayev 2006]. Several types of equipment are available to explore the shear properties of fluid samples [Mezger 2006]. In this study, the Advanced Rheometric Expansion System (ARES) by Rheometrics Scientific and the Low Shear Contraves LS 40 by Mettler-Toledo were used to characterize the basic rheological properties of the sample fluids. All the fluid properties were determined with the additives incorporated into the fluid sample. A brief description of the ARES and the LS 40 are given below.

5.4.1 Advanced Rheometric Expansion System (ARES), Rheometrics Scientific

The Advanced Rheometric Expansion System (ARES, Rheometrics scientific) is a rotational rheometer which is capable of measuring a variety of rheological properties, such as shear flow curve (steady shear viscosity) and normal stresses, dynamic properties and relaxation properties. This rheometer is equipped with a 100 FRTN1 transducer. The torque range is from 0.004 to 100 g-cm and the normal force range from 0.1 to 100 gmf. Several measuring systems are available with ARES (e.g. cone-and-plate, parallel-plate and Couette geometries). The temperature is bath controlled with a Polyscience (digital temperature controller) circulating bath.

The parallel plate measuring system (plate diameter = 50 mm and gap = 1 mm) was used in this investigation. The rheological measurements of PEO fluids, in the semi-dilute regime (i.e. 1.0wt%, 0.8wt% and 0.6wt% PEO in 55 wt% glycerol water), in steady and dynamic modes were carried out at constant temperature of 25 °C with a shear rate range of $0.1 \leq \dot{\gamma} \leq 100 \text{ s}^{-1}$ and frequency of $0.1 \leq \omega \leq 100 \text{ rad/s}$ respectively. The steady shear viscosities were

determined using strain-controlled-steady sweep test and the dynamic shear viscosity was measured using dynamic frequency sweep test. After loading the sample fluid and setting up the measuring recipe, approximately 5 ~10 minutes was taken for the system to reach equilibrium before the start of each test. Details regarding operation, maintenance and performance specification of the rheometer can be found in the instrument manual (902-30026 REV A) and user guide (902-00107).

5.4.2 Contraves LS 40

The low shear Contraves 40 is a rotational concentric cylinder type rheometer which was mainly used for measurements in the low shear rate domains, especially to get zero shear viscosity. The rheometer is equipped with an inverted bob to eliminate end effects and is able to measure steady and dynamic properties using small sample size. In this investigation, the rheometer was used for zero shear characterization of dilute aqueous PEO sample fluids (i.e. 0.1 wt% and 0.3 wt % PEO in water) at 25 °C. However, the relaxation time of such diluteness could not be determined with our facilities for these fluids.

5.4.3 Typical results of rotational shearing flow measurements

Typical results of shearing flow measurements on η and N1 for various concentrations of PEO in a mixture of 55 wt% glycerol and water were presented in Figure 5-2. Figure 5-2(d) shows that at low shear zero-shear plateaus, with increasing concentration of PEO the viscosity increased and the shear rate value at which shear thinning appear decreased, which are in good agreements with values reported in the literature. In the present investigation, the zero-shear viscosity, η_o , was determined via a nonlinear regression of the three parameter Carreau model. The evaluated values were different from the values reported in our earlier papers [Gan *et al.* 2006a, Gan *et al.* 2006b] which were fitted by a Ellis model. Better regression fit (1%

improvement in fitting results) was obtained from the Carreau model. Rheological results were summarized in Table 5-1

The Carreau fluid model was first proposed by Pierre Carreau [Bird *et al.* 1987]. The full Carreau Model is typically expressed in terms of four parameters by the following equation

$$\eta = \eta_{\infty} + (\eta_o - \eta_{\infty}) \left[1 + (\lambda \dot{\gamma})^2 \right]^{\frac{n-1}{2}} \quad (5.10)$$

where, η_o is the zero shear (Newtonian) viscosity, η_{∞} is the limiting viscosity at high shear rates and λ is a time constant. The high shear viscosity is generally associated with a breakdown of the fluid and is frequently taken as zero [Boger 1977]. Therefore, equation (5.10) reduces to

$$\eta = \eta_o \left[1 + (\lambda \dot{\gamma})^2 \right]^{\frac{n-1}{2}} \quad (5.11)$$

At low shear rate, $\dot{\gamma} \ll 1/\lambda$, Carreau fluid behaves as a Newtonian fluid and at high shear rate, $\dot{\gamma} \gg 1/\lambda$, behaves as a power-law fluid [Myers 2005].

Figure 5-2. Typical rotational shear measurements for various PEO sample fluids in semi-dilute concentration regime, (a)-(c) oscillatory shear and (d) steady shear.

5.5 Uniaxial Elongational Flows – Capillary Breakup Extensional Rheometer (CaBER 1)

The standard rheological measurements (by rotational rheometer) and the theoretical calculations are inadequate or insufficient for providing a reliable measurement of the relaxation time for the present study. In the experiments of multiple streams flow through abrupt contraction geometry, the viscoelastic sample at the core-stream (or center stream) of the microdevice underwent strong extensional stretching exhibiting nearly pure elongational straining. As such extensional strain measurement was desired. Unlike the typical shear flow measurement, the polymer coils are stretched not sheared during the measurement and the time required for the polymer coils to relax to the equilibrium state can be expected to be very different. The Capillary Break-up Extensional Rheometer (CaBER) provides a tool to

investigate the characteristic timescale of the fluid in a string extensional flow as a function of polymer concentrations, with a brief review on extensional strain measurement contained in Chapter 2 section 4.2.

In the present study, extensional rheology tests were performed on HAAKE CaBER-1 (Thermo Haake GmbH, Karlsruhe, Germany) with a system response of 10 ms. Measurable shear viscosity ranges is from 10 to 10^6 mPas. Typical results of extensional strain measurements for various concentrations of PEO in a mixture of 55 wt% glycerol and water were illustrated in Figure 5-3. Due to the limitation of the equipment, the extensional rheological properties of sample fluids in the dilute regime, i.e. 0.1% PWS and 0.3% PWS, could not be characterized. Therefore, its values were taken from the measurements by Rodd *et al.* [Rodd *et al.* 2005]. As the raw material used and measured viscosity (using LS 40) was in good agreement with Rodd *et al.* [2005] these values were hence taken to be acceptable for later analysis.

The CaBER-1 rheometer was equipped with two 6 mm ($2 \times R_0$) circular parallel plates. In order to minimize the influence of gravity and shear flow during the early stages of stretch, the plates were set to an initial gap of $h_0 = 3$ mm, resulting in an initial aspect ratio $\Lambda_0 = 0.5$ ($h_0/2R_0$). Fluid samples were carefully loaded between the plates using a disposable pipette to ensure the absence of trapped air and contamination. The upper plate was raised suddenly to a pre-set height of 10.43 mm (factory pre-set height) to create a filament. Laser beam aiming at the middle point of the filament measured the changes in diameter. With this experimental arrangement, the extensional flow of the filament was under the influence of the surface tension acting on the fluid surface [Bazilevsky *et al.* 1990, Rodd *et al.* 2005]. A brief review of the extensional strain measurement is contained in Chapter 2 section 4.2.

Figure 5-3. (a) Typical plot of normalized filament diameter versus time -- Semi-logarithmic plot of necking for three sample fluids, 1% PGWF, 0.8% PGWF and 0.6% PGWF. (b) Typical plot of apparent extensional viscosity versus strain.

5.6 Fluid Rheology Summary

The important physical rheological properties were summarized in Table 5-1. All the shear and extensional tests were repeated at least three times and their average was used for analysis. The static surface tension and density of sample fluids were determined using DCAT21 tensiometer (Dataphysics Instruments GmbH) with Wilhelmy plate and Du Noüy ring, and density determination set (DIS11) respectively.

Comparing the viscosity evaluated from steady shearing at very low shear plateau and extensional straining measurements, the ratio of measured apparent viscosity, η_e , to steady-shear viscosity (commonly known as the Trouton ratio, see equation (2.9)) was found to be 3 approximately. Based on the properties summarized in Table 5-2, fluid characterizations for the present investigations were desired and more adequate to reflect the flow characteristics.

Table 5-1. Fluid composition and rheological properties of dilute polyethylene oxide in solvent of water or mixtures of glycerol and water for rotational shear measurements.

Fluid	c/c^*	ρ [kg/m ³]	η_o [mPas]	λ_z [ms]	λ_w^0 [ms]
0.1% PWS	0.898	997 ± 10	2.24 ± 0.3	0.335	-
0.3% PWS	2.693	990 ± 10	8.0 ± 0.2	0.335	-
1% PGWF	8.974	1137 ± 20	903 ± 100	2.733	220
0.8% PGWF	7.179	1133 ± 20	402 ± 50	2.716	153
0.6% PGWF	5.385	1132 ± 20	175 ± 80	2.618	50

Note: λ_w^0 was calculated based on equation (2.19); evaluated intrinsic viscosity $[\eta] = 897.43$ cm³/g; PEO in 55 wt% glycerol water with green fluorescence dye is denoted as PGWF; PEO in water with 3µm microspheres is denoted as PWS.

Table 5-2. Fluid composition and rheological properties of dilute polyethylene oxide in solvent of water or mixtures of glycerol and water for extensional strain measurements.

Fluid	c/c^*	σ_s [mN/m]	ρ [kg/m ³]	η_e [mPas]	λ_e [ms]
0.1% PWS	0.898	61.844 $\pm$ 0.02	997 $\pm$ 10	2.3 $\pm$ 0.2 [Rodd <i>et al.</i> 2005]	1.5 [Rodd <i>et al.</i> 2005]
0.3% PWS	2.693	61.540 $\pm$ 0.02	990 $\pm$ 10	8.3 $\pm$ 1.0 [Rodd <i>et al.</i> 2005]	4.4 [Rodd <i>et al.</i> 2005]
1% PGWF	8.977	57.433 $\pm$ 0.03	1137 $\pm$ 20	2590 $\pm$ 80	103 $\pm$ 6
0.8% PGWF	7.181	57.630 $\pm$ 0.04	1133 $\pm$ 20	956 $\pm$ 60	64 $\pm$ 5
0.6% PGWF	5.386	57.845 $\pm$ 0.02	1132 $\pm$ 20	525 $\pm$ 80	25 $\pm$ 4

where PEO in 55 wt% glycerol water with green fluorescence dye is denoted as PGWF; PEO in water with 3 μ m microspheres is denoted as PWS.

CHAPTER 6

RESULTS AND DISCUSSIONS

It has been recently shown that the small lengthscale inherent to microfluidic devices has key implications on the flow behavior of fluids containing a very low concentration of high molecular weight polymer, refer to Chapter 2 for a brief review. Elastically induced flow instability was observed in a planar entry flow of dilute viscoelastic fluids in microchannels at low Re but high Deborah (De) number. The majority of the works were focused solely on studying single homogeneous viscoelastic fluid flow. There is much less attention on the multiple-stream flow instability of viscoelastic fluids through planar contraction/expansion microdevices and its application for mixing enhancement via this viscoelastically induced flow instability.

Albeit the elastic fluid's flow instability and enhancement of mixing at microscale curvilinear flow-path were reported recently [Burghilea *et al.* 2004, Pathak *et al.* 2004]. A relatively long mixing path with a large number of turnings at moderate flowrate is the major drawbacks. It appears that hitherto the viscoelastic effects of a fluid have not been exploited effectively. Indeed, to exploit effectively the viscoelastic flow instability, smaller geometries with geometrical discontinuity should be employed. Stress singularities developed at these sharp corners at geometrical discontinuity have been the source of elastic instabilities in many macro

scale experiments, while rounded corners tend to suppress elastic behavior [Bird *et al.* 1987]. This complex interplay that arises between the elasticity/viscosity of the fluids and the ratio of the elasticity of the mainstream and the side streams are the keys for viscoelastic flow instability and hence for an efficient mixing of fluid streams in microchannels. Furthermore, on micro-lengthscale, flow regimes previously not achievable on macro-lengthscale could be explored. For example, with proper design of the channel and flow conditions, viscoelastic flows with negligible inertial effects could be achieved. This type of flows can be characterized by the Deborah number, De , alone, which is analogous to Reynolds number for viscous-inertial (Newtonian) fluid flow. Therefore microfluidic planar contraction/expansion also provides an opportunity to investigate the critical Deborah number for the onset of multiple-stream flow instability, and thus for mixing on micro-lengthscale.

6.1 Dimensionless parameters

Four dimensionless quantities were commonly used to characterize the dynamics of planar contraction/expansion multiple-stream flow of viscoelastic fluids in microchannel: the Deborah number (De), Reynolds number (Re), Elasticity number (El) and Peclet number (Pe).

For an aqueous or a viscous solution, the onset of flow instability can be characterized by the Reynolds number, Re , which measures the relative importance of inertial and viscous effects in a fluid flow. It can be defined as

$$Re = 2\rho\dot{Q}/\eta_o(w_c + d) \quad (6.1)$$

where d is taken as channel depth, w_c is the contraction width, ρ is the fluid density, η_o is the fluid viscosity and $\dot{Q}$ is the total volumetric flowrate.

For a given geometry, the viscoelastic effects of a fluid flow can be characterized by the Deborah Number, De . The Deborah number is a dimensionless parameter which typifies the

relative importance of the elastic stresses of the fluid with the time scale of the flow system [Bird *et al.* 1987]. Generally, smaller dimension results in a higher characteristic deformation rate for the same flowrate, resulting in higher elastic effects and thus a higher De.

Deborah number may be defined in terms of a characteristic polymer fluid relaxation time (λ_e) and an average characteristic shear rate ($\dot{\gamma}_{char}$) in the contraction channel. As the channel depth governed the shear rate in the channel, it was taken as the characteristic length (d). Thus, the characteristic shear rate may be written as $\dot{\gamma}_{char} = \bar{V}/(d/2) = 2\dot{Q}/w_c d^2$. Hence, Deborah number may be expressed as,

$$De = \lambda_e \dot{\gamma}_{char} = 2\lambda_e \dot{Q}/w_c d^2 \quad (6.2)$$

A smaller channel has smaller flow characteristic length and time. Thus, Re is smaller and it is difficult to have inertia/viscous flow instability. Conversely, De becomes larger and it is easier to have elastic/viscous instability. The relative dominance of elastic to inertial effects is typified by the elasticity number, El, i.e. the ratio of fluid elasticity to fluid inertia. El is expressed as

$$El = De/Re = \frac{\lambda \eta_o (w_c + d)}{\rho w_c d^2} \quad (6.3)$$

The elasticity number is constant for a given fluid and geometry and is dependent only on the fluid properties and the inverse of the characteristic cross-sectional area.

For mixing in laminar flow, diffusion is an important mechanism. Peclet number, Pe, indicates the relative importance of advection to diffusion, and is given by

$$Pe = \dot{Q}W / D(w_c d) \quad (6.4)$$

where W is the upstream channel width and D is the diffusion coefficient. The higher the Pe , the less significant the diffusion effects. The diffusion coefficient of the dye in water was $D = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$ [Wu *et al.* 2004]. Since diffusion coefficient is inversely proportional to the viscosity [Einstein 1956], we estimated that $D = 1.66 \times 10^{-12} \text{ m}^2/\text{s}$ for 1% PGWF.

In addition, we proposed here the ratio of De (De_{ratio}) of two streams to typify the flow characteristics of planar contraction-expansion multiple-stream flows, De_{ratio} is defined as,

$$De_{\text{ratio}} = \frac{De_{\text{main}}}{De_{\text{side}}} = \frac{\lambda_{\text{main}}(\bar{V}_{\text{main}})}{\lambda_{\text{side}}(\bar{V}_{\text{side}})} \quad (6.5)$$

To have a common ground for comparison in the subsequent analysis, all parameters were calculated based on the average velocity of the flow system. The computed parameters could be over-estimated for semi-dilute sample fluid stream (i.e. 1% and 0.8% PGWF) and under-estimated for dilute sample fluid stream (i.e. 0.1% and 0.3% PWS). However, this computation was performed due to the difficulty involved in measuring precisely the actual flow in the contraction channel for each flow stream.

To have an appreciation for the range of the dimensionless parameters investigated, experiments conducted with 1% PGWF mainstream and 0.1% PWS side streams in silicon-glass microdevices had $20.4 < De < 244.1$, $0.004 < Re < 0.030$ and $5.8 \times 10^3 < El < 8.0 \times 10^3$. These high El values are typically not accessible in the equivalent macro-scale experiments and are very large compared to the reported values on abrupt planar contraction/expansion flow. Thus, the flow regime investigated here has negligible inertial effects and can be characterized by De alone. Moreover, the Peclet number (Pe) for all flowrates investigated were large ($Pe > 8.9 \times 10^6$). Thus, mixing based on molecular diffusion was negligible.

6.2 Proof of Concepts

The ease of fabrication and the shorter design cycle (within 48 hours) using direct laser micromachining on polymer substrate offer an economical alternative for researchers to prove their ideas and concepts. Thus, the concepts of viscoelastically induced multiple-stream flow instability and thus mixing enhancement in microchannels were first realized on a polymer-based device with a simple convergent/ divergent channel configuration [Gan *et al.* 2006a].

In the preliminary experiments, a PMMA microdevice of 200 μm in depth with an abrupt contraction of 1600 μm : 200 μm : 1600 μm was employed to introduce convergent/divergent flows, see Figure 6-1 [Gan *et al.* 2006a, Lam *et al.* 2006]. The microchannel was fabricated using two 1 mm thick PMMA layers, with the channels machined by CO₂ laser onto the top layer, and sealed by the bottom layer. The length of the contraction is 800 μm . Side streams were introduced into the central main stream through two side channels, each at either side of the main channel. The side channels were 800 μm in width, and 3400 μm upstream from the centerline of the contraction, see Figures 6-1(a) and (b) for illustrations.

Figure 6-1. (a) Geometry of the PMMA-based microdevice, (b) Ready-to-use PMMA microdevice. The mainstream, which has higher viscosity and elasticity, consists of 1 wt% PEO in 55 wt% glycerol water with green fluorescent dye (1% PGWF for brevity). The side streams, consisting of 0.1 wt% PEO in water with 3 μm fluorescent microspheres solution (0.1% PWS for brevity), enter the main microchannel through the two side channels. The molecular weight

(M_{wt}) of PEO employed is approximately 2×10^6 g/mol. The trace amounts of fluorescent dye and microspheres have negligible effects on the fluids' properties. The sample liquids were delivered by a precision micro-syringe pump (Lomir Biomedical Inc.). The main stream flowrate was $0.5 \dot{Q}$. The flowrate of the two side streams was the same and each having $0.25 \dot{Q}$. Thus, the total flowrate in the device was $\dot{Q}$.

6.2.1 Observation of viscoelastically induced flow instability

At $\dot{Q} = 10$ ml/hr ($Re = 0.04$, $De = 34.7$ and $El = 932$), small viscoelastic vortices formed at the corners of the upstream contraction in a symmetrical fashion, see Figure 6-2(b) upstream. Flow instability and pulsation induced by viscoelastic effects were observed in the flow field. When the flow approached the contraction entrance, more and more fluorescent creeks (initially contained within the central main stream) were directed to the sides instead of flowing through the contraction. The diverted “creeks” were then circulated within the vortex (swirling stream) and then blended back into the central main stream. Competition between the main and the side streams was taking place at the entrance region next to the contraction. This competition increased with an increase in flowrate, and the entire flow field became increasingly unstable and with increasing size of the vortices ($\dot{Q} = 20$ ml/hr to 40 ml/hr with $De = 69.4$ to 139 and $El = 932$).

At $\dot{Q} = 40$ ml/hr ($Re = 0.149$, $De = 139$ and $El = 932$), salient and large corner vortices were formed, and “whipping” or repeated swinging of the fluorescent main central stream across 70% of the channel width was observed. This whipping effect resulted in the fluorescent mainstream “encapsulating” the fluid of the side streams. The main stream with the “encapsulated” fluid swung together continuously as the flow was progressing. As shown in Figure 6-2(c) upstream, a lower level of fluorescent intensity was observed at the proximity of the “swinging” mainstream, indicating some degree of mixing at upstream. By comparing

Figures 6-2(c)-(d) upstream, we observed significant overlapping occurring between the main and the side streams, indicating mixing.

Figure 6-2. DVD camcorder images of viscoelastic multiple-fluid flow in microchannels with 8:1 contraction ratio for specific case of 1% PGWF at mainstream (center stream) and 0.1% PGWS at side-stream at two different flowrates, (a-b) $\dot{Q} = 10$ ml/hr and (c-d) $\dot{Q} = 40$ ml/hr. [Gan *et al.* 2006a].

Viscoelastic flow instability was more significant downstream of the contraction, subsequent to the main and side streams competing and gushing through the contraction at high speed. At $\dot{Q} = 10$ ml/hr, there was expansion flow for the main stream immediately downstream of the contraction, see Figure 6-2(a) downstream. However, as shown in Figure 6-2(b) downstream, there was obvious penetration of the side stream fluid into the central portion of the channel, overlapping with the main stream fluid. This penetrated-stream fluctuated in location and was intermittent, indicating flow instability. Similarly, by comparing Figures 6-2(a)-(b) downstream, there was overlapping between the main and the side streams, indicating mixing, but not fully extended across the whole channel width downstream. At $\dot{Q} = 40$ ml/hr, as discussed previously, there was significant viscoelastic whipping of the mainstream at upstream. This caused flow fluctuation of the main stream through the contraction, and fluctuation of flow resistance to the two side streams. Indeed, this whipping of the main stream facilitated the side streams penetrating deeply into the central portion downstream, see Figures 6-2(c)-(d) downstream. These fluctuations resulted in chaotic flow (and possibly turbulence)

downstream of the contraction. This chaotic flow, together with the expansion-flow of the main stream, promoted effective mixing. As illustrated in Figures 6-2(c)-(d) downstream, other than a thin layer next to the edge of the channel wall, significant mixing had occurred over the entire cross-section. The occurrence of upstream corner vortices and whipping of the main stream is depicted schematically in Figure 6-3.

Figure 6-3. Pictorial images of viscoelastic flow field of low-viscosity PEO fluids at two different flow conditions. The light-color lines represent main stream and dark-thick arrow lines represent side streams. (a) $\dot{Q} = 10$ ml/hr showing corner vortices and some mixing downstream, and (b) $\dot{Q} = 40$ ml/hr, highlighting the viscoelastic instability (whipping) upstream and chaotic flow behavior downstream [Gan *et al.* 2006a].

6.2.2 Necessity of viscoelasticity

To study the necessity of fluid viscoelasticity for multiple-stream flow instability and subsequent mixing enhancement, two different Newtonian flow experiments were conducted at $\dot{Q} = 40$ ml/h [Lam *et al.* 2006].

(i) Viscous effects – 26 wt% and 96% wt% glycerol water solutions were employed in the main and the side streams respectively, see Figure 6-4(a). The viscosity ratio is approximately

the same as the viscoelastic flows mentioned in the previous section. With higher viscosity, flow inertia was suppressed completely, and no corner vortices were observed throughout. The entire flow field was stable, the interface between the streams was smooth and well defined, indicating that fluid viscosity alone was insufficient to trigger flow instability.

(ii) Inertia-viscous effects – DI water with fluorescent additives was employed for both streams, see Figure 6-4(b). Water has negligible elasticity and very low viscosity. It provided the largest flow inertia among the investigated flow conditions. At upstream of the contraction, the interface between the streams was well defined and stable. However, a pair of symmetrical corner vortices (lip vortices) were formed immediately downstream of the contraction due to expansion flow effects and is in good agreement with the literature [Drikakis 1997, Hawa and Ruzak 2001]. There were some spread of the main streams at downstream due to possible chaotic advection and diffusion along the flow. However, no penetration of the side streams into the mainstream could be observed at downstream of the contraction.

Cases (i) and (ii) indicate that fluid viscosity and low fluid inertia were insufficient to induce multiple-stream flow instability and thus did not generate mixing enhancement in microchannels. This indicates that the viscoelasticity of the fluids is essential for flow instability and for mixing enhancement.

Our preliminary investigations demonstrated viscoelastically induced multiple-stream flow instabilities for convergent/divergent viscoelastic fluids flow. Mixing enhancement was also illustrated qualitatively. However, there is a lack of a clear in-depth understanding and quantification of the nonlinear interaction between the shear and extensional rheology of the fluids with the generation of viscoelastic instability and mixing for a multi-streams flow in microfluidic channels. Indeed, mixing in this type of device is also yet to be characterized and optimized. However, as the PMMA-based device was laser machined resulting in rough

surfaces and poor micro-geometrical profile definition, the quantitative characterization of the flow behavior and mixing were difficult.

Thus, in subsequent investigations, we employed instead high precision micromachined silicon/glass chips with good surface finish, geometrical definition and optical transmittance. Fluorescent dye and micro-spheres were used with mercury lamp (for dye-concentration measurement) and Nd-YAG lasers (for μ -PIV measurement) to characterize the dynamical flow field and mixing efficiency.

Figure 6-4. Flow behaviors for viscous fluids and water at $\dot{Q} = 40 \text{ ml/h}$. The observed flow fields were steady and stable. (a) Viscous fluid flow with negligible elastic and inertial effect with no mixing observed. (b) Water for both main and side streams. Due to inertial/viscous effects, vortices formed at corners downstream of contraction [Lam *et al.* 2006].

6.3 Silicon-Glass Microdevices

For rigorous investigations and better characterizations of the actual flow field, three different silicon-glass microdevices with different contraction ratio (CR), were employed to introduce the convergent/divergent flow instability. The three CRs are 4:1:4, 5:1:5 and 8:1:8, with a uniform depth of 150 μm and a fixed dimension of 1000 μm for upstream and downstream widths. The length of the contraction was 1000 μm . Side streams were introduced into the central mainstream through two side channels, each at either side of the main channel. The side channels were 1000 μm in width and were located 3000 μm upstream from the centerline of the contraction. The channel structures were machined in a silicon wafer, see Figure 6-1, using the deep reactive ion etching (DRIE) technique and sealed by a Pyrex glass wafer using anodic bonding (refer to Chapter 5 for detailed discussions). The silicon/glass stack was then diced into 10 mm $\times$ 10 mm single test chips. A polymeric holder with tubings was designed and fabricated as the micro/macro fluidic interface.

For a neat and brief illustration of μ -PIV and dye-dilution experiments, experimental measurements of specific flow case of 1% PGWF with 0.1% PWS in CR 8:1 silicon-glass microdevice would be presented as typical results in sections 6.3 and 6.4.

Figure 6-5. Configuration of silicon-glass abrupt convergent/divergent microdevice. (a) Silicon-glass chip and Teflon device holder, (b) physical dimensions of 8:1:8 micro-geometry configuration and (c) the assembled microdevice [Gan *et al.* 2006b].

6.3.1 Streak flow and fluorescent-dyed flow imaging

Figure 6-6 presents consecutive snapshots (DVD-camcorder imaging) of particle streak flow and fluorescent dyed flow in a CR 8:1 silicon-glass microdevice. Good surface finish (machining marks were eliminated) and image contrast were obtained from the high precision micro-machined silicon-glass device. The flow field images in the same experiment were visualized using the green fluorescent dye (mainstream) and the red fluorescent microspheres (side streams). The images of individual flow stream were captured at the same location by switching the epi-fluorescent attachments of the microscope, and Chapter 4 contains a description of the imaging techniques. Both green and red filters have a bandwidth of 25 nm. The separated fluorescent bands of the red particles (540/610 nm) and of the green dye (490/520 nm) allowed a clear discrimination of the sample fluids.

(i) Particle streak flow (sidestream) (ii) Fluorescent dyed flow (mainstream)

Figure 6-6. DVD camcorder images of two-dissimilar viscoelastic fluid flow, with 1% PGWF and 0.1% PWS, through a CR 8:1 convergent/divergent microgeometry at $\dot{Q} = 10$ ml/h. (i) Microsphere (3 μ m) added to side streams, 0.1% PW (ii) Green fluorescent dye added to main stream, 1% PGW [Lam *et al.* 2007].

For the case of 1% PGWF with 0.1% PWS, similar viscoelastically induced flow instabilities to those observed on PMMA microdevices were observed in silicon-glass microdevices, see Figure 6-6. Salient and large corner vortices with repeated whipping of the mainstream across the channel width were observed at upstream of the contraction. Viscoelastic flow instability was more prominent at downstream of the contraction, due to the hybrid effects of expansion flow and competition of the streams through the contraction at a high flow velocity. Consistent with the previous observations, at downstream of contraction, other than a thin layer next to the edge of the channel wall, significant overlapping of two streams occurred over the entire channel cross section indicating good mixing.

With good surface finish, geometrical definition and optical transmittance of the silicon-glass microdevice, multiple-stream flow instability and induced micro-mixing in planar contraction-expansion microchannel could be analyzed quantitatively. There will be discussed in the following sections.

6.4 Micro-PIV Measurement

We analyzed the multiple-stream flow dynamics of two dissimilar viscoelastic fluids, 1% PGWF with 0.1% PWS, based on the measurements of velocity flow field. With reference to the mainstream fluid (1% PGWF) properties, experiments were performed over a range of De and Re ($40.69 < De < 244.1$, $0.005 < Re < 0.031$). The elasticity number ($El = 7.998 \times 10^3$) was constant as discussed in the previous section. With this enormous elasticity number, we had ventured into a flow regime with negligible inertial effects which can be characterized by De alone. As the Peclet number (Pe) for all viscoelastic fluid flow experiments were large ($Pe > 1.78 \times 10^7$), mixing based on molecular diffusion was negligible.

6.4.1 Measurement of the velocity field

As fluorescent microspheres were added only to the side streams (0.1% PW) for μ PIV investigations, only the flow field of the side streams would be measured. The microspheres have a maximum excitation wavelength close to the characteristic wavelength of Nd:YAG laser. The measurement was carried out with a 4 $\times$ objective lens and two 30 mJ laser pulses with a delay time of 4 ms. At least 200 images were collected for every flow condition. The fluorescent microspheres solution was not added to the higher viscosity 1% PGW. This would ensure that any velocity measured was related to particles originated from the side streams. This would allow us to evaluate easily the penetration of the side streams to the main stream. In addition, if the solution was added to the main stream, it would compromise the viscosity of the main stream due to the exponential relationship of viscosity to the concentration of the polymeric solution, particularly the solvent glycerol.

Figure 6-7 shows the typical results obtained from the μ PIV measurements both upstream and downstream of the contraction. For viscoelastic two-fluid flow at $\dot{Q} = 10$ ml/h, asymmetrical vortices was observed and confirmed with post-analysis (streamlines and velocity vector field)

using a commercial PIV software (Flow Manager, FlowMap). The formation of these asymmetrical vortices based on empirical observations was discussed in our previous sections.

Figure 6-7. Typical results of two-dissimilar viscoelastic fluid flow ($\dot{Q} = 10$ ml/h, trace microspheres are in the side streams): (a) raw particle image, (b) evaluated streamlines of the flow field, (c) evaluated velocity field, and (d) surface plot of the velocity magnitude.

Figure 6-8 presents the consecutive velocity fields and CCD streak flow snapshots of viscoelastic two-fluid flow at $\dot{Q} = 10$ ml/h ($De = 203.5$ and $Re = 0.025$). Salient and large corner vortices with viscoelastic “whipping” at upstream of the contraction were evident. Successive snapshots showed a large fluctuation of both magnitude and direction of the velocity vectors. This fluctuation indicates the highly unstable nature of the viscoelastic flow. The chaotic competition of the two fluids at the contraction and across the downstream channel was illustrated. These results were in good agreement with our earlier observations.

(a) **Downstream**

Upstream

Figure 6-8.
Consecutive
snapshots at a
time interval of 2.4
s for viscoelastic
fluids flow of $\dot{Q} =$
10 ml/h for 1%
PGWF
(mainstream) with
0.1% PWS (side
streams, with trace
microspheres). (a)
PIV measurements
and (b) CCD
streak-flow.

Figure 6-9, Figure 6-10 and Figure 6-11 show the statistical analyses of the velocity flow profile for three different flowrates, 0.5, 5 and 10 ml/h, respectively. At $\dot{Q} = 0.5$ ml/h ($De = 40.69$ and $Re = 0.005$), the entire flow field was stable and steady. The flow was laminar and the measured results show a small variance in velocity, see Figure 6-9. For the upstream velocity profile shown in Figure 6-9(a), no data points were shown at the central portion due to the lack of fluorescent microspheres in the mainstream. The downstream velocity profile (Figure 6-9(b)) shows large variances at the central portion of the channel. This phenomenon was caused by the penetration of fluorescent microspheres from the side streams into the mainstream. This penetration was intermittent but consistent. However, in general, the entire flow field shows little flow instability.

Figure 6-9. Velocity profile across the channel at $\dot{Q} = 0.5$ ml/h (each plot represents statistic over 50 image pairs and 1,000 data points): (a) upstream of the contraction and (b) downstream of the contraction.

At higher flowrates, i.e. $\dot{Q} = 5$ ml/h ($De = 101.7$ and $Re = 0.013$), salient corner vortices were formed upstream of the contraction. The upstream vortices formed were larger than in $\dot{Q} = 0.5$ ml/h but remained rather constant in size. The entire flow field was still rather laminar-like. This fact was supported by the symmetrical velocity profile plot with an increasing, but still relatively small variance, see Figure 6-10. As shown in Figure 6-10(a), at upstream of the contraction, there was a region at the center portion of the channel with much higher velocity. This indicates that the side streams particles had penetrated into the mainstream and their velocity increased due to the transfer of momentum from the mainstream to these side stream particles. As shown in Figure 6-10(b), at downstream of the contraction, one can observe more penetrations of the side streams into the central portion of the channel, with increasing fluctuation of the flow field at the center portion of the channel.

Figure 6-10. Velocity profile across the channel at $\dot{Q} = 5$ ml/h (each plot represents statistic over 50 image pairs and 1,000 data points): (a) upstream of the contraction and (b) downstream of the contraction

However, when $\dot{Q}$ increased further to 10 ml/h ($De = 203.5$ and $Re = 0.025$), the upstream vortices were the largest and unstable in nature, as discussed previously with “viscoelastic whipping” of the central mainstream at upstream of the contraction. The flow pattern reflected a competition between the main and the side streams at the entrance of the contraction with significant velocity fluctuation, see Figure 6-11(b). The entire flow field was unstable and chaotic. The whipping effects allowed the side streams to penetrate deeply into the central portion downstream. Extensive flow instability occurred downstream of the contraction as indicated by the large velocity variance. Indeed, the well defined parabolic average velocity profile (solid line) in Figure 6-11(a) was much less obvious in Figure 6-11(b), suggesting the possibility of the onset of chaotic flow. In addition, with deep penetration of the side streams into the main stream, and with flow instability, it was expected that effective mixing would result in the microchannel.

Figure 6-11. Velocity profile across the channel at $\dot{Q} = 10$ ml/h (each plot represents statistic over 50 image pairs and 1,000 data points). (a) upstream of the contraction and (b) downstream of the contraction.

6.5 Dye-Dilution Measurements

In dye-dilution experiments, concentration measurements were conducted in order to evaluate the efficiency of mixing for the flowrate investigated. In this section, silicon-glass microdevice (CR = 8:1) at flowrate of $\dot{Q} = 10$ ml/h was used as an example. The dynamics of the various two-fluid flows was also qualitatively investigated, based on the competition of the dominant forces in the flow field, namely viscous/elastic, viscous/viscous and viscous/inertial. Fluorescent dye and microspheres were used with mercury lamp (as illumination source) to visualize the flow.

The measured area was illuminated by a mercury lamp. The mainstream with green fluorescent dye images as recorded by CCD camera, Figures 6-12 (a-iii), (b-iii) and (c-iii), were employed for evaluating the mixing performance. The DVD camcorder images in Figure 6-12 were for visualization only. The side streams with red microspheres, which appeared as red streak flow would track the flow of the side streams. DVD-camcorder images (color streak flow and fluorescent-dyed flow) and CCD images (concentration measurement) were recorded at the same location (in the same experiment) at different times.

To confirm the necessity of fluid viscoelasticity for multiple-stream flow instability, viscous fluids, namely 96.1% and 26.1% glycerol/water solutions (96.1%GW and 26.1%GW), with no measurable elastic effects were first investigated. The viscosity ratio is approximately the same as for the viscoelastic flows. The entire flow field was stable for all flowrates investigated, for example $\dot{Q} = 10$ ml/h ($Re = 0.032$, De and $El \approx 0$), see Figure 6-12 (a). The interface between the streams was stable and was well defined, with no mixing observed. Similar to PMMA device, fluid viscosity alone was insufficient to trigger flow instability.

For benchmarking, de-ionized water (DI water), which is a Newtonian liquid with negligible elasticity and low viscosity, was also investigated ($Re = 20.20$ at $\dot{Q} = 10$ ml/h), see Figure 6-12(b). The entire flow field was dominated by the viscous-inertial effects. At upstream of the contraction, the interface between the streams was well defined and stable. A pair of symmetrical corner vortices (lip vortices) were formed immediately downstream of the contraction due to the expansion flow effects and is in good agreement with previously reported results. There were some spreads of the main stream at downstream of the contraction possibly due to the sudden expansion flow immediately after the contraction. However, no penetration of the side streams into the main stream was observed.

Flow characterization for the viscoelastic fluids (1% PGWF and 0.1% PWS) were shown in Figure 6-12(c). At upstream of the contraction, salient and large corner vortices with repeated whipping of the mainstream across the channel width were observed. Mixing was expected as there was overlapping region of the green fluorescent dye (main-stream) and red microspheres (side-stream). Indeed, it was observed that the main stream also penetrated into the two corner vortices of the side streams at the proximity of the contraction entrance. At downstream of the contraction, due to pronounced viscoelastic flow instability, other than a thin layer next to the edge of the channel wall, significant mixing had occurred over the entire channel cross section, see Figure 6-12(c) downstream. The observed mixing regions were consistent with the viscoelastic instability regions and phenomena observed through the measurements of the velocity field as described in the previous section.

Figure 6-12. Typical images of three different fluid flows at $\dot{Q} = 10$ ml/h: (a) glycerol water (b) DI water and (c) viscoelastic fluids (1% PGWF and 0.1% PWS) in a CR 8:1 silicon-glass microdevice. (i) DVD camcorder particle streak flow images, (ii) DVD camcorder fluorescent-dyed flow images and (iii) CCD measurement of fluorescence concentration.

6.5.1 Dye-concentration probability density function (PDF)

After recording the high resolution CCD images on a PC (Figure 6-12(iii)), the probability density function (PDF) (concentration distribution profile) of the intensity images (the entire upstream and downstream channels, with an analysis window of $2000\ \mu\text{m} \times 950\ \mu\text{m}$ approximately) were evaluated using a customized program written in MATLAB. The noise in the measured image was removed with an adaptive noise-removal filter. For each pixel, a local mean value was calculated with a window of 5×5 pixels. The noise distribution was assumed to have a Gaussian characteristic. Mixing performance was evaluated using the evaluated PDFs. The intensity of the grayscale in the recorded images was proportional to the dye concentration. Thus, the PDF provided quantification on the degree of mixing. For example a function with two prominent peaks that are far apart (one of the dyed fluid and the other of the non-dyed fluid) means that the two fluids are not mixed. A single peak at the mid-range of concentration means good mixing.

Figure 6-13 compares the PDFs for the DI water and viscoelastic fluids flow at upstream and downstream of contraction at a total flowrate of $\dot{Q} = 10\ \text{ml/h}$. For both cases, the PDF of upstream of the contraction had two obvious peaks of the dyed fluid and the non-dyed fluid, indicating insignificant mixing. One should take note that at upstream of contraction the PDF peaks were not symmetrical, although input volumetric ratio of the two fluids was 1:1. This anomaly was attributed to the entry flow effects causing the bending of flow streams at the contraction entrance region, see Figure 6-12. Side-stream occupied a bigger portion (corner of upstream contraction) when approaching the contraction channel. While at downstream of the contraction, the two peaks of the DI water flow remained despite of a significant reduction of the non-dyed fluid peak. This was mainly caused by the downstream expansion flow vortices.

However, for viscoelastic fluids flow, the viscoelastic flow instability leads to a single peak in the PDF indicating significant mixing. Enhanced mixing was achieved even at a very low Reynolds number ($Re \approx 0.025$) and a large Peclet number ($Pe \approx 89.20 \times 10^6$).

Figure 6-13. Probability density function (PDF) of concentration of the fluorescent dye at upstream and downstream channel at a total flowrate of $\dot{Q} = 10$ ml/h for (a) DI water and (b) 1% PGWF with 0.1% PWS (Each curve for (a) or (b) is a statistic of over 10^7 data points for 200 images).

6.5.2 Mixing efficiency evaluation

After normalization of the intensity of the dye to range from 0.0 (100% side stream) and 1.0 (100% main stream), the mixing efficiency ϵ_{eff} is quantified based on the following definition [Gan *et al.* 2006b],

$$\epsilon_{eff} = \left[1 - \frac{\sum_{C_i=0}^{C_i=1} |C_i - C_\infty| P(C_i)}{C_\infty} \right] \times 100\% \quad (6.6)$$

where C_i is the observed concentration on the normalized scale, C_∞ is the concentration on the normalized scale for perfect mixing, and $P(C_i)$ is the probability density function. In our investigation, for equal flowrate of the main and the side streams, perfect mixing concentration is $C_\infty = 0.5$. In equation (6.6), $\epsilon_{eff} = 0\%$ for no mixing and $\epsilon_{eff} = 100\%$ for perfect mixing.

Therefore, based on Figure 6-13, for viscoelastic fluid flow with a total flowrate of $\dot{Q} = 10$ ml/h, the mixing efficiency ϵ_{eff} was found to be 22% at upstream of the contraction and improved significantly to 70% at downstream of the contraction. However, for DI water flow, ϵ_{eff} was found to be 15% at upstream of contraction and 25% at downstream of contraction.

6.5.3 Progression of mixing performance along flow path

Figure 6-14 compares the progression of ϵ_{eff} along the flow path for the Newtonian fluids (DI water) and the viscoelastic fluids at the same total flowrate of $\dot{Q} = 10$ ml/h. This was achieved by evaluating ϵ_{eff} across the channel at various locations along the flow path for both upstream and downstream channels. The size of analysis window was reduced to an area of $30 \mu\text{m} \times 950 \mu\text{m}$ across the channel which was different from the analysis window in section 6.4.2 (area of

2000 μm x 950 μm). The analysis windows were distributed evenly at a spacing of 100 μm except at the proximity of the contraction plane, where the spacing interval was halved, see Figures 6-14 (a) & (b).

Figure 6-14(c) shows the progression of ε_{eff} . At upstream of contraction, for the laminar flow of DI water, there was insignificant mixing (approximately 12% on average). For the viscoelastic fluids flow, on average more than 15% of mixing was found along the upstream channel. Maximum mixing of 30% were observed at a distance of 1.2 mm approximately (section 11 upstream) away from the contraction plane. Indeed, one would expect that ε_{eff} could only increase as flow progressed. Thus, it was interesting to observe that as flow progressed from sections 11 to 1 upstream, ε_{eff} decreased. The surge of ε_{eff} at section 11 was due to the relatively large fluctuation in the flow field or viscoelastic whipping as compared to the region near to the contraction. The scale of whipping was constrained by the converging flow path when approaching the contraction plane. In addition, close to the contraction, the mainstream, and fluids next to the mainstream, which consisted of a mixture of mainstream and sidestreams, were “compressed” and flow at a higher velocity. As such, more of the unmixed side streams would dominate spatially resulting in lower computed mixing efficiency ε_{eff} .

At downstream of contraction, mixing performance for the DI water flow had improved due to the expansion flow effects. Mixing region at the interface of the two streams was stretched out. ε_{eff} had improved from 10% to 30%. Highly concentrated main and side streams could still be identified easily from the CCD images, see Figure 6-14(a). This low efficiency of mixing was as expected for Newtonian flow at this low Reynolds number ($Re \approx 20.20$) and large Peclet number ($Pe \approx 98.80 \times 10^3$).

Figure 6-14. Mixing efficiency along the flow path at $\dot{Q} = 10$ ml/h for (a) DI water and (b) viscoelastic fluids at upstream and downstream channels. In pictures (a) & (b) – Rectangular box represents the analyzed window for the evaluation of mixing efficiency at a specific location. (c) Progression of mixing performance along the flow path.

For viscoelastic fluids flow downstream of the contraction, viscoelastic flow instability together with the expansion flow effects had promoted mixing effectively. Next to the contraction, ε_{eff} was approximately 50%. This was mainly caused by the inhomogeneous volume of fluids discharged through the contraction intermittently, due to the frantic

competition of the two streams at upstream of the contraction. As flow progressed further downstream, mixing was further promoted through viscoelastically induced flow instability, and ε_{eff} increased steadily from 50% to 70%, see Figure 6-14(c). Indeed, the CCD image in Figure 6-14(b) had shown extensive overlapping of the two fluids. Thus, despite of the very low Reynolds number ($Re \approx 0.025$) and a large Peclet number ($Pe \approx 89.20 \times 10^6$), significant mixing was achieved. Homogeneity of mixed stream was obtained at approximately 1.5 mm away from the contraction plane.

In the subsequent discussion for mixing efficiency, the location of analysis window with an area of $80 \mu\text{m} \times 950 \mu\text{m}$ was fixed at approximately 1.5 mm away from the downstream contraction plane to minimize any adverse effects induced by the outlet port (located 3 mm downstream of the contraction plane).

6.6 Viscoelasticity Effects on Multiple-Stream Flow Instability

With negligible elasticity in the fluid stream, mixing performance of two Newtonian flows (i.e. DI water and glycerol-water solutions) was found to be well below 35%. By comparing these two flows, better mixing quality was obtained in DI water than in viscous-fluid (mixture of glycerol in water). Expansion flow vortices formed at salient corner downstream of contraction had mildly improved the diffusion effects between the two DI water streams. These inertial vortices growth in size (symmetrically) with increasing flowrate resulted in slight mixing enhancement. This was reflected as a gentle positive gradient of mixing efficiency in Figure 6-15. However, for glycerol-water solutions, the higher viscosity of glycerol had completely suppressed the expansion flow effects due to smaller Reynolds number (viscous forces dominated). 25% (approximately) of mixing performance was mainly caused by hydraulic focusing effects (narrowing of mixing channel will improve the diffusion effects) in viscous-

viscous fluid flow for all flowrate (Chapter 3 contains a brief review on hydro-focusing mixing mechanism). Both Newtonian flow cases indicated that fluid viscosity and low fluid inertia were insufficient to induce multiple-stream flow instability in microfluidic planar contraction/expansion flow and thus effective mixing was unattainable. This indicates that the viscoelasticity of the fluids is essential for flow instability and hence for mixing enhancement.

The complex interplay that arises between the elasticity/viscosity of the fluids and the ratio of the elasticity of the mainstream and the side streams are the keys for multiple-stream flow instability. As such, the competing effects of the viscoelasticity of the streams viscoelasticity (inertial effects was negligible due to very small Re) on vortex growth and the structure of flow instabilities in multiple-stream flow of viscoelastic fluids were first studied and followed by the geometry (contraction ratio) effects. Lastly, in order to properly characterize the multiple-stream flow instability of viscoelastic fluids, a new parameter De_{ratio} (ratio of viscoelasticity of the mainstream over side-stream) is proposed. In addition, a De_{ratio} - De space is will be presented which summarizes the typical flow behavior or regime of planar contraction-expansion multiple-stream flow. This De_{ratio} - De space could serves as a guide for multiple-stream flow instability of viscoelastic fluids in planar contraction/expansion microchannel.

Figure 6-15. Effects of viscoelasticity of mainstream (center stream) flow on viscoelastically induced flow instability in a CR 8:1 microdevice.

6.6.1 Viscoelastic property of sample fluids

To facilitate the discussion in the following sections, important rheological properties of sample fluid were summarized in Table 6-1. The relaxation time (λ_e) is the key parameter for characterizing a viscoelastic fluid, which was directly proportional to the concentration of PEO contained. The larger the relaxation time the greater the elasticity of a fluid with a more apparent viscoelastic behavior. Generally, for a fluid with large λ_e , the stresses relax slowly and the elastic effects can be detected even at low deformation rates.

Table 6-1. Rheological properties (at 25 °C) of solution containing PEO of $M_{wt} = 2 \times 10^6$ g/mol.

Sample fluid	Relaxation time, λ_e (ms)	Zero-shear viscosity, η_o (mPas)
1.0% PGWF	103	903
0.8% PGWF	64.0	402
0.1% PGWF [Rodd <i>et al.</i> 2005]	23.1	18.2
0.3% PWS [Rodd <i>et al.</i> 2005]	4.40	8.10
0.1% PWS [Rodd <i>et al.</i> 2005]	1.50	2.24

6.6.2 Viscoelasticity effects of mainstream fluids

Mainstream viscoelasticity effects were investigated by employing three different mainstream fluids (i.e. 1%, 0.8% and 0.1% PGWF) with a fixed 0.1%PWS at the side streams. The evolution of flow behaviors, from a stable Newtonian-like flow to a prominent viscoelastic instability flow, and its corresponding mixing performance were illustrated in Figure 6-16. The photographic illustration of flow pattern at the respective point of interest is presented. The importance of mainstream viscoelasticity on multiple-stream flow instability and thus mixing was revealed. Larger value of De_{ratio} (68.7 for 1% PGWF, 42.7 for 0.8%PGWF and 15.4 for 0.1%PGWF) exhibited a stronger cross-stream interaction, resulting in substantial interfacial areas of flow streams at downstream of contraction. Hence, an effective and efficient mixing enhancement was promoted.

From the flow images shown in Figure 6-16, it was found that the evolution of the dynamical behavior of the multiple-stream flow was strongly dependent on the elasticity of viscoelastic fluids of the two streams. For a give De_{ratio} as the flow increased (i.e. De_{main} increased), mixing performance increased and the flow became unstable. Similarly, for a given flowrate (i.e. De_{main}), mixing performance improved and flow became unstable with an increase in De_{ratio} . Typically four specific flow regimes were observed, they are (i) Newtonian-like, (ii) onset

elastic instability, (iii) formation of “lip” vortices and development of corner vortices and (iv) unsteady vortices growth with viscoelastic flow instability.

Generally, at upstream of contraction, the behavior of the multiple-stream flow appeared Newtonian-like for $De < 20$ approximately and streamlines converged in a laminar fashion at upstream of contraction, see Figure 6-16(a3). As De increased, the streamlines began to detach from the laminar flow pattern. The onset of elastic effects was evident and the flow stream was depicted with pronounced curvature streamlines as shown in Figures 6-16(a2) and (c3). At sufficiently high De ($De \sim 40$ for 1%PGWF), a pair of small “lip vortices” was formed at the entrance of the contraction, and growth toward the salient corner with increasing De ($50 < De < 200$ approximately). These upstream corner vortices continued to growth in size and extended upstream in a symmetric manner with increasing flowrate, and remained stable, see Figures 6-16(a1)-b(1) and (b2)-c(2). In Figure 6-16(c1), a diverging flow was observed immediately before De_{opt} was reached (Optimum De , De_{opt} , was defined as the De for optimum mixing, which was typically accompanied by an extensive overlapping of streams at downstream of contraction. $De_{opt} \approx 150 \sim 200$). There was no single vortex (asymmetric bistable vortex) development observed in the span of De investigated, this observation was similar to the results reported by Rodd *et al.* (2005) in single homogeneous viscoelastic fluid flow through planar contraction in microchannel. Bistable single vortex growth was reported to be observed at a relatively low El value ($El = 3.8$) by Rodd *et al.* (2005).

When De_{opt} was reached, salient corner vortices at upstream of contraction were suddenly reduced in size, and became unstable and unsteady in nature, see Figures 6-16(d1) and (d2). Viscoelastically induced multiple-stream flow instability was apparent. One or both sides of corner vortices began to collapse (vanish) randomly and a repeatedly “swinging” of flowing stream (viscoelastic whipping) was induced, see Figure 6-6 and Figure 6-8 for consecutive

snapshots illustration. However, as shown in Figures 6-16 (e1) and (e2), no perceptible change of behavior at upstream of contraction was observed as De was further increased.

At downstream of contraction, when the flowrate was low, the entire flow field was stable and laminar. Three distinct flow streams (mainstream (center) and side streams (upper and lower)) were clearly observed, see Figures 6-16(a1) and (a3). As De increased, flow stream interfaces became wavy and more laminate flow streams (5 flow streams) were formed at downstream of contraction, see Figures 6-16(a1)-(c1) and (a2)-(c2). The repeatedly swinging of streamlines at downstream of contraction intensified with increasing flowrate. At De_{opt} extensive multiple-stream flow instability was reached. Magnified flow streams fluctuation with upper and lower side streams, overlapping one another was observed, see Figures 6-16(d1) and (d2). Prominent cross-stream interaction and large interfacial areas were promoted. Other than a thin layer next to the edge of the channel wall, significant mixing had occurred over the entire channel cross section. As shown in Figures 6-16(e1) and (e2) at higher De ($De > De_{opt}$), the intensity of cross-stream interaction at downstream of contraction did not further improve with increasing flowrate, but a significant suppression of cross-stream interaction was observed and resulting in a reduction of mixing efficiency. This observation was contrary to intuition as it would be natural to expect better mixing with higher De and flowrates. This will be further discussed and analyzed in later sections (sections 6.6.3 and 6.6.4).

Indeed, at upstream of contraction, side-stream fluids were experiencing a shear-dominated flow because of the zero channel wall velocity (assuming no slip condition). However, in the center-stream, viscoelastic fluids was experiencing mainly extensional stretching resulting in much higher strain energy stored within the fluid than that within a shear-stretched fluid. As a result, when both streams gushing out of the contraction, a discontinuity of energy was induced at the stream-stream interface due to a sudden and different amount of elastic energy released by the main and side-stream fluids. These sudden re-coil (or relaxation) of

viscoelastic fluids and the energy discontinuity at the stream-stream interfaces generated a strong convection flow within the system and promoted viscoelastic flow instability. Hence, the relaxation status of individual stream when discharging through the contraction would have significant effects on the discontinuity of energy dissipation at the stream interfaces. As such it could significantly affect the chaotic flow instability at downstream of contraction.

Figure 6-16. Effects of viscoelasticity of mainstream (center stream) flow on viscoelastically induced flow instability in a CR 8:1 microdevice. With aid of photographic imaging of flow pattern and respective Deborah, Reynolds and Elasticity numbers.

6.6.3 Flow residence time in contraction channel

As discussed previously, the relaxation status of individual streams after flowing through the contraction has an important bearing on the flow behavior at downstream of contraction. Here, we consider the relaxing effects of viscoelastic fluids when they entered the contraction channel, prior to the discussion of reduction of mixing quality at $De > De_{opt}$.

The total residence time, t_{res} , in the contraction channel was examined as one of the crucial factor responsible for multiple-stream flow instability. It reveals the status of elongated or stretched viscoelastic fluid when discharged out of the contraction channel. This computation is only an approximation as each fluid in the device was evaluated independently from the other fluid. The computed average velocity could be underestimated for dilute sample fluid stream, and over-estimated for semi-dilute sample fluid stream. This simplification was adopted due to the difficulty in measuring the precise flow velocity at the entrance and exit of the contraction. However, it could serve as a basis for comparison.

The residence time for the fluids in the contraction channel was defined based on the average velocity of a single fluid flow in the device,

$$t_{res} = \frac{L_c}{\bar{V}_c} = \frac{L_c (w_c \times d)}{\dot{Q}} \quad (6.7)$$

L_c is the length of the contraction (i.e., 1 mm), w_c is the contraction channel width, d_c is the channel depth and $\bar{V}_c$ is the average velocity in the contraction channel.

The mainstream fluid, which underwent highly elongational stretching, was assumed to have a similar trend of stress relaxation as in a simple shear flow. Thus, to illustrate the stress

relaxation behavior for different sample fluids, a simple Maxwell liquid stress relaxation model was adopted.

A dimensionless parameter, Γ_{rel} , for the characterization of the instantaneous stress magnitude of a stretched viscoelastic fluid over time (as it flows through the contraction channel) is defined as,

$$\Gamma_{\text{rel}} = \frac{\tau}{G_o} = e^{-t_{\text{res}} / \lambda_e} \quad (6.8)$$

where G_o is the instantaneous modulus (the initial value of relaxation modulus).

The magnitude of Γ_{rel} determined the proportion of non-relaxed stress as the streams flows through the contraction. With Γ_{rel} close to unity, the sample fluid would have less relaxation as it discharges out of the contraction as compared with low value of Γ_{rel} .

Γ_{rel} at the exit of the contraction for different sample fluids employed is presented in Figure 6-17. Generally, for example at moderate flowrate of 10 ml/h, semi-dilute sample fluids (1% PGWF and 0.8% PGWF) would have insignificant relaxation, while dilute sample fluids (0.1% PWS and 0.3% PWS) would have relaxed significantly within the contraction channel.

Figure 6-17. Γ_{rel} (at exit of the contraction) versus total flowrate. When $\Gamma_{rel} \rightarrow$ unity, sample fluids would little relaxing and when $\Gamma_{rel} \rightarrow 0$, they relaxed almost completely.

The multiple-stream flow experiments (as shown in Figure 6-16 and as discussed in the previous section) will now be re-examined in the light of Γ_{rel} evaluated. At De_{opt} ($\dot{Q} = 10$ ml/h for 1%PGWF with 0.1%PWS and 12 ml/h for 0.8%PGWF with 0.1 %PWS), Figure 6-17 shows that little relaxation occurred at the contraction for the mainstream fluid (1% or 0.8% PGWF) but significant relaxation for the side-stream fluids (0.1% or 0.3% PWS). Indeed for 0.1% PWS, it had relaxed approximately 95% as it flowed through the contraction channel before it was discharging into the downstream channel.

For semi-dilute fluids (mainstream), without much relaxation in the contraction, a substantial amount of stored elastic energy would be released comparatively quickly at exit of the contraction due to a sudden lost of physical constraint. Thus, at the interfaces between the mainstream and side streams there would be a discontinuity in the elastic energy stored and

subsequently released and dissipated. At downstream of contraction, the released of a substantial amount of elastic energy from the mainstream (compared to the relaxed side streams) would have induced a strong transverse flow and displaced the relaxed side streams next to it. The random penetration of the mainstream (dependent on the recoil of stretched polymer coils) into the side-streams would result in chaotic cross-stream flow instability at downstream flow field, see Figures 6-16(d1) & (d2). Hence, this discontinuity would have a strong bearing on the multiple-stream flow instability of two-dissimilar viscoelastic fluids.

The whole process was depicted graphically in Figure 6-18. Large cross-stream interactions and interfacial areas were generated and thus significant mixing enhancement was achieved.

Figure 6-18. Graphical illustration of the deformation process of a semi-dilute sample fluid polymer-coil (white color ring) through a planar contraction/expansion flow, (i) initial equilibrium configuration at further upstream of contraction, (ii) extensively elongated through abrupt contraction (contraction channel) (iii) random penetration of mainstream fluid into side streams at downstream of contraction.

6.6.4 Reduction of mixing efficiency at $De > De_{opt}$

Further increased of De ($> De_{opt}$) resulted in similar flow instabilities at upstream of contraction, see Figures 6-16(e1) & (e2). However, at downstream of contraction it was confined to the channel center region and streak lines were more coherent and showed less pronounced viscoelastic relaxation fluctuation. Consequently, a poorer mixing performance was obtained. This observation was contrary to intuition as it would be natural to expect better mixing with increasing De and flowrate. However, this anomaly could be attributed to the

delayed of relaxation process of higher viscoelasticity fluid (mainstream) further downstream due to the shorter flow residence time. For mixing efficiency evaluation, the location of the analysis window was fixed at 1.5 mm downstream of contraction to minimize any adverse effects from the outlet port (3 mm downstream of contraction). Limitation of flow length from the contraction to the analysis window restricted the relaxation process. The stretched polymer coils was flushing through the analysis window before it could be significantly relaxed. This delayed of relaxation can be characterized by the retardation Γ_{rel} .

Retardation Γ_{Ret} , is defined as

$$\Gamma_{\text{Ret}} = \frac{\tau}{G_o} = e^{(-t_{\text{res}} + \Delta t) / \lambda_e} \quad (6.9)$$

where Δt is the time required for the stream to flow from the contraction exit to the analysis window.

Γ_{Ret} evaluated at 1.5 mm downstream of contraction is shown in Figure 6-19. The results of this analysis was consistent the hypothesis that at high $De > De_{\text{opt}}$, the stretched polymer coils was flushing through the analysis window before it could be significantly relaxed, hence resulting in a lower mixing efficiency as shown in Figure 6-16.

Figure 6-19. Γ_{Ret} (at 1.5 mm downstream of contraction) versus total flowrate. When $\Gamma_{Ret} \rightarrow$ unity, sample fluids would have less relaxation.

6.6.5 Viscoelasticity effects of side-stream fluids

In the last section, we concluded that due to the difference in the viscoelastic property and elongation of the two streams, at downstream of the contraction, a discontinuity existed in the elastic energy stored and subsequently released and dissipated at the stream-stream interfaces. This discontinuity is a crucial factor in triggering the multiple-stream flow instability through a planar contraction-expansion microchannel. Hence, an increment of side-stream viscoelasticity resulting in a reduction of the severity of the energy discontinuity was expected to suppress the flow instability.

The effects of the side streams were examined by having the same mainstream fluid (1%PGWF or 0.8%PGWF) but with different side-stream solutions (i.e. 0.1% PWS or 0.3% PWS). As illustrated in Figure 6-20, the experimental results were consistent with expectation.

With insufficient discontinuity of energy induced at the interfaces, multiple-stream flow instability was not triggered. 0.3%PWS side-stream had poorer mixing performance as compared to 0.1%PWS side-stream, indicating relatively less cross-stream interactions was induced in the downstream channel. This difference in mixing efficiency was exaggerated with an increase in the flow velocity due to the hybrid effects of lower energy discontinuity and shorter flow residence time (as discussed in sections 6.6.3 and 6.6.4).

In addition, by comparing the two sets of data (1%PGWF and 0.8%PGWF mainstreams), the multiple-stream flow instability of viscoelastic fluids was found to be strongly dependent on the ratio of viscoelasticity of the mainstream to the side-stream fluids. De_{ratio} for the two cases differed by a factor of 1.6. (De_{ratio} for 1%PGWF = 68.67 and 0.8%PGWF = 42.67), resulting in a 25% difference in the respective optimum mixing efficiency. Hence, in order to properly characterize the multiple-stream flow instability of viscoelastic fluids, the ratio of viscoelasticity of the mainstream and the side-stream, De_{ratio} , should be employed.

Figure 6-20. Effects of side-stream's viscoelasticity on multiple-stream flow instability. For same mainstream of 1% PGWF or 0.8% PGWF with different side-stream of 0.1% PWS or 0.3% PWS.

6.7 Geometry Effects -- Contraction Ratio (CR)

In Figure 6-21, mixing performance for three different contraction ratio (CR) microdevices was presented for the specific case of 1% PGWF (mainstream) with 0.1% PWS (side streams). From the experimental observations, the bigger the contraction channel, the higher the flowrate was required to achieve significant multiple-stream flow instability for effective mixing.

Average velocity of the flow system was essentially affected by the geometry. In bigger contraction channel (e.g. CR = 4:1), a lower deformation rate and longer flow residence time were induced in the flow system as compared to CR = 8:1. Since the stresses of a viscoelastic fluid relaxes exponentially, see equation (6.8), viscoelastic fluid relaxation could be significant even for a small different in the flow residence time. For example at $\dot{Q} = 10$ ml/h, for CR = 8:1 and CR = 4:1, t_{res} in the contraction is 6.75 ms and 13.5 ms respectively and the deformation rate is 1973 s^{-1} and 988 s^{-1} , respectively.

For CR 4:1 microdevice, the lower deformation rate imposed on the sample fluids and the smaller proportion of stress remained due to higher relaxation after flowing through the contraction would result in a reduction of the severity of the energy discontinuity at downstream of contraction. As a result, poorer transverse flow induced, and thus mixing, was expected for smaller CR. This was consistent with the experimental results obtained as illustrated in Figure 6-21.

Figure 6-21. Geometry effects on mixing performance of flow instability at downstream of contraction. For a typical of 1%PGWF (mainstream) and 0.1% PWS (side streams).

6.8 $De_{ratio} - De_{main}$ Space

The promotion of viscoelastic instability by utilizing microchannels with abrupt contraction/expansion geometry was demonstrated with very high values of Elasticity numbers ($El = De / Re$, a ratio of elastic to inertial forces of the system), which are approximately 932 (PMMA device) and 7998 (silicon-glass device). At such a high Elasticity number, inertial effects were negligible. Thus, Reynolds number is no longer relevant in describing the flow behaviors. The multiple-stream flow dynamics and viscoelastically induced mixing enhancement of two dissimilar viscoelastic fluid streams were essentially governed by the competition of the viscous and elastic forces in the flow field. As such, Deborah number, which is a ratio of elastic to viscous forces of the system, would be the dominant governing parameter. In addition, the chaotic flow instability of viscoelastic fluids in planar contraction-expansion flow was found to be strongly dependent on the ratio of viscoelasticity of

mainstream to side-stream fluids. Thus, in order to properly characterize multiple-stream flow instability of viscoelastic fluids, a new parameter, namely the ratio of viscoelasticity of the mainstream over the side-stream ($De_{ratio} = De_{main} / De_{side}$), was employed.

To provide a guide for the prediction of the onset of multiple-stream flow instability in planar contraction-expansion flows, a De_{ratio} - De_{main} operating space was proposed to characterize the flow behavior.

The evolution in the dynamical behavior of multiple-stream flow of two dissimilar viscoelastic fluids was characterized in the De_{ratio} - De_{main} space shown in Figure 6-22. The space shows clearly the development of four specific flow regimes – (i) steady Newtonian-like flow, (ii) onset elastic instability, (iii) lip vortices and stable symmetric vortex growth and (iv) unsteady vortex growth with viscoelastic flow instability. In Figure 6-22, we illustrated these flow regimes and their locations by blue color slanted dashed-line in the De_{ratio} - De_{main} space. The slanted boundaries imply that the development of the flow regime was strongly dependent on both De_{main} and De_{ratio} . As shown in the space, De_{main} for the inception of each flow regime decreased with an increase in De_{ratio} . The larger the De_{ratio} , the lower the deformation rate required to triggered the elastic instability, because the required level of energy discontinuity at downstream of contraction were much easier to attain.

The four main flow regimes identified will now be further discussed.

A) *STEADY NEWTONIAN-LIKE FLOW REGIME*

At very small De_{main} , multiple-stream flow exhibited Newtonian-like flow behavior. Elastic effects in the flow were comparable to viscous effects and thus the behavior of the multiple-stream flow behaved as a highly viscous Newtonian liquid flowing through an abrupt contraction/expansion. The fluid in the upstream of contraction converged in a laminar fashion

and accelerated directly towards the contraction. At downstream of contraction, the flow field was stable and steady.

B) ONSET OF ELASTIC INSTABILITY

As the flowrate increased and the elastic effects in the flow became important, a dramatic change occurred in the shape of the streamlines. The elastic instability initiated at the re-entrant corner (corner at contraction entrance), the flow field no longer monotonically converged towards the contraction. The streamlines near the centerline diverged and bended. However, at downstream of contraction, the flow streams were apparently stable and steady with some waviness of stream-stream interfaces.

C) LIP VORTICES AND STABLE SYMMETRIC VORTEX GROWTH

Subsequently, an intense vortex (lip vortices) formed at the re-entrant corner. In addition to the formation of lip vortices, the fluid flowed out from the centerline towards the channel corners at upstream of contraction. As De_{main} increased, the lip vortices increased in size and growth towards the channel corners. Eventually, the lip vortices filled the entire upstream contraction plane (channel wall between the upstream channel and the contraction) and the flow entered the stable symmetric vortex growth regime in which further increases in De_{main} led to rapid increased in the size of vortex towards upstream.

At downstream of contraction, three distinct flow streams as in Newtonian-like regime was laminated into more streams with the onset of elastic instability. As the flowrate increased, the flow stream interfaces became wavy. The repeatedly swinging of streamlines at downstream of contraction intensified with increasing flowrate. There was obvious penetration of the side streams fluid into the central portion of the channel, overlapping with the mainstream fluid. This penetrated-stream fluctuated in location and was intermittent and not fully extended across the whole channel width downstream.

D) UNSTEADY VORTEX GROWTH / CHAOTIC INSTABILITY

When the flowrate increased further, the salient corner vortices at upstream of contraction reduced in size abruptly and became unstable and unsteady in nature. One or both sides of the corner vortices began to collapse (vanish) randomly and a repeatedly “swinging” of flowing stream (viscoelastic whipping) was induced. Viscoelastic “whipping” or repeated swinging of the main central stream across the channel width was observed. However, no perceptible change of behavior at upstream of contraction was observed as the flowrate increased further.

Viscoelastic flow instability was more significant downstream of the contraction, subsequent to the main and side streams competing and gushing through the contraction at high speed. Significant viscoelastic whipping at upstream of contraction caused flow fluctuation of the main stream through the contraction, and fluctuation of flow resistance to the two side streams. These fluctuations resulted in chaotic flow downstream of the contraction. Magnified flow streams fluctuation with upper and lower side streams, overlapping one another was observed. Prominent cross-stream interaction and large interfacial areas were promoted. As shown in Figure 6-22 at higher De_{main} , the intensity of cross-stream interaction at downstream of contraction did not further improve with increasing flowrate, but a significant suppression of cross-stream interaction was observed. The possibility (as analyzed previously) of this anomaly could be attributed to the hybrid effects of the delayed of relaxation process of higher viscoelasticity fluid (mainstream) due the shorter flow residence time. The stretched polymer coils was flushing through the analysis window before it could be significantly relaxed and induced flow instability.

Figure 6-22. Summary of flow regimes in $De_{ratio} - De_{main}$ space for multiple-stream flow of viscoelastic fluids through planar contraction-expansion (CR 8:1) microchannels.

6.8.2 Effective Mixing Characterization

The performance of mixing enhancement through viscoelastically induced multiple-stream flow instability of two dissimilar viscoelastic fluids could be similarly characterized in the De_{ratio} - De_{main} space, see Figure 6-23. This space clearly illustrates the effects of De_{ratio} and De_{main} associated with the induced mixing enhancement. The performance of mixing was greatly improved with increasing De_{ratio} and/or De_{main} . Noting that for a few observations at the chaotic flow instability regime, the reduction in mixing performance with increased flowrate was due to the location of the analysis window. This reduction, as analyzed in sections 6.6.3 and 6.6.4, might not be an actual reduction in mixing performance. Thus, in subsequent discussions on the trend of mixing performance, these observations will not be included. These observations are shown as red-color boxed data points in Figure 6-23.

For a constant De_{ratio} , Figure 6-23 indicated that with an increase in flowrate, thus De_{main} , the flow regime evolved from Newtonian-like to onset elastic instability, then followed by symmetric vortex growth and finally chaotic instability. Mixing was relatively low at the Newtonian-like flow regime ($\approx 25\%$). There was an abrupt improvement on mixing when crossing from this regime to the onset instability flow regime with mixing performance achieving $\approx 40\%$ except those at very low De_{ratio} . Subsequently, the improvement of mixing performance was rather gentle when De_{main} increased further, and the flow regimes progressed to symmetric vortex growth and chaotic instability flow regimes. Only at very high De_{ratio} , mixing performance was significant much higher ($\approx 60\% \sim 70\%$). However, it was noticed that even for a constant high De_{ratio} , there was only mild increase in mixing performance as De_{main} increased.

Thus, Figure 6-23 indicates that De_{ratio} is a more significant parameter for mixing performance. For a given De_{main} , mixing performance increased significantly with an increase in De_{ratio} .

regardless if there was any change from one flow regime to another as a consequence of the increment in De_{ratio} .

As analyzed in section 6.6.3, De_{ratio} links directly with the viscoelastic energies of the two streams and the energy discontinuities at the interfaces of the streams at downstream of contraction. This is believed to have a direct bearing on the inter-penetration of the streams at downstream of contraction and thus the degree of mixing. As such, it is not a surprise to observe in Figure 6-23 that De_{ratio} is the more significant parameter than De_{main} .

Hence, as demonstrated in this section, the De_{ratio} - De_{main} operating space is also useful to characterize mixing performance of multiple-stream flow of viscoelastic fluids.

Figure 6-23. De_{ratio} — De_{main} operating space with mixing efficiency for different flow conditions (in percentage) in a typical device of CR 8:1.

6.9 Summary

This chapter presents the realization of chaotic flow instability in microchannels, and rigorous and systematic investigations on multiple-stream flow instability of viscoelastic fluids at flow regime with negligible inertial effects.

Fluid viscosity and low fluid inertia were found to be insufficient to induce multiple-stream flow instability, resulting in minimum mixing enhancement in microchannels. This indicates that the viscoelasticity of the fluids is essential for flow instability and for mixing enhancement. The multiple-stream flow dynamics, and thus viscoelastically induced mixing enhancement, of two dissimilar viscoelastic fluid streams were mainly governed by the competition of the viscous and elastic forces in the flow field. The complex interplay that arises between the elasticity and viscosity of fluids and the contraction ratio of the channel were investigated. These multiple-stream flow behaviors were characterized in terms of steady Newtonian-like flow patterns, onset of viscoelastic instabilities, symmetric vortex growth and viscoelastically induced chaotic flow instability. The chaotic flow instability was found to be strongly dependent on the ratio of the viscoelasticity of the mainstream to the side-stream fluids.

To properly characterize the multiple-stream flow instability of viscoelastic fluids, a new parameter, namely the ratio of viscoelasticity of the mainstream over side-stream ($De_{ratio} = De_{main} / De_{side}$) was employed. The effects of the viscoelasticity of the fluids have been quantified and summarized in the proposed De_{ratio} - De_{main} space, see Figure 6-22. This space may be employed as a guide to predict the onset of multiple-stream flow instability in planar contraction/expansion flows. In addition, the same space was utilized to characterize mixing performance, see Figure 6-23.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The focus of this dissertation is to examine the planar contraction/expansion multiple-stream flow instability of two dissimilar viscoelastic fluids in microchannels and the mixing of these two fluids.

Experimental observations demonstrated the existence of viscoelastically induced chaotic flow instability in planar contraction/expansion microchannels. The underlying mechanism was depended on the ratio of viscoelasticity of mainstream to side-stream fluids and the viscoelastic energies of the flow streams. A new governing parameter, $De_{ratio} = De_{main} / De_{side}$, was employed to characterize the dynamical flow behaviors, where De_{main} and De_{side} are Deborah number associated with the mainstream and the side streams respectively. Furthermore, a De_{ratio} - De_{main} operating space was employed to provide a guide for the prediction of multiple-stream flow instability and thus mixing performance.

This chaotic flow instability was generated at very high values of Elasticity number (El, a ratio of elastic to inertial forces of the flow system), which are approximately 932 (PMMA device) and 7998 (silicon-glass device). With hitherto little unexplored flow regime at such an enormous El, Re is no longer relevant in describing the flow behaviors. With this De_{ratio} – De_{main} operating space, the evolution in dynamical flow behavior was well characterized. The operating space illustrated the development of four specific flow regimes. They are steady Newtonian-like flow regime, onset elastic instability flow regime, symmetric vortex growth flow regime and chaotic flow instability flow regime. Slanted regime boundaries were identified in the space to categorize these four flow regimes. These slanted boundaries imply that De_{ratio} and De_{main} are important parameters governing the development of these flow regimes.

The performance of mixing enhancement of the streams through viscoelastic instability was similarly characterized in the De_{ratio} – De_{main} operating space. The effects of De_{ratio} and De_{main} on mixing were projected in the operating space. Mixing performance was greatly improved with increasing De_{ratio} and/or De_{main} . However, as illustrated in the operating space, De_{ratio} was found to be a more significant parameter for mixing performance. For a given De_{main} , mixing performance increased significantly with an increased De_{ratio} , regardless if there was any from one flow regime to another as a consequence of the increment in De_{ratio} .

Our analysis suggests that this mixing enhancement was attributed to the direct correlation between De_{ratio} and the viscoelastic energies of the two streams and the energy discontinuity at the stream-stream interfaces at downstream of contraction. This correlation has a direct bearing on the chaotic inter-penetration of the streams at downstream of contraction. Efficient and effective mixing of fluid streams was achieved through viscoelastically induced flow instability with negligible diffusion and inertial effects (i.e. at enormous Peclet $> 8 \times 10^6$ and very small $Re < 0.1$), which could potentially be implemented in a μ TAS platform with

minimum requirements for design and fabrication. Such viscoelastic mixing was achieved over a short effective mixing length (< 5 mm) and relatively fast flow velocities ($\sim 10^1$ mm/s).

7.2 Recommendations

Although the basic issues related to planar contraction/multiple-stream flow instability of viscoelastic fluids in microchannels have been investigated, there are still a number of related issues yet to be explored,

- 1) Turbulence flow instability – Viscoelastically induced multiple-stream flow instability observed in this investigation appeared to be chaotic/turbulence in nature. However, due to the limitation of existing facilities available, flow turbulence could not be proven conclusively. Further investigation is required
- 2) Effects of contraction length – As discussed in section 6.6.3, the flow residence time in the contraction and thus the energies discontinuity at the interfaces of the streams are a function of the contraction length. Thus, it is recommended that the effects of varying the length of the contraction be investigated.
- 3) Currently, the ratio of the volumetric flowrate of the mainstream and side streams was fixed at 1:1. It will be interesting to investigate the effects of the volumetric flowrate ratio on flow instability and mixing performance.
- 4) Shear thinning fluids (e.g. PW, PGW) were employed in the course of current study. It will be advantageous to employ Boger fluids (fluids with constant viscosity to observe the behavior of viscoelastic flow instability and mixing performance) without the complication of shear thinning.

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Viscoelastic fluid flow

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Appendix A

SILICON MICROMACHINING

The entire silicon micromaching process was conducted in the Micromachines Lab, School of Mechanical and Aerospace Engineering, Nanyang Technological University. The equipments involved are Spin coater, Karl Suss Mask aligner, STS DRIE, Karl Suss Wafer Bonder and Dicing machine.

A.1 Si Micromachining

(A.1.1) Outline of experiment procedures:

(a1) Hole Patterning Mask A₁

The details of each step are described below,

(1) Mask A₁ Patterning (Wafer thickness of 400 μm)

(i) Hexamethydisilazane (HMDS) priming

HMDS priming consisted of two stages, i.e. baking and N₂ purging to remove surface moisture, followed by HMDS coating which acted as an adhesive layer between Silicon wafer and resist.

Table A1-1. Equipment used is VPO recipe 1.

	Stage 1	Stage 2
Temperature (°C)	100	100
Time (s)	60	10

After HMDS priming, the substrate was left in open air for 60 seconds.

(ii) Resist coating

Photoresist was coated on the whole substrate surface using spin-coater. In this experiment, the resist used is AZ 9260, a positive resist in which the exposed region would be removed during photolithography.

Resist thickness of 10 μm was selected to ensure that the wafer was not damaged during the etching process. Equipment used was Karl Suss Spin coater (Program 1). There were two stages of coating process to ensure that the resist is uniformly distributed on the substrate.

Table A1-2. Recipe of Karl Suss Spin coater program 1.

	Stage 1	Stage 2
Spin speed (rpm)	500	1500
Acceleration (rpm/s)	100	1000
Time (sec)	10	30

(iii) Soft bake

After the resist coating, soft-bake or also known as the pre-bake process was performed to remove the residual solvent and to increase adhesion between the resist and the wafer.

The wafer was baked on the hot plate for 4 minutes at 110 °C.

(iv) Exposure

Exposure time was 30 seconds. After exposure, the substrate was left in open air for 4 minutes to relax the residual stress formed on the wafer during exposure. The mask used for hole patterning is shown below,

Figure A1-1. Mask A₁ for hole arrangement.

(v) Developing

AZ400K developer was used as the solvent. The substrate was soaked inside the solution for 3 minutes before rinsing and drying.

(2) Back Wafer for Mask A₁

(i) HMDS coating

Equipment used is VPO (Recipe 1). The parameters used are the same as described in Table A1-1.

(ii) Resist coating

The resist thickness was 3.5 μm . Equipment used was Delta 80 spin coater (Recipe 14), with spin speed of 4000 rpm for 30 seconds.

(iii) Back wafer bonding

After resist coating, the back wafer was immediately pasted onto wafer A1. The next step was to bake the wafer with the back wafer with a temperature profile shown in Figure A1-2.

Figure A1-2. Temperature profile of back wafer bonding process.

(3) First Etching

Equipment used was the DRIE system by Surface Technology Systems (STS). In this system, each process cycle contained an etching step and a polymer deposition step. The etching step employed SF₆ gas, and the polymer deposition step employed C₄F₈. The polymer protected the sidewalls from etching.

Table A1-3. Parameters used in STS-DRIE.

No.	Parameters	Etch Step		Passivation Step	
1	FlowRate (sccm)	SF6	130	C4F8	100
		O2	13		
2	Time (s)	14		8	
3	Pressure (mTorr)	41		29	
	APC Angle (%)	75		75	
5	Coil Power (W)	800		800	
	(L%, T%)	33, 38		35, 40	
6	Platen Power (W)	11.4		-	
	(L%, T%)	48, 45		-	
7	Vpp (V)	114		-	
	Vbias (V)	435		-	

The etch rate employed was 5 $\mu\text{m}/\text{min}$. Thus, with a target depth of 400 μm , the bonded wafer was placed inside the chamber for 1.5 hour.

(4) Photoresist (PR) Strip

After the etching process, the bonded wafer was soaked in acetone for 1 day to remove the back wafer. Subsequently, the wafer was cleaned inside a piranha etch bath for 20 minutes.

(a2) Channel Patterning Mask A₂

The details of each step are described below,

(1) Back Wafer and (2) Patterning for Mask A₂

The experimental procedure is similar to **steps (a1-1) and (a1-2)**, except that the back wafer was pasted first before the patterning process. The reason for performing this is that the etched wafer has many holes and that it could not be vacuumed during the resist coating process. The mask used for channel patterning is shown in Figure A1-3.

Figure A1-3. Mask A₂ for channel structures and parting lines (for dicing process) arrangements.

(3) Second Etching

The etching time for second etching was 30 minutes with a target depth of 150 μm .

(4) Potor resist (PR) Strip

The experimental procedure is the same as **step (a1-4)**.

(a3) Anodic Bonding of Silicon Wafer to Pyrex Glass

One of the requirements for anodic bonding process is that the surface must be clean and dust-free. Thus, before undergoing the bonding process, O₂ plasma etching was performed on the wafer to ensure that the wafer surface was clean.

Karl Suss wafer bonder was utilized to bond the wafer with Pyrex glass wafer. The cleaned wafer with glass wafer on top was placed on the fixture. Subsequently, the fixture was loaded to the chamber. The overall process time was 1.5 hours.

Table A1-4. The recipe chosen is anodic-bonding-glass-wafer which consists of 10 steps.

Steps	1	2	3	4	5	6	7	8	9	10
Top Temp (°C)	400	400	400	400	400	400	400	400	400	200
Bottom Temp (°C)	400	400	400	400	400	400	400	400	400	100
Press/Vac(mbar)	1000	0.01	0.01	0.01	0.01	0.01	0.01	0.01	1000	1000
Tool Press (mbar)	0	0	0	0	0	0	250	250	0	0
Voltage (V)	0	0	-2000	-2000	0	0	0	-1000	0	0

(a4) Dicing of Silicon-Glass Wafer

Silicon-on-glass wafer was then diced to a 10 × 10 mm chips using a dicing machine from SIMTech. A maximum of 52 chips were fabricated per wafer.