Functional block copolymers, heterogeneous catalysts and chain-end functionalized polymers in organocatalyzed living radical polymerization

Chang Jun Jie

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**FUNCTIONAL BLOCK COPOLYMERS, HETEROGENEOUS
CATALYSTS AND CHAIN-END FUNCTIONALIZED
POLYMERS IN ORGANOCATALYZED LIVING RADICAL
POLYMERIZATION**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of Doctor of
Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from [3] paper(s) published in the following peer-reviewed journal(s) where I was the first author or co-first author with equal contribution.

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The contributions of the co-authors are as follows:

Assoc. Prof. A. Goto provided the initial project.

I performed all the experimental work and analysis at the Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Singapore.

Assoc. Prof. A. Goto, Dr. L. Xiao and Dr. C.-G. Wang provided guidance in the interpretation of the experimental data.

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Assoc. Prof. A. Goto provided guidance in the interpretation of the experimental data.

Dr. S. Chatani and Dr. H. Niino performed the GPEC and viscosity analysis.

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Dr. C.-G. Wang and I prepared the manuscript drafts. Assoc. Prof. A. Goto edited and finalized the manuscript.

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Abstract

Reversible complexation mediated polymerization (RCMP) is an organocatalyzed living radical polymerization system. The motivation of this Ph.D. thesis is to further develop RCMP. The objectives include extending the applications of RCMP, increasing its ease of use, and improving its practicality to industry.

In Chapter 1, the concept of radical polymerization is introduced and the principle as well as mechanisms of several living radical polymerization (LRP) systems will be discussed. The concept of block copolymers, macromonomers, heterogeneous catalysis and chain-end functionalized polymers along with examples of their applications are also mentioned. The motivations and aims of each chapter in this thesis will be discussed.

In Chapter 2, a method of preparing block copolymers via RCMP was developed. A stable poly(methyl methacrylate) bearing a vinyl end-group (PMMA–Y) was employed as a macroinitiator precursor. PMMA–Y was transformed in situ into the active macroinitiator PMMA-iodide (PMMA–I) via addition-fragmentation chain transfer (AFCT), followed by RCMP with butyl acrylate (BA) to obtain block copolymers. Both the transformation and polymerization occur in one-pot and quantitative studies were conducted on the mechanism of transformation. The use of stable PMMA–Y overcomes the drawback of using isolated PMMA–I which lacks long-term stability, thereby making this block copolymerization method suitable for practical use due to its increased ease of operation.

In Chapter 3, the scope of monomers was expanded for block copolymerization with PMMA–Y. AFCT of PMMA–Y generates the desired block copolymers, while propagation results in branched copolymers. Kinetic studies revealed the temperature dependence of AFCT and propagation of PMMA–Y in the styrene (St) polymerization, allowing efficient synthesis of PMMA–PSt block copolymers at higher temperatures, while branched

copolymers were predominantly obtained at lower temperatures. AFCT of PMMA–Y was also found to be dominant at the temperatures used in the acrylonitrile and acrylate polymerizations, allowing for the respective block copolymers to be synthesized. The polymerization of BA using PMMA–Y with higher molecular weights was also performed, demonstrating the usefulness of this method for block copolymer synthesis.

RCMP is typically performed using homogeneous catalysts such as tetrabutylammonium iodide (BNI). BNI was also the catalyst used in the block copolymerizations with PMMA–Y in Chapters 2 and 3, and one issue is the removal of such homogeneous catalysts after polymerization. In Chapter 4, polymer resin particles containing tertiary amine (R_3N) and quaternary ammonium iodide ($R_4N^+I^-$) functionalities were developed as supported catalysts for heterogeneous RCMP. The supported catalysts produced low dispersity homopolymers and block copolymers of several methacrylates and acrylonitrile. The catalysts were also easily recovered from the reaction mixtures and were recycled for 5 polymerizations without any significant decrease in their catalytic activity. The developed supported catalysts are attractive particularly for industrial applications of RCMP.

Control over the polymer architecture was demonstrated in Chapter 3 through the selective synthesis of block copolymers and branched copolymers using high and low polymerization temperatures respectively. The next objective was the chain-end modification of polymer-iodides obtained from RCMP. In Chapter 5, the chain-end transformation of polyacrylate-iodides were carried out via an organocatalyzed radical addition to alkynes to obtain vinyl-iodide-terminated polymers. This transformation reaction was also amenable to functional alkynes bearing hydroxyl and trifluoromethyl functionalities. The chain-end transformations were comprehensively studied via matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Such vinyl-iodide bearing polymers are

potential precursors for cross-coupling reactions towards the development of functional polymer materials.

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List of Abbreviations

AFCT	Addition-fragmentation chain transfer
AIBN	2,2'-azobis(2-methylpropionitrile)
AN	Acrylonitrile
ATRP	Atom transfer radical polymerization
BA	Butyl acrylate
BNI	Tetrabutylammonium iodide
BPO	Benzoyl peroxide
BzMA	Benzyl methacrylate
CCTP	Catalytic chain transfer polymerization
CP-I	2-iodo-2-methylpropionitrile
$\bar{D}$	Polymer dispersity
EBA	4-ethynylbenzyl alcohol
EC	Ethylene carbonate
EHMA	2-ethylhexyl methacrylate
F_{fr}	Fraction of fragmentation
GPC	Gel permeation chromatography
GPEC	Gradient polymer elution chromatography
HEMA	2-hydroxyethyl methacrylate
ITP	Iodine transfer polymerization
k_{fr}	Fragmentation rate constant
k_{p}	Propagation rate constant
LMA	Lauryl methacrylate
LRP	Living radical polymerization

MALDI-TOF MS	Matrix assisted laser desorption/ionization time-of-flight mass spectrometry
MEA	2-methoxyethyl acrylate
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
NMP	Nitroxide mediated radical polymerization
NMR	Nuclear magnetic resonance
PA	Phenylacetylene
PAN	Poly(acrylonitrile)
PBA	Poly(butyl acrylate)
PBZ	<i>tert</i> -butyl peroxybenzoate
PEGA	Poly(ethylene glycol) methyl ether acrylate
PMA	Poly(methyl acrylate)
PMEA	Poly(2-methoxyethyl acrylate)
PMMA	Poly(methyl methacrylate)
PPEGA	Poly(poly(ethylene glycol) methyl ether acrylate)
PSt	Poly(styrene)
RAFT	Reversible addition-fragmentation chain transfer polymerization
RCMP	Reversible complexation mediated polymerization
SEM	Scanning electron microscope
St	Styrene
T	Temperature
t	time
TEA	Triethylamine
TFT	4-ethynyl-trifluorotoluene

V40	1,1'-azobis(cyclohexanecarbonitrile)
V65	2,2'-azobis(2,4-dimethylvaleronitrile)
XPS	X-ray photoelectron spectroscopy
η	Intrinsic viscosity

Chapter 1. General Introduction

Synthetic polymers are prevalent in modern society. Global plastics production reached 348 million tons¹ with a value of nearly 523 billion US dollars² in 2017, and these numbers are projected to increase even further.

Radical polymerization accounts for nearly half of all polymers produced industrially (on the basis of the value). This dominance is due to its advantages over other methods of polymerization. Radical polymerization is tolerant to water and other small amounts of impurities, thereby requiring less stringent reaction conditions. Furthermore, it is amenable to a wide range of monomer families, allowing many useful polymers and copolymers to be produced. These factors combined make radical polymerization economically attractive for large scale production.³

In conventional radical polymerization, a radical initiator such as azobisisobutyronitrile (Figure 1.1) decomposes either by heat or light, generating free radicals (initiation) (Scheme 1.1). The generated radicals add to the monomers to form a growing chain (propagation). The propagating polymer chain eventually comes to an end (termination) either by chain transfer (to polymer, monomer or solvent), or via radical coupling or disproportionation with another propagating chain. Polymers produced by conventional radical polymerization can have a high degree of polymerization (DP). This refers to the number of monomer units that are incorporated into the polymer. However, one major disadvantage is that the polymer molecular weights and molecular weight distribution cannot be controlled in conventional radical polymerization. Termination occurs randomly among the propagating polymer radicals, giving a wide distribution in the chain length. The dispersity ($\bar{D}$) of the chain length is 1 when all polymers have equal chain lengths, and is generally larger than 1.5 when polymers are produced via conventional radical polymerization.

Figure 1.1. Commonly used radical initiators.

Scheme 1.1. Scheme of conventional radical polymerization.

To overcome the aforementioned drawback of conventional radical polymerization, living radical polymerization (LRP), also termed reversible-deactivation radical polymerization or controlled radical polymerization was developed. The term “living” was borrowed from living anionic polymerization which was discovered and coined by Szwarc in 1956.⁴ That anionic polymerization did not involve a termination step, allowing the polymer chain to continue growing when more monomer was added.

The general concept of LRP is based on a dormant polymer species (Polymer–X) which is reversibly activated to generate a propagating polymer radical (Polymer[•]) that can undergo addition of monomer (Scheme 1.2), where X is a capping agent. Polymer[•] adds to monomers and is capped by X, forming back Polymer–X. The capping agent establishes an equilibrium between the propagating polymer radicals and dormant polymer species via the persistent radical effect. The rate constant of activation k_a is much lower than the rate constant of deactivation k_{da} , thus the equilibrium is heavily shifted to the left, meaning that the large majority of polymer chains are dormant at any point during the polymerization. By having a large number of activation-deactivation cycles, each polymer chain has an equal opportunity to propagate, and low dispersity polymers ($D < 1.5$) with predictable molecular weights can be synthesized. Examples of LRP systems will be described below.

Scheme 1.2. Reversible activation in LRP.

1.1. Nitroxide Mediated Radical Polymerization (NMP)

Nitroxide mediated radical polymerization (NMP) was attempted in 1984 by Solomon and coworkers at CSIRO and is one of the earliest studied LRP systems.⁵ NMP relies on the reversible termination between Polymer[•] and nitroxides (serving as X) to form alkoxyamines. Nitroxides are stable radicals (persistent radicals) (Figure 1.2). The earliest studied NMP system yielded oligomers (Scheme 1.3).⁶

Figure 1.2. Structures of several nitroxides.

Scheme 1.3. Scheme of NMP.

Georges et al. employed the nitroxide (X) 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (Figure 1.2) in 1993, successfully generating polystyrenes (polymers instead of oligomers) with low dispersities.⁷ Polymer-X is activated by heat and good dispersity control was achieved at temperatures around 125 °C. However, TEMPO was not as effective in the polymerizations of acrylates.

To address these limitations, much effort has been made in the development of other nitroxides, targeting effective control of other monomers.⁸ For example, two other nitroxides shown in Figure 1.2, i.e., *N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide* (DEPN) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) enabled the control in the polymerization of acrylamides, acrylates, dienes and acrylonitrile while also requiring lower polymerization temperatures.⁹⁻¹¹

1.2. Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) was independently developed by Sawamoto¹² and Matyjaszewski¹³ in 1995 based on the principles of atom transfer radical addition (ATRA) in organic synthesis. ATRP employs alkyl halides as the initiator ($X = \text{Cl}, \text{Br}$ or I). A transition metal catalyst (LM_t^n) with a ligand (L) is employed to abstract the halogen atom from Polymer-X via a redox process to reversibly generate Polymer $\cdot$ and the oxidized metal species $\text{LM}_t^{n+1}\text{X}$. (Scheme 1.4).

Scheme 1.4. Scheme of ATRP.

A metal frequently employed in ATRP is Cu, while other transition metals such as Pd, Fe, Ni, and Ru are also effective.¹⁴⁻¹⁵ The ligand influences the dispersity control and polymerization rate.¹⁶ Many monomers including styrenes, methacrylates, acrylates, acrylonitrile and methacrylamides¹⁷⁻¹⁸ are amenable to ATRP in both organic and aqueous media.¹⁹ The halide terminal group of Polymer-X can also be further converted to other functionalities via post treatment, giving well-defined, end-functional polymers.²⁰⁻²¹

1.3. Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

Reversible addition-fragmentation chain transfer (RAFT) polymerization was developed in 1998 by several researchers at CSIRO,²² and relies on the degenerative chain

transfer of $\text{Polymer}^\bullet$ to thiocarbonylthio compounds ($\text{S}=\text{C}(\text{Z})\text{S}-\text{Polymer}'$) which function as chain transfer agents. $\text{Polymer}^\bullet$ undergoes addition to $\text{S}=\text{C}(\text{Z})\text{S}-\text{Polymer}'$ to generate an intermediate radical ($\text{Polymer}-\text{S}-\dot{\text{C}}(\text{Z})-\text{S}-\text{Polymer}'$), and the intermediate radical subsequently undergoes fragmentation into $\text{Polymer}''$ and $\text{S}=\text{C}(\text{Z})\text{S}-\text{Polymer}'$ (Scheme 1.5).

Scheme 1.5. Degenerative Chain Transfer in RAFT polymerization.

RAFT polymerization depends on the Z group.²³⁻²⁴ Examples of the Z groups are dithioesters ($\text{Z} = \text{R}$), trithiocarbonates ($\text{Z} = \text{SR}$), and xanthates ($\text{Z} = \text{OR}$). The xanthate system is also known as the macromolecular design by interchange of xanthates (MADIX) system.²⁵⁻
²⁶ RAFT polymerization is applicable to many monomers including methacrylates, acrylates, dienes, vinyl pyridines, vinyl acetate and acrylamides using appropriate RAFT agents.²⁷⁻³⁰

1.4. Iodine Transfer Polymerization (ITP)

Iodine transfer polymerization (ITP) using alkyl iodides as initiators ($\text{X} = \text{iodide}$) was developed in 1995.³¹ The principle of ITP is the degenerative chain transfer between $\text{Polymer}^\bullet$ and $\text{Polymer}'-\text{X}$ (Scheme 1.6). This chain transfer is reversible, and iodide (X) is exchanged between the polymer chains.

Scheme 1.6. Degenerative chain transfer in ITP.

Instead of using isolated alkyl iodide, an azo compound (R–N=N–R) with an iodine molecule I₂ can also generate the alkyl iodide initiator in situ. This technique is termed reverse iodine transfer polymerization (RITP).³² This technique addresses one limitation of ITP, namely the instability of the alkyl iodides upon long-term storage.

1.5. Reversible Complexation Mediated Polymerization (RCMP)

Goto, et al.³³⁻³⁵ (our research group) developed the first LRP system that uses organic (non-metal) catalysts. This organocatalyzed LRP system employs alkyl iodides as initiators (X = iodide) and organic compounds such as amines or the iodide anion (I[−]) as catalysts. Bu₄N⁺I[−] is typically used as a source of the iodide anion (I[−]). The catalyst coordinates to the iodide of Polymer–I through halogen bonding, forming a complex (Polymer–I⋯catalyst) that can generate Polymer[•] in a reversible manner (Scheme 1.7). Mechanistically, RCMP is similar to that of ATRP as Polymer–X is activated by a catalyst.

Scheme 1.7. Reversible activation in RCMP.

The initial RCMP system using amines as catalysts was mainly limited to methacrylates and styrene monomers.³⁴ More reactive ionic catalysts were later discovered with greater electron donating abilities (greater halogen-bonding abilities), granting control over the polymerization of acrylates, acrylonitrile and other functional monomers.³⁵⁻³⁸ Not only heating, but also photoirradiation can be used to drive and control the polymerization through the use of amines³⁹ or organic photocatalysts.⁴⁰ RCMP can be applied for several monomers in polar solvents such as water or ethanol.^{38,41}

The weak carbon-iodine bond at the polymer chain-end is exploited in RCMP to generate Polymer-I. An additional benefit of the weak carbon-iodide bond is the further conversion of Polymer-I to other functional groups.^{37,42-43} A drawback of this weak carbon-iodine bond is the requirement of low temperatures and dark conditions for storage of the alkyl iodide initiators.

RCMP is advantageous for the use of inexpensive compounds and no use of metals or odorous compounds.^{34,44-45} Furthermore, the catalysts generally have low toxicity. As such, RCMP serves as an industrial synthetic method. RCMP has been utilized by Dainichiseika Color & Chemicals Mfg. Co., Ltd in Japan to manufacture block copolymers for pigment dispersants in water-based ink applications.⁴⁶⁻⁴⁷

LRP also allows for topological control through the use of multi-functional initiators, allowing for complex structures such as star polymers⁴⁸ and dendrimers⁴⁹ to be obtained. These branched polymers exhibit lower viscosity when dissolved in solution compared with linear polymers due to the greater steric repulsion between the branched polymers. This property allows for their application as lubricants or coatings.

In summary, LRP is a versatile method with functional and architectural control to obtain well-defined polymers, attracting both academic and industrial interests. A search on

Scopus using the keywords “Living Radical Polymerization”, “Reversible-deactivation Radical Polymerization” and “Controlled Radical Polymerization”, revealed more than 12000 publications from the year 1995 to 2019.

1.6. Block Copolymers

A key feature of polymers synthesized via LRP is that the capping agent (X) remains on the dormant polymer chains (Polymer–X) after the polymerization. Polymer–X can then continue to grow when more monomer is added. Through the addition of a different second monomer, block copolymers can be obtained (Figure 1.3).

Figure 1.3. Synthesis of block copolymers by LRP.

Diblock copolymers have two different segments with different properties. Using blocks of hydrophobic and hydrophilic monomers in the two segments, amphiphilic block copolymers can be synthesized. Such amphiphilic polymers can form micelles via self-assembly when dispersed in solution (Figure 1.4). By adjusting the lengths of the hydrophilic and hydrophobic segments, other structures like worms or vesicles can also be obtained.⁵⁰ Such vesicles can encapsulate small molecules such as drugs. Using biocompatible non-toxic polymers, the obtained vesicles may be used in drug delivery systems. Some in vivo studies in mice for the treatment of tumours⁵¹ have successfully demonstrated the improvement in the spatial memory of rats impaired with scopolamine.⁵² Another medical application is

loading magnetic nanoparticles in the vesicles for use as contrast agents in magnetic resonance imaging.⁵³

Figure 1.4. Micelle formation from block copolymer self-assembly.

Another application of block copolymers is as dispersants for coatings and pigments. The polymer chains adsorb onto the surfaces of pigment nano-particles, creating a polymer layer surrounding the pigment surface. The polymer layer protects the pigment particle from re-agglomeration with other pigment particles via osmotic and entropic effects.⁵⁴ Figure 1.5 illustrates this process. This strategy has also been used for the dispersion of other nano-materials. For example, poly(4-vinyl pyridine)-*block*-poly(ethylene oxide) was synthesized as an amphiphilic block copolymer to disperse high concentrations of graphene in ethanol and water.⁵⁵ Despite the facile aggregation of graphene sheets in solution, the sheets remained well dispersed even after 3 months. In another example, an amphiphilic poly(lauryl methacrylate)-poly(2-hydroxyethyl methacrylate) block copolymer was used to finely disperse hydrophilic cellulose nanofibers (CNF) in hydrophobic high-density polyethylene (HDPE).⁵⁶ The well dispersed CNF acted as a filler in HDPE, forming a composite material with enhanced compressive and tensile strengths compared to pure HDPE.

Figure 1.5. Dispersion of pigment by a block copolymer.

Block copolymers can attach to a solid surface to form a polymer layer (coating), thus modifying the surface properties. Membrane fouling from the accumulation of biological compounds such as proteins or microorganisms is common in water purification and marine environments. This results in lowered efficiencies from the clogging of water filtration membranes,⁵⁷ or the increased hydrodynamic drag on the hulls of ships.⁵⁸ Because the adhesion of biological compounds is promoted by the hydrophobicity of the surface material,⁵⁹ one strategy to suppress the fouling is the coating of the top layer of the material with block copolymers containing hydrophilic segments.⁶⁰⁻⁶¹ This can also be extended to antibacterial coatings for medical devices or materials via the use of biocompatible polymers.⁶²

Stimuli-responsive polymers exhibit changes in chemical or physical properties upon encounter with external stimuli like pH or temperature. Thus they are used to form “smart” materials or sensors that are able to respond when triggered by an external stimuli.⁶³ For example, a dual pH and temperature polymeric sensor was developed using a diblock copolymer synthesized via RAFT polymerization, in which one block was pH sensitive and the other was temperature sensitive.⁶⁴ That diblock copolymer exhibited solubility changes in a temperature range from 10–20 °C as well as solvatochromatic shifts for pH values from 1–7.

Block copolymers can also stabilize polymer blend interfaces. Polymer blends are a mixture of two or more different polymers and exhibit unique physical properties compared to a single polymer. However, in most cases, the polymers in such mixtures are not fully miscible with each other, resulting in separation over time into different phases.⁶⁵⁻⁶⁶ Block copolymers can stabilize the polymer blend interfaces and enables high miscibility of the polymer blends (Figure 1.6).

Figure 1.6. Block copolymers stabilizing the interface of immiscible polymer blends.

Like polymer blends, block copolymers themselves also exhibit phase separation. Each segment in the block copolymer is covalently bonded in the polymer backbone and they form micro-phase separations with domains ranging from 5 – 50 nm.⁶⁷ When a thin layer of block copolymers are applied onto a surface or substrate, these nanoscale micro-phase separations can align in parallel or perpendicular orientation to the surface (Figure 1.7). These micro-phase separations find applications such as nanolithography for microelectronics. For example, domains with perpendicular cylinders (Figure 1.7b) was used for a nanoporous filtration membrane.⁶⁸ Domains with cylinders lying in parallel (Figure 1.7c) are of particular interest for the development of nanowires.⁶⁹⁻⁷⁰

Figure 1.7. Various orientations of block copolymer thin films. (a) Lamella lying in parallel orientation, (b) cylinders lying in parallel orientation, (c) perpendicular cylinders, and (d) spheres.⁶⁹

Thus, block copolymers possess unique properties that make them useful in many applications. LRP is a versatile technique that allows such block copolymers to be synthesized, providing great control over the length of each block segment and the chain length distribution.

1.7. Macromonomers

Macromonomers are polymers containing a polymerizable chain end such as an unsaturated carbon–carbon double bond (Figure 1.8). Catalytic chain transfer polymerization (CCTP) using cobalt porphyrin catalysts was discovered in 1975 and is a useful method to synthesize macromonomers containing a terminal vinyl group.⁷¹ Adjusting the amount of catalyst used also allows for control of the polymer molecular weights. CCTP is amenable to many monomers including methacrylates, acrylates, styrenes as well as vinyl esters under tailored reaction conditions.⁷²

Figure 1.8. Structure of a methacrylate macromonomer.

The mechanism of the catalytic cycle in CCTP is shown in Scheme 1.8, using a methacrylate monomer as an example. First, a hydrogen atom is abstracted by the cobalt catalyst (Co^{II}) from the α -methyl group of the propagating radical ($\text{P}^\bullet$), forming the macromonomer (P^-) and the cobalt hydride complex ($\text{Co}^{\text{III}}\text{-H}$). The $\text{Co}^{\text{III}}\text{-H}$ complex then reinitiates polymerization on a monomer (M), forming a new propagating radical ($\text{M}^\bullet$). $\text{M}^\bullet$ becomes $\text{P}^\bullet$ after further addition of monomers.⁷¹⁻⁷²

Scheme 1.8. Mechanism of CCTP.

The vinyl chain end on macromonomers can be converted to other functional groups through thiol-ene click reactions,⁷³ e.g., with α -keratin, a protein found in human hair containing a high concentration of sulfide groups for potential hair care applications.⁷⁴ The vinyl chain end has also been reacted with a divinyl monomer as a crosslinker to generate star polymers.⁷⁵ Such star polymers can be applied as rheology modifiers to alter the viscosity in coatings or oil additive applications.

Another interesting use of macromonomers is as polymerizable surfactants (also called surfmers). In emulsion polymerization, a surfactant is used to disperse the hydrophobic monomer in water. An amphiphilic block copolymer macromonomer works as both monomer and surfactant for (additional) surfactant-free emulsion polymerizations.⁷⁶⁻⁷⁷ The amphiphilic macromonomers initially stabilize the hydrophobic monomer droplets. As the monomer droplets (cores) become polymers, the macromonomers are also polymerized and grafted onto the polymer core by a covalent chemical bond. The formation of the covalent bonds better stabilize the growing polymer core compared with traditional surfactants, and the resulting latexes displayed increased hydrophobic properties and stability.⁷⁸ Such latexes can be applied in water-based paints or protective coatings.

Oligomers synthesized by CCTP were employed in conventional radical polymerization as chain transfer agents to produce low dispersity polymers.⁷⁹⁻⁸¹ The reaction of a methyl methacrylate trimer (MMA–Y, where $Y = \text{CH}_2\text{C}(\text{=CH}_2)\text{COOCH}_3$) with a 2-cyanopropyl radical ($\text{CP}^\bullet$) was studied by Cacioli, et al. (Scheme 1.9).⁸² When $\text{CP}^\bullet$ is added to the vinyl group of MMA–Y, the intermediate radical $\text{CP}-(\text{Y}^\bullet)\text{--MMA}$ is generated (where $\text{Y}^\bullet = (\text{CH}_2)_2\text{C}^\bullet(\text{COOCH}_3)$). The intermediate radical subsequently undergoes the fragmentation into $\text{CP} \text{--} Y$ and $\text{MMA}^\bullet$. This process is known as addition-fragmentation chain transfer (AFCT). AFCT using $\text{C}=\text{S}$ bond instead of $\text{C}=\text{CH}_2$ is used in RAFT polymerization, as mentioned above.⁸³⁻⁸⁵

Scheme 1.9. AFCT of MMA-Y and CP[•].

AFCT allows for block copolymers to be synthesized through the polymerization of vinyl monomers with macromonomers, e.g., PMMA-Y (Scheme 1.10).⁸⁶⁻⁸⁷ A radical source such as BPO (Figure 1.1) provides free radicals (R[•]) which react with monomers (M_B) to generate a polymer radical P_B[•]. P_B[•] adds to PMMA-Y, forming the radical species P_B-(Y')-PMMA (Scheme 1.10a). P_B-(Y')-PMMA undergoes fragmentation to P_B-Y and PMMA[•] (Scheme 1.10b). Finally, the propagation of PMMA[•] with M_B generates the block copolymer (Scheme 1.10c).

Another reaction pathway of the macromonomers is propagation with the monomers to form comb shaped polymers (Scheme 1.10d).^{82,88} Whether AFCT or propagation occurs is heavily dependent on the steric hindrance of the intermediate radical.^{80,88-90} A larger steric hindrance favors fragmentation (AFCT) to relieve the internal strain of the intermediate radical (P_B-(Y')-PMMA in Scheme 1.10a). Thus, block and comb shaped polymers can be synthesized, depending on the macromonomer/monomer pairing based on the aforementioned principles.⁹¹

Scheme 1.10. (a) – (c) AFCT of PMMA–Y and polymer radical ($P_B^\bullet$) to form block copolymers. (d) Copolymerization of PMMA–Y and $P_B^\bullet$ to form comb shaped copolymers.

1.8. Heterogeneous Catalysis

Catalysis can be categorized into homogeneous and heterogeneous catalysis. In homogeneous catalysis, the concentrations of the catalyst and other reactants are evenly distributed in the media. In contrast, in heterogeneous catalysis, the concentrations of the catalyst are not evenly distributed but localized in the media. Another important difference in homogeneous and heterogeneous catalytic systems is related to diffusion. As a result of the catalyst localization, the reactants in the media must diffuse to the non-diffusive (or very slowly diffusive) catalyst. Furthermore, in the case of porous solid catalysts, the catalytic sites are also within the core of the solid. Hence the reactants will need to penetrate into those sites.⁹²

An advantage of heterogeneous catalysis is the recoverability of the catalysts. Using a solid-supported catalyst in a liquid medium, the supported catalyst can be removed in a facile manner from the reaction mixture. Thus, the heterogeneous catalysts facilitate the purification of the product compared with the homogeneous catalysts. This offers reduced cost and energy savings, which are beneficial in industrial processes.

One motivation for the development of solid-supported catalysts in ATRP systems is the high cost of the removal of potentially toxic and colored transition metal catalyst from the obtained polymers. The use of solid-supported catalysts is a desirable solution to facilitate the catalyst removal.⁹³ In most cases, ligands are chemically bound to the support, and metals are coordinated with the ligand. Silica,⁹⁴⁻⁹⁸ polymer^{95,97} and magnetic particles such as iron oxides⁹⁹⁻¹⁰⁰ have been employed as the supports for the polymerizations of methacrylates, acrylates and styrene monomers. An interesting application of using iron oxide supports is the isolation and collection of the catalytic particles by applying a magnetic field.

A disadvantage of the supported catalysts is that the control over the polymerization is poorer than that of relevant homogeneous catalysts. While the rate of activation (k_a) (Scheme 1.4) is not significantly affected, the rate of deactivation (k_{da}) is significantly reduced by slow diffusion of the deactivating species.¹⁰¹ The slow deactivation of the propagating polymer (Polymer[•]) thus results in increased dispersity. To overcome the slow diffusion, a greater concentration of deactivator is required so that Polymer[•] can quickly return to the dormant species (Polymer–X) in a sufficiently short time.

Supported RAFT agents are used in RAFT polymerizations. The immobilized agents are not catalysts but RAFT (chain transfer) agents, aiming at isolating the colored and odorous sulfur containing RAFT agents from the obtained polymers. The Z group (Scheme 1.5) in the chain transfer agent (S=C(Z)S–R) has been immobilized onto silica¹⁰²⁻¹⁰⁴ and

polymer^{102,105} supports.¹⁰⁶ An additional advantage is that the dormant polymer chains remain bound onto the solid support through the Z group. These dormant chains can then be separated from terminated polymer chains present in solution via filtration.¹⁰⁵

1.9. Chain-end Functionalized Polymers

Polymers synthesized via LRP possess a capping agent (X) on the chain-end. X has been converted to functional groups such as azide, thiol or dienes, yielding chain-end functionalized polymers.^{37,107-108} Polymers bearing such clickable functionalities were used as building blocks to create complex macromolecular architectures. For example, azide-functionalized polymers were grafted onto a multi-alkyne compounds via azide-alkyne cycloaddition to form 3-miktoarm star polymers and polymeric dendrimers.¹⁰⁹ For another example, poly(*N*-isopropylacrylamide) with a thiol chain-end was linked with a protein such as bovine serum albumin, forming a bioactive polymer-protein conjugate that exhibited thermoresponsive behavior.¹¹⁰ Chain-end functionalized polymers are useful building blocks to generate complex functional polymer materials and composites.

1.10. Thesis Objectives

Reversible complexation mediated polymerization (RCMP) is a metal-free LRP system employing only low toxicity compounds such as alkyl iodides as initiators, and amines or the iodide anion (I^-) as catalysts. In this Ph.D. thesis, the primary motivation was the further development of RCMP. The extension of applications in RCMP, its increased ease of use and its industrial applicability were the areas of focus in this work.

1.11. Aims in Chapter 2 and 3

One of the disadvantages of RCMP in block copolymer synthesis is the instability of the macroinitiator (Polymer-I) upon long-term storage because of the weak carbon-iodine bond of Polymer-I.¹¹¹⁻¹¹² Thus, usually, purified Polymer-I is required to be stored at low temperatures and in the dark.

Chapter 2 demonstrates the application of a poly(methyl methacrylate) (PMMA) possessing a terminal vinyl group (PMMA-Y) as a macroinitiator precursor. The stable PMMA-Y can be stored for long periods, overcoming the drawback of using isolated PMMA-I, and is thus useful for practical synthesis of block copolymers. PMMA-Y is first converted to PMMA[•] via AFCT. PMMA[•] then reacts with I[•] to form PMMA-I. PMMA-I functions as the macroinitiator in the organocatalyzed LRP of butyl acrylate (BA) monomer to form PMMA-PBA block copolymers. The in situ conversion of PMMA-Y to PMMA-I and the subsequent polymerization to PMMA-*b*-PBA are conducted in one pot.

Chapter 3 studied the kinetics of AFCT and propagation for PMMA-Y with several monomers. An interesting finding in the polymerization of styrene was that while propagation was dominant at milder temperatures (below 60 °C), AFCT was dominant at elevated temperatures (120 °C). This kinetic finding enabled the temperature selective synthesis of block and comb (branched) copolymers with styrene. With the other studied monomers, i.e., acrylonitrile and functional acrylates, AFCT was also dominant, allowing block copolymers of PMMA with the respective monomers to be synthesized.

1.12. Aim in Chapter 4

RCMP utilizes amines and iodide anions as catalysts. In chapters 2 and 3, tetrabutylammonium iodide (BNI) was used as the homogeneous catalyst to synthesize block

copolymers from the macroinitiator precursor PMMA–Y. However, the separation of BNI (and other homogeneous catalysts) from the obtained polymers is not very simple. Chapter 4 reports the development of supported (heterogeneous) RCMP catalysts that can facilitate the catalyst separation. The recovered catalysts were also successfully used in a recycled manner in the polymerizations, enabling the waste reduction.

1.13. Aim in Chapter 5

Vinyl iodides are useful precursors in organic chemistry for cross-coupling reactions catalyzed by transition metals. *N*-heterocycles¹¹³, vinyl sulfides¹¹⁴, vinyl amides¹¹⁵ or vinyl azides¹¹⁶ can be formed through the cross-coupling reactions, for example. Amongst the vinyl halides (with Cl, Br and I), vinyl iodides have the weakest carbon-halogen bond,¹¹⁷ generally leading to the fastest cross-coupling reactions or requiring the lowest temperatures. In polymer chemistry, the incorporation of vinyl iodides in the polymer backbone have been achieved via the solid-phase polymerization of diiodobutadiyne¹¹⁸, step-growth iodo-yne polymerizations of 1,9-decadiyne and diiodoperfluorohexane¹¹⁹ as well as through post-polymerization transformations.¹²⁰⁻¹²¹ However, the installation of vinyl iodides at the polymer chain end has not been reported. In chapters 2–4, polymers with chain-end iodide groups (Polymer–I) were obtained. The terminal iodide group can be further converted into other functional groups. Chapter 5 reports the transformation of Polymer–I into Polymer–vinyl iodides via an organocatalyzed radical addition to alkynes.

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Chapter 2. Use of Poly(methyl methacrylate) with an Unsaturated Chain-End as a Macroinitiator Precursor in Organocatalyzed Living Radical Block Polymerization

Abstract

A poly(methyl methacrylate) (PMMA) with an unsaturated chain-end (PMMA–Y) was transformed to PMMA-iodide (PMMA–I) in situ in the organocatalyzed living radical polymerization of butyl acrylate; the generated PMMA–I worked as a macroinitiator to successfully generate a PMMA–PBA–I block copolymer, where PBA is poly(butyl acrylate). The use of PMMA–Y overcomes the drawback of the direct use of the isolated PMMA–I, i.e., its general lack of long-term stability upon storage, and thus significantly improves the ease of operation. This method is highly suitable for practical use. A quantitative mechanistic study on the transformation of PMMA–Y into PMMA–I was also conducted.

2.1. Introduction

Living radical polymerization (LRP), also known as reversible-deactivation radical polymerization, is a useful technique for synthesizing well-defined block copolymers with narrow molecular weight distributions.^{1–15} LRP is based on the reversible activation of a dormant species (Polymer–X) into a propagating radical (Polymer[•]) (Scheme 2.1a). LRP includes nitroxide mediated polymerization,² atom transfer radical polymerization (ATRP),^{3–6} and reversible addition fragmentation chain transfer (RAFT) polymerization.^{7,8} We have developed an organocatalyzed LRP using iodide as a capping agent (X) and organic molecules as catalysts (Scheme 2.1b).^{16–21} Mechanistically, polymer-iodide (Polymer–I) is activated using a catalyst to reversibly generate Polymer[•]. The catalysts include tertiary amines such as tributylamine¹⁷ and organic salts such as tetrabutylammonium iodide (Bu₄N⁺I[–] (BNI)).¹⁸ This polymerization is attractive because of no use of special capping

agents or expensive catalysts, ease of operation, and amenability to a wide range of monomers and polymer structures and would be useful for various applications.

This polymerization yields polymer-I bearing iodide at the chain-end. Polymer-I can be used as a macroinitiator in a subsequent polymerization to generate a block copolymer. However, because the carbon-iodine bond is relatively weak, Polymer-I generally lacks long-term stability upon storage.^{9,22} A poly(methyl methacrylate) (PMMA) with an unsaturated chain-end (PMMA-Y), typically prepared by cobalt-mediated catalytic chain-transfer polymerization,^{23–27} is a promising precursor to synthesize PMMA-I via possible chain-end transformation, where Y is $\text{CH}_2\text{C}(\text{=CH}_2)\text{COOCH}_3$. PMMA-Y is stable upon long-term storage and can be transformed to PMMA-I when necessary.

(a) Reversible activation (general scheme)

(b) Organocatalyzed LRP

Scheme 2.1. Reversible activation: (a) General scheme of LRP and (b) organocatalyzed LRP.

In the field of radical polymerization, PMMA-Y is used as a chain transfer agent in the polymerizations of methacrylates (Scheme 2.2a).^{28–32} A propagating polymethacrylate radical (e.g., $\text{PMMA}^\bullet$) undergoes addition to the C=C double bond of PMMA-Y to generate an intermediate radical $\text{PMMA-(Y}^\bullet\text{)-PMMA}$, which is followed by fragmentation into $\text{PMMA}^\bullet$ and PMMA-Y. This process is reversible and named reversible addition-fragmentation chain

transfer (reversible AFCT). This process is used as a reversible activation in LRP of methacrylates.^{33–40}

Unlike the polymethacrylate radical, a polyacrylate radical results in “irreversible” AFCT (Scheme 2.2b).^{41,42} A poly(butyl acrylate) radical (PBA[•]) undergoes addition to PMMA–Y to generate the intermediate radical PBA–(Y[•])–PMMA, followed by fragmentation into PMMA[•] and PBA–Y. Because PMMA[•] is energetically more stable than PBA[•], the fragmentation selectively produces PMMA[•] rather than PBA[•], leading to irreversible AFCT. A useful aspect of this process is that the generated PMMA[•] can provide a block copolymer in the polymerizations of acrylates.

PMMA–Y also possibly acts as a macromonomer instead of a chain transfer agent. The intermediate radical Polymer–(Y[•])–PMMA can propagate (added to a monomer), forming a branched polymer. However, it was reported that PMMA–Y predominantly acts as a chain transfer agent in the polymerizations of methacrylates (nearly 100%)⁴³ and acrylates (approximately 90%),⁴¹ because the intermediate radical rapidly releases the sterically hindered PMMA[•] (Schemes 2.2a and 2.2b). In contrast, the polyacrylate PBA–Y predominantly acts as a macromonomer rather than a chain transfer agent in the polymerizations of acrylates, forming a branched polymer,^{41,42} because the intermediate radical PBA–(Y[•])–PBA propagates faster than the release of the less sterically hindered PBA[•] (Scheme 2.2c).

Scheme 2.2. AFCT of (a) PMMA[•] and PMMA-Y, (b) PBA[•] and PMMA-Y, and (c) PBA[•] and PBA-Y.

Herein, we report the use of PMMA-Y as a precursor for the macroinitiator in the organocatalyzed LRP. We in situ transformed PMMA-Y into the PMMA-I macroinitiator and synthesized block copolymers in one pot. The studied monomer was butyl acrylate (BA). The use of PMMA-Y overcomes the drawback of the use of isolated PMMA-I, i.e., its general lack of long-term stability upon storage, and thus can significantly improve the ease of operation and be highly suitable for practical use. We also conducted a quantitative mechanistic study of the transformation of PMMA-Y to PMMA-I. Methacrylate-acrylate block copolymers are useful polymers and widely synthesized via LRP under carefully designed conditions.^{1-14,44-46}

2.2. Results and discussion

Organocatalyzed LRP using 2-iodo-2-methylpropionitrile (CP-I).

We heated a mixture of BA (monomer (200 equiv.)), PMMA-Y (precursor (1 equiv.)), 2-iodo-2-methylpropionitrile (CP-I) (alkyl iodide (1 equiv.)), and BNI (catalyst (8 equiv.)) at 110 °C (Table 2.1 (entry 1)). The M_n and dispersity ($D = M_w/M_n$) of the PMMA-Y precursor were 3900 and 1.67, respectively, where M_n and M_w are the number-average and weight-average molecular weights, respectively. CP-I reacts with BNI to generate the carbon-centred CP $\cdot$ radical and I $\cdot$ species (Scheme 2.3a). CP $\cdot$ reacts with BA, forming PBA $\cdot$ (Scheme 2.3a). PBA $\cdot$ undergoes irreversible AFCT with PMMA-Y, generating PMMA $\cdot$ and PBA-Y (Schemes 2.2b and 2.3b). PMMA $\cdot$ is capped with the I $\cdot$ species to form the PMMA-I macroinitiator (Scheme 2.3c). The block polymerization of BA from PMMA-I proceeds via organocatalyzed LRP with a catalytic role of BNI, generating a PMMA-PBA-I block copolymer (Scheme 2.3d).

Table 2.1. Polymerizations of BA with PMMA–Y ($M_n = 3900$ and $\bar{D} = 1.67$) (110 °C).

Entry	[BA] ₀ /[PMMA–Y] ₀ /[CP–I] ₀ /[AIBN] ₀ /[I ₂] ₀ / [BNI] ₀ (mM)	<i>t</i> (h)	Conv (%)	M_n^a ($M_{n,theo}^b$)	$\bar{D}^a$
1	8000/40/40/0/0/320	2	14	5100 (7500)	1.42
		4	22	6700 (9500)	1.43
		8	39	9700 (14000)	1.60
		16	68	18000 (21000)	2.33
		24	75	29000 (23000)	2.54
2	8000/40/0/28.8/20/320	2	21	6300 (9300)	1.54
		4	35	8400 (13000)	1.73
		8	61	13000 (20000)	2.46
		16	69	19000 (22000)	2.34
		24	90	24000 (27000)	2.66
3	8000/40/0/10/0/0	70 s	62	17000 (20000)	2.79
		1	73	25000 (23000)	3.19
		16	88	35000 (26000)	5.61

^a PMMA-calibrated THF-GPC values. ^b Theoretical M_n calculated with [BA]₀, [PMMA–Y]₀, and monomer conversion.

Scheme 2.3. Mechanisms in the organocatalyzed LRP of BA using PMMA–Y as a precursor.

Figure 2.1a shows the gel permeation chromatography (GPC) curves at different reaction times from zero to 24 h. The GPC curves shifted from the lower molecular weight side to the higher molecular weight side with an increase of the reaction time. At 24 h, the monomer conversion reached 75%, M_n was 29000, and $\bar{D}$ was 2.54. Upon the peak resolution of the GPC curve at 24 h (Figure 2.1b), we estimated the remaining PMMA–Y to be at most 10%, suggesting successful chain extension from PMMA–Y to PMMA–PBA–I with a high block efficiency (>90%). For the peak resolution, we used the curve of PMMA–Y (red solid line) for determining the remaining PMMA–Y (red dashed line) and subtracted the remaining PMMA–Y from the whole polymer (black solid line) for determining the PMMA–PBA–I block copolymer (blue dashed line). To confirm that the extended polymer is the PMMA–PBA block copolymer, we fractionated a higher-molecular-weight species (molecular weight > 5000) (green shadow in Figure 2.1b) from the original PMMA–Y ($M_n = 3900$) with preparative GPC and analyzed the higher-molecular-weight species with ^1H NMR (Figure 2.1c). Both PMMA (at 3.50–3.65 ppm for OCH_3) and PBA (at 3.83–4.20 ppm for OCH_2) segments were observed, confirming the formation of the PMMA–PBA block copolymer.

Figure 2.1. (a) GPC chromatograms for the BA/PMMA-Y/CP-I/BNI system (110 °C). The reaction condition is given in Table 2.1 (entry 1). (b) GPC chromatograms at $t = 0$ h and 24 h. The peak resolution is given for 24 h. The red and blue dashed lines are for remaining and extended polymers, respectively. (c) ^1H NMR spectrum of the fractionated polymer (green area in (b)).

We probed the AFCT mechanism for the transformation of PMMA–Y to PMMA–I. If AFCT takes place (Scheme 2.3b), the Y group is transferred from PMMA to PBA. Thus, the generation of PBA–Y will be a proof of AFCT.⁴¹ We analyzed the obtained polymer (after purification with preparative GPC to remove small molecules) with ¹H NMR (Figure 2.2). At the onset of the reaction (Figure 2.2a), the C=CH₂ protons (*a* and *b*) of PMMA–Y appeared at 5.45–5.53 and 6.18–6.23 ppm. During the reaction (Figure 2.2b), two new peaks appeared at 5.53–5.57 and 6.15–6.18 ppm and corresponded to the C=CH₂ protons (*c* and *d*) of PBA–Y.⁴¹ We also confirmed the generation of PBA–Y by matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 2.3). The observation of PBA–Y clearly demonstrates the occurrence of AFCT.

At the onset of the reaction (Figure 2.2c), the OCH₃ proton (*e'*) at the ω -terminal MMA unit of PMMA–Y appeared at 3.71–3.75 ppm. During the reaction (Figures 2.2d and 2.2e), a new peak appeared at 3.73–3.75 ppm, which corresponded to the OCH₃ proton (*e''*) at the ω -terminal MMA unit adjacent to iodide.⁴⁷ This result demonstrates the transformation from PMMA–Y to PMMA–I, as assumed in Scheme 2.3.

Figure 2.2. ^1H NMR spectra in the range of 5.40–6.30 ppm at $t =$ (a) 0 and (b) 8 h, 3.50–3.80 ppm at $t =$ (c) 0 and (d) 8 h, and (e) 3.70–3.76 ppm at $t = 8$ h for the BA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 2.1 (entry 1).

Figure 2.3. MALDI-TOF MS spectra of (a) PMMA–Y and (b) the polymer obtained in the organocatalyzed LRP (Table 2.1 (entry 1) at 8 h).

Figure 2.4 summarizes the monomer conversion, consumption of PMMA–Y, and generation of PBA–Y at different reaction times. The consumption of PMMA–Y and generation of PBA–Y were determined from the NMR peak area (Figures 2.2a and 2.2b). The first order plot of the monomer concentration $[M]$ was linear (Figure 2.4a). The concentration of PMMA–Y decayed with time (Figure 2.4b), and 90% of PMMA–Y was consumed for 24 h, quantitatively agreeing with the GPC peak resolution result (Figure 2.1b). PBA–Y was accumulated to almost the same extent as PMMA–Y that was consumed in the first 4 h (Figure 2.4c). Because PBA–Y acts (and hence is consumed) as a macromonomer in acrylate

polymerizations (Scheme 2.2c), the accumulation of PBA–Y then slowed down and started to decay after 16 h. After 24 h, most of the PBA–Y was consumed, meaning that the block copolymer could contain PBA branches in the PBA segment. Because one PMMA–Y generates one PBA–Y (macromonomer), the block polymer can contain approximately one PBA branch in a PBA segment on average.

Figure 2.4. Plots of (a) $\ln([M]_0/[M])$, (b) fraction of PMMA–Y, and (c) fraction of PBA–Y vs. time for the BA/PMMA–Y/CP–I/BNI system (110 °C) The reaction condition is given in Table 2.1 (entry 1).

Organocatalyzed LRP using I₂ and Azo Compound.

Instead of the isolated CP–I (alkyl iodide), we may employ molecular iodine (I₂) and 2,2'-azobis(2-methylpropionitrile) (AIBN (CP–N=N–CP)) as the starting compounds to generate CP–I in situ in the polymerization.^{9,18,22,48–50} Because I₂ and AIBN are inexpensive,

this method is attractive for practical use. Upon thermal heating, AIBN generates the alkyl radical CP[•], and CP[•] reacts with I₂ to yield CP-I.

We heated a mixture of BA (200 equiv.), PMMA-Y (1 equiv.), I₂ (0.5 equiv.), AIBN (0.72 equiv.), and BNI (8 equiv.) at 110 °C (Table 2.1 (entry 2)). Because the efficiency of AIBN to produce free CP[•] is approximately 0.6–0.7, 0.72 equiv. of AIBN and 0.5 equiv. of I₂ are stoichiometric to produce 1 equiv. of CP-I. At 110 °C, AIBN completely decomposes within 10 min, during which time CP[•] will predominantly react with I₂ (rather than the monomer) and CP-I gets accumulated. Figure 2.5 shows the result. The GPC curve smoothly shifted to the higher molecular weight side with time, and after 24 h, the monomer conversion reached 90%, *M_n* was 24000, and *D* was 2.66. Virtually 100% of both PMMA-Y and PBA-Y was consumed for 24 h. The polymerization was controlled in a manner similar to that in the CP-I system, showing the effectiveness of the I₂/AIBN approach for in situ generating CP-I. Again, this I₂/AIBN method is practically useful because of no requirement of the isolation of CP-I.

Figure 2.5. (a) GPC chromatograms and (b) plots of (a) $\ln([M]_0/[M])$, fraction of PMMA-Y, fraction of PBA-Y vs. time t for the BA/PMMA-Y/AIBN/I₂/BNI system (110 °C) The reaction condition is given in Table 2.1 (entry 2).

Model Conventional Radical Polymerization.

In comparison with the organocatalyzed LRP system, a model conventional radical polymerization containing an azo compound but not iodine or catalyst was performed. We heated a mixture of BA (200 equiv.), PMMA–Y (1 equiv.), and AIBN (0.25 equiv.) at 110 °C (Table 2.1 (entry 3)). AIBN acted as a conventional radical initiator to run the polymerization. Thermal initiation of BA monomer would also act as a (slow) radical source. After 16 h, the monomer conversion reached 88%, M_n was 35000, and $\bar{D}$ was 5.61. The $\bar{D}$ of 5.61 was much larger than that ($\bar{D}$ of 2.54) in the organocatalyzed LRP system (Table 2.1 (entry 1)) and is in agreement with the $\bar{D}$ values previously reported for the conventional radical polymerization of BA with PMMA–Y mediated via AFCT.³⁸ The GPC curve (Figure 2.6a) shifted to the higher molecular weight side with an increase in time. PMMA–Y was completely converted to PMMA–PBA–Y after 16 h, and a large portion of PMMA–PBA–Y was incorporated into the polymer after 16 h (Figure 2.6b).

Figure 2.7 compares the GPC charts for the organocatalyzed LRP system with CP–I (red line) and conventional radical polymerization system (blue line) at high monomer conversions (conv. = 75 and 88%, respectively), using the same GPC column (higher-molecular-weight column). The GPC chart for the organocatalyzed LRP system given in Figure 2.1a uses a different column (lower-molecular-weight column). As a marked observation, very high molecular weight species were generated at a later stage of polymerization in the conventional polymerization, giving a large $\bar{D}$ value (= 5.61).

Figure 2.6. (a) GPC chromatograms and (b) plots of (a) $\ln([M]_0/[M])$, fraction of PMMA-Y, fraction of PBA-Y vs. time t for the BA/PMMA-Y/AIBN system (110 °C) The reaction condition is given in Table 2.1 (entry 3). A higher-molecular-weight column system was used in Figure 2.6.

Figure 2.7. GPC chromatograms for organocatalyzed LRP vs. conventional radical polymerization. A higher-molecular-weight column system was used in all cases. (A lower-molecular-weight column system was used for organocatalyzed LRP in Figure 2.1.)

Scheme 2.4 illustrates the polymerization behaviours in the organocatalyzed LRP and conventional radical polymerization systems. Scheme 2.4 is a conceptual illustration, and there should be deviations in the actual polymerization.

In the organocatalyzed LRP system (Scheme 2.4a), PMMA-Y, CP-I, and BA (and catalyst) generate PMMA-PBA-I (short block copolymer) and CP-PBA-Y (macromonomer) through the consumption of PMMA-Y via AFCT (Scheme 2.3) (step 1). The PBA segment of the block copolymer subsequently grows in a controlled manner via the organocatalyzed LRP (step 2). In the growth process, the PBA segment can incorporate the macromonomer. Therefore, not only a linear block copolymer but also branched block copolymers can be generated. The average number of the branch is approximately one, as discussed.

A possible deviation in the actual polymerization is the non-clear separation of step 1 (consumption of PMMA-Y via AFCT) and step 2 (chain growth via the organocatalyzed

LRP). As Figure 2.4b shows, PMMA–Y was actually gradually consumed during the polymerization, and hence step 1 only gradually shifted to step 2. Another deviation is that AFCT to PMMA–Y occurs not only with CP–PBA[•] to generate CP–PBA–Y but also with PMMA–PBA[•] to generate another macromonomer PMMA–PBA–Y, which will also be consumed in step 2 (Scheme 2.4a). The observed relatively large $\bar{D}$ of 2.54 (Table 2.1 (entry 1)) would be due to these deviations and also the random distribution in the number of branches. These effects are unavoidable and led to larger $\bar{D}$ values than those ($\bar{D} < 1.5$) in usual living systems.

In the conventional radical polymerization system (Scheme 2.4b), PMMA–Y and BA (and conventional radical initiator) generate PMMA–PBA–Y (block copolymer macromonomer) through AFCT (step 1). Subsequently, the PMMA–PBA–Y macromonomer and BA are consumed in the conventional radical polymerization, forming branched polymers (step 2). The molecular weight of the branched polymers can be very high because of the conventional radical polymerization, as was actually observed at a later stage of polymerization (Figure 2.5a). The formation of branched polymers in the conventional radical polymerization was previously confirmed by Haddleton, et al. in a clear manner using viscosity measurements.³⁸

A notable difference in the two systems (Schemes 2.4a and 2.4b) is that the organocatalyzed LRP system tends to provide PMMA–PBA diblock copolymers (with possible PBA branches in the PBA segment) while the conventional radical polymerization system tends to provide comb-shaped multi-block copolymers (with multiple PMMA segments), as will be discussed below. Once again, Scheme 2.4 just highlights the concept, and there should be deviation in the actual polymerization.

Scheme 2.4. Schematic illustration for (a) organocatalyzed LRP and (b) conventional radical polymerization.

Composition Distribution Analysis.

Gradient polymer elution chromatography (GPEC) is a useful method to analyze co-monomer composition and distribution of polymers. The principle of GPEC is to separate polymers based on their polarity with a gradient eluent. An acetonitrile/THF eluent (from 100/0 to 0/100) was used in the present study. Figure 2.8 shows the GPEC curves for the polymers obtained in the organocatalyzed LRP using CP-I (Table 2.1 (entry 1)) and conventional radical polymerization (Table 2.1 (entry 3)) systems. The dashed and dotted red lines show pure PMMA (PMMA-Y) (with a peak at 4.0 min) and pure PBA (independently prepared, $M_n = 53000$, $D = 1.58$) (with a peak at 7.2 min), respectively. In the organocatalyzed LRP system (Figure 2.8a), the peak of PMMA-Y decayed with an increase in time and virtually disappeared after 24 h, agreeing with the NMR result (Figure 2.4b). Instead, a new peak appeared between 4.0 min (pure PMMA) and 7.2 min (pure PBA), corresponding to PMMA-PBA block copolymers. For a short polymerization time of 2 h, the peak was broad and tailed to a short elution time because the number of BA units in the chains is small. The GPEC elution time also depends on the molecular weight and tends to be shorter for a lower molecular weight. Therefore, short PBA homopolymers also appeared below 7.2 min. The observed formation of the short block copolymers and short PBA homopolymers agrees with the illustration in Scheme 2.4a at an early stage of polymerization. Subsequently, the GPEC peak shifted to a longer elution time (more BA units) with an increase in the polymerization time, suggesting that the PBA segments grew as shown in Scheme 2.4a. At 24 h, we observed two peaks reaching 6.9 min, which is ascribed to the grown block copolymers, and 7.2 min, which is ascribed to the grown PBA homopolymers. The peak intensity at 7.2 min increased from 4 h to 16 h and decreased from 16 h to 24 h, which is also consistent with the NMR result (time variation in the amount of PBA-Y) shown in Figure 2.4c. At 24 h, the integral (not the peak height) at 6.9 min (for block copolymers) is

larger than that at 7.2 min (PBA homopolymers), agreeing with the decay in PBA–Y and the generation of block copolymers as main components. These GPEC results support the conceptual illustration in Scheme 2.4a.

In the conventional radical polymerization system (Figure 2.8b), at 70 s, the PMMA–PBA–Y block copolymer macroinitiator (Scheme 2.4b) appeared at 7.0 min with a slight formation of PBA homopolymers at 7.2 min. With a further increase in the polymerization time, the GPEC peak did not significantly shift, while we observed a significant increase in the molecular weight with GPC (Figure 2.6a). This means that the co-monomer composition did not significantly change with an increase of the molecular weight and suggests that the observed higher molecular weight species are polymers connecting the PMMA–PBA–Y macromonomers. These GPEC results support the conceptual illustration in Scheme 2.4b.

Figure 2.8. GPEC chromatograms for (a) organocatalyzed LRP and (b) conventional radical polymerization. The reaction conditions are given in Table 2.1 (entries 1 and 3, respectively).

2.3. Conclusions

PMMA–Y was successfully utilized as a precursor of the macroinitiator for synthesizing PMMA–PBA block copolymers (with possible PBA branches in the PBA segment) in the organocatalyzed LRP. The use of the stable PMMA–Y overcomes the drawback in the direct use of the isolated PMMA–I macroinitiator, i.e., general lack of long-term stability upon storage, and significantly improves the ease of operation. The I₂/AIBN method uses inexpensive compounds (I₂ and AIBN) and is particularly attractive for practical applications. This method would be applicable to a range of functional acrylates and other monomers and to other molecular weight PMMA–Y precursors. We are currently studying other monomers and other molecular weight precursors for seeking a broad scope in the monomer and precursor molecular weights.

2.4. Experimental Section

Materials.

Methyl methacrylate (MMA) (>99%, Mitsubishi Chemical Corporation (MCC), Japan), sodium 2-(methacryloyloxy)ethanesulfonate (>98%, MCC), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) (>98%, Wako Pure Chemical, Japan), 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate (Perocta O) (>90%, NOF Corporation, Japan), cobalt (II) acetate tetrahydrate (>99%, Wako), diphenyl glyoxime (>98%, Tokyo Chemical Industry (TCI), Japan), boron trifluoride diethyl ether complex (>98%, TCI), potassium hydroxide (>85%, Wako), sodium sulfate (>99.5%, TCI), diethyl ether (>99.5%, TCI), butyl acrylate (BA) (>99%, TCI), tetrabutylammonium iodide (BNI) (>98%, TCI), 2,2'-azobis(2-methylpropionitrile) (AIBN) (98%, Wako), iodine (I₂) (>98%, TCI), 2-iodo-2-methylpropionitrile (CP–I) (>95%, TCI), hexane (>99%, International Scientific Pte Ltd.,

Singapore), and tetrahydrofuran (THF) (>99.5%, Kanto Chemical, Japan) were used as received.

Synthesis of Dispersant for Dispersion Polymerization.

61.6 g of 17% aqueous potassium oxide solution, 19.1 g of MMA, and 19.3 g of deionized water were charged into a reaction vessel equipped with a stirrer, condenser tube, and thermometer. The mixture was stirred at room temperature. After the confirmation of an exothermic peak, the mixture was stirred for additional 4 h. Subsequently, the mixture was cooled to room temperature to obtain an aqueous potassium methacrylate solution.

900 g of deionized water, 60 g of sodium 2-(methacryloyloxy) ethanesulfonate, 10 g of the aforementioned aqueous potassium methacrylate solution, and 12 g of MMA were placed in a reaction vessel equipped with a stirrer, condenser tube and thermometer. The mixture was heated to 50 °C under a nitrogen atmosphere. 0.08 g of V-50 was added into the reaction vessel and the mixture was further heated at 60 °C. Subsequently, MMA was continuously added dropwise for 75 min at a rate of 0.24 g/min using a syringe pump. After holding the reaction mixture at 60 °C for 6 h, the mixture was cooled to room temperature to obtain a dispersant as a transparent aqueous solution with a solid content of approximately 10%.

Synthesis of Cobalt Complex for Dispersion Polymerization.

2.00 g (8.03 mmol) of cobalt (II) acetate tetrahydrate, 3.86 g (16.1 mmol) of diphenyl glyoxime, and 100 mL of diethyl ether deoxygenated by nitrogen bubbling were placed in a reaction vessel equipped with a stirrer. The mixture was kept stirring for 2 h at room temperature under a nitrogen atmosphere.

Next, 20 mL of boron trifluoride diethyl ether complex was added, and the mixture was kept stirring for additional 6 hours. The resulting mixture was filtered, and the solid was

washed with diethyl ether and then vacuum-dried for 12 h at 20 °C to obtain 5.02 g (7.93 mmol, yield: 99%) of cobalt complex as a brown solid.

Dispersion Polymerization for Synthesis of PMMA-Y.

145 g of deionized water, 0.1 g of sodium sulfate, and 0.26 g of the dispersant synthesized above were placed in a reaction vessel equipped with a stirrer, condenser tube, and thermometer, and the mixture was stirred to obtain a homogeneous aqueous solution. To this solution, 100 g of MMA, 0.005 g of cobalt complex, and 0.1 g of Perocta O were added to obtain an aqueous dispersion, which was subsequently heated to 80 °C under a nitrogen atmosphere. The temperature was held at 80 °C for 4 h and then heated to 92 °C and was held for additional 2 h. The aqueous dispersion was cooled to 40 °C and filtered with a filter cloth. The filtrate was washed with deionized water and dried for 16 h at 40 °C to obtain PMMA-Y as white beads ($M_n = 3,900$).

Measurement.

The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The monomer conversion was determined from the peak area. The column system was calibrated with standard polystyrenes and poly(methyl methacrylate)s (PMMA)s.

NMR.

The NMR spectra were recorded on a Bruker (Germany) BBFO spectrometer (400 MHz) at ambient temperature. CDCl₃ (Cambridge Isotope Laboratories, USA) was used as a

solvent, and the chemical shift was calibrated using the residual undeuterated solvent or tetramethylsilane (TMS) as the internal standard.

Gradient Polymer Elution Chromatography (GPEC).

The GPEC analysis was performed at 40 °C on a HPLC alliance e2695 liquid chromatograph (Waters, Milford, USA) equipped with a TSKgel ODS-100V column (TOSOH, Tokyo, Japan) (150 × 4.6 mm; bead size = 5 μm). The eluent was a gradient solvent of acetonitrile/THF from 100/0 to 0/100 in 10 min at a flow rate of 1 mL/min. Sample detection was conducted using a PDA 2998 detector (Waters).

MALDI-TOF MS.

The matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL, Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared the polymer solutions (PMMA–Y: 10 g/L in THF and organocatalyzed LRP reaction mixture: 10 g/L in THF), matrix solution (DCTB: 60 g/L in THF), and cationization agent solution (NaTFA: 10 g/L in THF). The MALDI-TOF MS samples were prepared by the dried droplet method.⁵¹ The polymer solutions (in THF), NaTFA solution (in THF) and the DCTB solution (in THF) were mixed in a ratio of 1/1/2 (v/v/v). The mixed solution was deposited on the target plate spot and dried in the air at room temperature.

General Procedure for Polymerization.

In a typical run (Table 2.1 (entry 1)), a mixture of BA (2.00 g), PMMA-Y (0.304 g), CP-I (0.0152 g), and BNI (0.231 g) was heated in a Schlenk flask at 110 °C under an argon atmosphere with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the

solution was taken out by a syringe, quenched to room temperature, diluted by THF to a known concentration, and analyzed by GPC.

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Chapter 3. Synthesis of Block Copolymers Using Poly(methyl methacrylate) with Unsaturated Chain-End through Kinetic Studies

Abstract

A poly(methyl methacrylate) (PMMA) with an unsaturated chain-end (PMMA–Y) was used as a macroinitiator in the polymerizations of several monomers to generate block copolymers via addition-fragmentation chain transfer (AFCT). PMMA–Y also worked as a macromonomer to generate branched polymers via propagation. A kinetic study revealed that the occurrence of AFCT and propagation significantly depends on temperature in the styrene polymerization; namely, while propagation was predominant below 60 °C as previously reported, AFCT was predominant at elevated temperatures such as 120 °C as newly revealed in the present work. This new kinetic finding opened up an efficient synthesis of block copolymers of PMMA with polystyrene at an elevated temperature. AFCT was also predominant over propagation in the polymerizations of acrylonitrile and acrylates. Thus, block copolymers of PMMA with polyacrylonitrile and functional polyacrylates were successfully obtained. The polymerization was controlled using iodine transfer polymerization (ITP) for styrene and reversible complexation mediated polymerization (RCMP) for the other monomers. PMMA–Y with different molecular weights were also tested. This approach to obtain block copolymers is practically attractive for the ease of operation.

3.1. Introduction

Living radical polymerization (LRP), also termed reversible-deactivation radical polymerization, is a versatile method to synthesize polymers with predictable molecular weights and narrow molecular weight distributions and also importantly synthesize block copolymers.¹⁻⁹ Our research group developed an organocatalyzed LRP using alkyl iodides (R-I) as initiators and organic molecules as catalysts (Scheme 3.1).¹⁰⁻¹⁶ In this LRP, polymer-iodide dormant species (Polymer-I) coordinates a catalyst via halogen bonding to form a complex (Polymer-I...catalyst). The complex reversibly generates a propagating radical (Polymer[•]). We termed this polymerization as reversible complexation mediated polymerization (RCMP). The catalysts include organic salts such as tetrabutylammonium iodide (Bu₄N⁺I (BNI)).¹¹ This polymerization is attractive for no use of special capping agents or expensive catalysts and for amenability to a wide range of monomers and polymer structures.

Polymer-I can function as a macroinitiator to synthesize block copolymers. However, owing to a weak carbon-iodide bond, Polymer-I is generally not very stable upon long-term storage.^{6,17} In Chapter 2, we reported the use of a poly(methyl methacrylate) (PMMA) containing an unsaturated chain-end (PMMA-Y) as a macroinitiator in RCMP of butyl acrylate (BA), where Y is CH₂CH(=CH₂)COOCH₃ (Scheme 3.2).¹⁸ PMMA-Y is typically prepared via cobalt-mediated catalytic chain-transfer polymerization.¹⁹⁻²³ PMMA-Y was converted to PMMA[•] via an addition fragmentation chain transfer (AFCT)²³⁻³² of a poly(butyl acrylate) radical (PBA[•]) to PMMA-Y (Scheme 3.2a). The generated PMMA[•] subsequently added BA monomers to yield a PMMA-PBA block copolymer in one pot. Because PMMA-Y is stable under long-term storage, its use as a macroinitiator is a convenient and practical method to obtain block copolymers.

Scheme 3.1. Reversible activation in RCMP.

Scheme 3.2. (a) AFCT (addition-fragmentation chain transfer) via the fragmentation of the intermediate radical and (b) propagation of the intermediate radical.

PMMA-Y can also act as a macromonomer. A propagating radical ($\text{Polymer}^\bullet$) adds to the C=C double bond of PMMA-Y to generate the intermediate radical $\text{Polymer}-(\text{Y}^\bullet)\text{-PMMA}$ (Scheme 3.2). When $\text{PMMA}^\bullet$ is fragmented, the process is AFCT (Scheme 3.2a). When the intermediate radical adds to a monomer, the process is propagation, generating a branched polymer (Scheme 3.2b). In this chapter, we define the fragmentation rate constant as k_{fr} (Scheme 3.2a), the propagation rate constant as k_{p} (Scheme 3.2b), and the fraction of the intermediate radical to undergo the fragmentation as $F_{\text{fr}} = k_{\text{fr}}/(k_{\text{fr}} + k_{\text{p}})$. In the case of polyacrylate radicals for $\text{Polymer}^\bullet$, AFCT is predominant ($F_{\text{fr}} > 90\%$) over propagation.²⁶ This is the reason why block copolymers were obtained in Chapter 2 when we used butyl

acrylate as the monomer. In the case of polystyrene radical (PSt[•]), it was reported that AFCT is less significant ($F_{fr} > 40\%$) than propagation at 60 °C.²⁶

In this chapter, we experimentally determined F_{fr} for several different Polymer[•], i.e., PSt[•], poly(acrylonitrile) radical (PAN[•]), and functional hydrophobic and amphiphilic polyacrylate radicals. A significant finding was that AFCT became predominant ($F_{fr} \sim 100\%$) over propagation at an elevated temperature (120 °C) for PSt[•], which is in sharp contrast to the F_{fr} value ($> 40\%$) at 60 °C, showing a markedly large temperature dependence of F_{fr} . This kinetic finding opened up the use of PMMA–Y as a macroinitiator to produce PMMA–PSt block copolymers by simply elevating temperature, which could not be achieved at mild temperatures such as 60 °C. AFCT was also predominant ($F_{fr} > 90\%$) for PAN[•] and the studied functional polyacrylate radicals, enabling the synthesis of block copolymers. This work successfully expanded the monomer scope for the synthesis of block copolymers from PMMA–Y. We also studied PMMA–Y with different molecular weights. The high stability of PMMA–Y upon storage and the encompassed monomer scope including important monomer families (acrylates, styrene (St), and acrylonitrile (AN)) with functional groups are attractive features in this approach.

3.2. Results and Discussion

Temperature Dependence of F_{fr} for PSt[•] and PMMA–Y.

We used a PMMA–Y with $M_n = 3900$ and dispersity $\bar{D} (= M_w/M_n) = 1.67$, where M_n and M_w are the number-average and weight-average molecular weights, respectively. We carried out bulk polymerizations of St (200 equiv.) with PMMA–Y (1 equiv.), a conventional radical initiator (peroxide or azo initiator) (0.3–10 equiv.), and 2-iodo-2-methylpropionitrile (CP–I) (1 equiv.) (Figure 3.1) at different temperatures (40–120 °C) (Table 3.1). CP–I was

added as an alkyl iodide dormant species of LRP (iodide transfer polymerization (ITP)⁶ in the styrene system) to control the molecular weight.

Figure 3.1. Structures of alkyl iodide, catalyst, and monomers used in this work.

Table 3.1. Reaction conditions for the polymerizations of St with PMMA–Y at different temperatures (Table 3.2 (entry 1) and Figures 3.2, 3.4 and 3.5)).

Entry	T (°C)	In ^a	[St] ₀ /[PMMA–Y] ₀ /[CP–I] ₀ /[In ^a] ₀ (mM)
1	40	V65	8000/40/40/400
2	60	V65	8000/40/40/36
3	80	AIBN	8000/40/40/12
4	100	V40	8000/40/40/20
5	110	V40	8000/40/40/12
6	120	PBZ	8000/40/40/40

^a Conventional radical initiator. V65 = 2,2'-azobis(2,4-dimethylvaleronitrile), AIBN = 2,2'-azobis(2-methylpropionitrile), V40 = 1,1'-azobis(cyclohexanecarbonitrile), and PBZ = *tert*-butyl peroxybenzoate (PBZ).

The conventional radical initiator generates radicals, which react with St to form PSt[•]. PSt[•] undergoes addition to the C=C double bond of PMMA–Y to form the intermediate radical PSt–(Y[•])–PMMA, which can undergo fragmentation or propagation (Scheme 3.2). After the reaction, the polymer was purified with a preparative gel permeation chromatography (GPC) to remove small molecules such as residual monomer and radical initiator. Figure 3.2 shows the ¹H NMR spectra (CDCl₃) of the polymers obtained at time zero (Figure 3.2a) and 10 min (Figure 3.2b, monomer conversion = 10%) at 120 °C. The resonance peaks of CH₂=C of PMMA–Y were observed at 5.45–5.53 and 6.18–6.23 ppm (Figure 3.2a). Through the fragmentation, the Y group is transferred from PMMA–Y to PSt[•], generating PSt–Y (Scheme 3.2a). At 10 min, two new resonances appeared at 5.03–5.15 and 5.88–5.98 ppm and corresponded to the CH₂=C of PSt–Y (Figure 3.2b).³³ Thus, the AFCT of

PMMA–Y to generate PSt–Y was clearly observed. The formation of PSt–Y was also confirmed by matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 3.3). In the NMR spectra (Figure 3.2), the decay in PMMA–Y corresponds to the sum of k_{fr} and k_p , and the generation of PSt–Y corresponds to k_{fr} . We followed the change in the $CH_2=C$ peak areas of PMMA–Y and PSt–Y using the OCH_3 peak area of PMMA as an internal standard (which was unchanged during the reaction) and obtained the F_{fr} value ($= k_{fr}/(k_{fr} + k_p)$).

Figure 3.2. 1H NMR spectra ($CDCl_3$) in the range of 5.0–6.4 ppm at $t =$ (a) 0 and (b) 10 min for the St/PMMA–Y/CP–I/PBZ system (120 °C) (Table 3.1 (entry 6)); $[St]_0/[PMMA-Y]_0/[CP-I]_0/[PBZ]_0 = 8000/40/40/40$ (mM). PBZ is *tert*-butyl peroxybenzoate.

Figure 3.3. MALDI-TOF MS spectra of (a) PMMA–Y and (b) the polymer obtained in the styrene/PMMA–Y/CP–I/PBZ system at 120 °C (Table 3.3 (entry 1) at 30 min).

Figure 3.4 shows the F_{fr} values obtained at different temperatures. In this kinetic study, we intentionally focused on low monomer conversion regions (i.e., below 15% monomer conversion), because the generated PSt–Y can be consumed as a macromonomer during the polymerization, which causes an underestimation of the F_{fr} value. For the same reason, we also extrapolate the plots (Figure 3.4). The F_{fr} value extrapolated at the zero monomer conversion should be the most reasonable and is summarized in Table 3.2 (entry 1). The F_{fr} value determined at 60 °C was 38%, which is consistent with the literature value (40%) at 60 °C (Table 3.2 (entry R2)).

Table 3.2. F_{fr} values for PMMA–Y with Polymer[•].

Entry	R–Y	Polymer [•]	T (°C)	F_{fr} (%)	Ref.
R1	PMMA–Y	PMA [•]	60	>90	26
R2		PSt [•]	60	>40	26
1	PMMA–Y	PSt [•]	40	13	This work
			60	38	This work
			80	57	This work
			100	67	This work
			110	78	This work
			120	~100	This work
2	PMMA–Y	PAN [•]	75	97	This work
3	PMMA–Y	PMEA [•]	110	~100	This work
4	PMMA–Y	PPEGA [•]	110	83	This work

A significant finding was that the F_{fr} value markedly increased with an increase in temperature and that the fragmentation is predominant over propagation ($F_{fr} \sim 100\%$) at 120 °C. This finding opens up the use of PMMA–Y to produce PMMA–PSt block copolymers exclusively by simply elevating temperature, as demonstrated below, which was impossible to achieve at 60 °C. Conversely, the fragmentation occurred in only 13% at 40 °C. Therefore, PMMA–PSt block copolymers are obtainable at 120 °C, while branched copolymers are obtainable as the major products at 40 °C, which will be discussed below.

Figure 3.4. Plot of F_{fr} vs. monomer conversion for the St/PMMA–Y systems at 40–120 °C (Table 3.1 and Table 3.2 (entry 1). The symbols are indicated in the figure.

Because the fragmentation of the PSt–(Y^{*})–PMMA intermediate radical is a bond breaking process, a greater energy would be required compared with the propagation (radical addition), which is a bond forming process. At the same time, fragmentation is entropically favored at higher temperatures ($\Delta S > 0$) compared to propagation ($\Delta S < 0$). This would rationalize the promoted fragmentation with an increase in temperature. Figure 3.5 shows the Arrhenius plot of the ratio of $k_{\text{fr}}/k_{\text{p}}$ (not $F_{\text{fr}} = k_{\text{fr}}/(k_{\text{fr}} + k_{\text{p}})$). The $k_{\text{fr}}/k_{\text{p}}$ value at 120 °C was not included, because F_{fr} was nearly 100% and hence $k_{\text{fr}}/k_{\text{p}}$ becomes mathematically infinity. The plot gives equation (1).

$$k_{\text{fr}}/k_{\text{p}} = 3.8 \times 10^5 \exp(-37.4 \text{ kJ mol}^{-1}/RT) \quad (1)$$

The activation energy of 37.4 kJ mol^{-1} is the energy difference between the two processes ($E_{\text{fr}} - E_{\text{p}}$).

Figure 3.5. Arrhenius Plot of $k_{\text{fr}}/k_{\text{p}}$ for the St/PMMA–Y system.

Block Copolymerization of St from PMMA–Y.

The mentioned kinetic finding inspired us to study the block polymerization of St using PMMA–Y at an elevated temperature of 120 °C. We heated a mixture of St (200 equiv.), PMMA–Y ($M_n = 3900$ and $\bar{D} = 1.67$) (1 equiv.), *tert*-butyl peroxybenzoate (PBZ) (conventional radical initiator) (1.5 equiv.), and CP–I (1 equiv.) at 120 °C (Table 3.3 (entry 1) and Figure 3.6a). This is ITP including CP–I as an alkyl iodide dormant species but without catalysts. As Figure 3.6a shows, the GPC curve shifted from the low molecular weight to high molecular weight side with an increase in the polymerization time. After 3 h, the monomer conversion reached 96%, M_n was 17000, and $\bar{D}$ was 1.60 (Table 3.3 (entry 1) and Figures 3.6a and 3.6b). In order to confirm the generation of the PMMA–PSt block copolymer, we fractionated a higher-molecular-weight species (molecular weight >5000) (green shaded region in Figure 3.6b) from the original PMMA–Y ($M_n = 3900$) using a preparative GPC and analyzed the higher-molecular-weight species with ^1H NMR (Figure 3.6c). Both PMMA (3.50–3.70 ppm for OCH_3) and PSt (6.25–7.50 ppm for C_6H_5) segments were observed, confirming the successful formation of the PMMA–PSt block copolymer.

Table 3.3. Polymerizations using PMMA–Y ($M_n = 3900$ and $D = 1.67$).

Entry	Monomer	In ^a	[Monomer] ₀ /[PMMA–Y] ₀ / [CP–I] ₀ /[In] ₀ /[BNI] ₀ (mM)	<i>T</i> (°C)	<i>t</i> (h)	Conv (%)	<i>M_n</i> ^b (<i>M_{n,theo}</i> ^c)	<i>D</i> ^b
1	St	PBZ	8000/40/40/60/0	120	15 min	24	4600 (8900)	2.00
					30 min	46	8500 (13000)	1.77
					1	56	14000 (16000)	1.63
					3	96	17000 (24000)	1.60
2	St	V65	8000/40/40/400/0	40	16	90	15000 (23000)	1.51
3	AN	AIBN	8000/40/40/4/160 ^d	75	1	46	5900 (8800)	1.74
					3	67	7900 (11000)	1.90
					5	83	14000 (13000)	2.04
					7	86	15000 (13000)	1.82
4	MEA	none	8000/40/40/0/320	110	2	17	4400 (8300)	1.48
					4	27	5600 (11000)	1.47
					8	45	7900 (16000)	1.61
					16	69	12000 (22000)	1.86
					24	72	15000 (23000)	1.96
5	PEGA	none	8000/80/80/0/640	110	2	12	7700 (9700)	1.25
					4	17	8700 (12000)	1.26
					8	23	9300 (15000)	1.28
					16	34	12000 (20000)	1.41
					24	41	13000 (24000)	1.53

^a Conventional radical initiator. PBZ = *tert*-butyl peroxybenzoate (PBZ), V65 = 2,2'-azobis(2,4-dimethylvaleronitrile), and AIBN = 2,2'-azobis(2-methylpropionitrile). ^b PMMA-calibrated GPC values. The eluent was tetrahydrofuran (THF) for entries 1, 2 and 4 and dimethylformamide (DMF) for entries 3 and 5.

^c Theoretical M_n calculated with [Monomer]₀, [PMMA–Y]₀, and monomer conversion. ^d Diluted in 50 wt% ethylene carbonate (EC).

Figure 3.6. (a) GPC chromatograms for the St/PMMA–Y/CP–I/PBZ system (120 °C). The reaction condition is given in Table 3.3 (entry 1). (b) GPC chromatograms at $t = 0$ and 3 h. (c) ^1H NMR spectrum of the fractionated polymer (green area in (b)).

Figure 3.7 shows the monomer conversion and the amounts of PMMA–Y and PSt–Y at different times. PMMA–Y gradually decayed and was nearly completely consumed after 1 h (monomer conversion = 56%) (Figure 3.7b), suggesting that nearly all of the PMMA–Y chains became PMMA–PSt block copolymers. PSt–Y was accumulated at the initial stages of polymerization and started to decay after 30 min (monomer conversion = 46%) (Figure 3.7c), meaning that the generated PSt–Y was consumed as a macromonomer in the St polymerization. Therefore, the PSt segment in the block copolymer could contain PSt branches originated from PSt–Y. Because one PMMA–Y generates one PSt–Y (macromonomer), the block polymer can contain approximately one PSt branch in a PSt segment on average.

Figure 3.7. Plots of (a) $\ln([M]_0/[M])$, (b) fraction of PMMA–Y, and (c) fraction of PSt–Y vs. time t for the St/PMMA–Y/CP–I/PBZ system (120 °C) (Table 3.3 (entry 1)).

Scheme 3.3 illustrates the polymerization behaviour. PMMA–Y, CP–I, and St generate PMMA–PSt–I and PSt–Y through the consumption of PMMA–Y via AFCT (step 1). The PSt segment of the block copolymer subsequently grows in a controlled manner via LRP (step 2). The PSt block segment can add to PSt–Y and contain a PSt branch.

A possible deviation in the actual polymerization is the concurrent occurrence of steps 1 and 2. Because PMMA–Y was gradually consumed, step 1 gradually shifted to step 2. Hence, the AFCT of PMMA–PSt^{*} to PMMA–Y can also occur to generate another macromonomer, i.e., PMMA–PSt–Y. The gradual consumption of PMMA–Y also means non-uniform initiation from the PMMA chain. The distribution of the number of PSt branches per block copolymer chain is also random, while the average is one (as mentioned). These unavoidable deviations explain the observed larger $\bar{D}$ values ($\bar{D} > 1.60$) (Table 3.3 (entry 1)) than those ($\bar{D} < 1.5$) in usual living systems.

The addition of catalysts (converting ITP to RCMP) did not significantly lower the $\bar{D}$ value in this styrene system. Because of the mentioned unavoidable deviations, it seems that the $\bar{D}$ value of 1.60 attained by this ITP system is already close to the lowest achievable value and hence could not be lowered even though the addition of catalyst could give a larger number of activation-deactivation cycles. In contrast, in the AN and acrylate systems described below, because the frequency of the iodide transfer (ITP) is not high enough, the addition of catalysts (RCMP) was effective to lower the $\bar{D}$ value.

Scheme 3.3. Schematic illustration for the generation of block copolymer from PMMA–Y.

Viscosity and Composition Analysis.

In the St system, PMMA–Y works as a macroinitiator and tends to generate linear PMMA–PSt block copolymers at 120 °C ($F_{fr} \sim 100\%$), although some block copolymers can have branches in the PSt segment (Scheme 3.3). In contrast, at 40 °C ($F_{fr} = 13\%$), PMMA–Y works as a macromonomer and tends to generate more branched polymers with the PS main chain and PMMA branches. Therefore, interestingly, we tend to obtain block and branched copolymers by just changing temperature.

To confirm the structural difference, we measured intrinsic viscosity $[\eta]$ for a polymer synthesized at 120 °C ($M_n = 17000$, $\bar{D} = 1.60$, conv = 96%) (Table 3.3 (entry 1) at 3 h) and a polymer synthesized at 40 °C ($M_n = 15000$, $\bar{D} = 1.51$, conv = 90%) (Table 3.3 (entry 2) at 16 h). Because the M_n and $\bar{D}$ values are similar, a difference in $[\eta]$ will result from the linear and branched structures. Figure 3.8 shows the Mark-Houwink plot. The $[\eta]$ value for the polymer at 120 °C was larger than that for the polymer at 40 °C by 18–33% in the studied range of molecular weight (12000–63000), supporting that the polymer synthesized at 120 °C tends to be more linear than that synthesized at 40 °C.

Figure 3.8. Mark-Houwink plot of the PMMA–PSt polymers synthesized at 40 °C and 120 °C.

The St/MMA composition of the polymer obtained at 120 °C was analyzed with gradient polymer elution chromatography (GPEC) (Figure 3.9). In GPEC, polymers are separated based on their polarity with a gradient eluent of acetonitrile/tetrahydrofuran (THF)

(from 100/0 to 0/100). The dashed and dotted lines show a pure PMMA (PMMA–Y) with a peak at 4.2 min and a pure PSt (GPC standard PSt ($M_n = 19000$ and $D = 1.01$)) with a peak at 7.9 min, respectively. After the 3 h polymerization, the peak for PMMA–Y at 4.2 min almost disappeared, which is consistent with the NMR result (Figure 3.7b). Instead, we observed a new peak at 6.5–7.7 min, i.e., between 4.2 min (pure PMMA) and 7.9 min (pure PSt), corresponding to PMMA–PSt block copolymers. This result confirms the generation of the copolymer. We also observed a PSt homopolymer (remaining PSt–Y (Figure 3.7c)) at 7.8 min. The integral (not the peak height) at 6.5–7.7 min (for block copolymer) is much larger than that at 7.8 min (for PSt homopolymer), agreeing with the generation of block copolymers as main components.

Figure 3.9. GPEC chromatograms for a pure PSt, the polymer obtained after 3 h at 120 °C (Table 3.3 (entry 1)), and a pure PMMA (PMMA–Y).

Determination of F_{fr} for PAN $\cdot$ and Block Copolymerization of AN from PMMA–Y.

We studied a polymerization of AN (200 equiv.) with PMMA–Y ($M_n = 3900$ and $D = 1.67$) (1 equiv.), 2,2'-azobis(isobutyronitrile) (AIBN) (0.1 equiv.), CP–I (1 equiv.), and BNI (4 equiv.) in ethylene carbonate (EC) (solvent, 50 wt%) at 75 °C (Table 3.3 (entry 3)). The system is RCMP using CP–I as an alkyl iodide dormant species and BNI as a catalyst. The temperature selected (75 °C) is suitable for the polymerization of AN via RCMP.¹¹ AIBN was added to increase the polymerization rate. EC was a solvent to dissolve the PAN segment. The obtained polymers were purified by reprecipitation.

Figure 3.10 shows the ^1H NMR spectra (DMSO- d_6) of the polymers obtained at time zero (Figure 3.10a) and 1 h (Figure 3.10b, monomer conversion = 46%). The $\text{CH}_2=\text{C}$ protons of PMMA–Y appeared at 5.52–5.60 and 6.08–6.17 ppm (Figure 3.10a). At 1 h, two new peaks appeared at 5.90–5.95 and 6.28–6.31 ppm and corresponded to the $\text{CH}_2=\text{C}$ protons of

PAN–Y (Figure 3.10b). The F_{fr} value obtained from the peak areas was 97% (Table 3.2 (entry 2) and Figure 3.11), meaning that the PAN–(Y $\cdot$)–PMMA intermediate undergoes fragmentation (AFCT) predominantly over propagation.

Figure 3.10. ^1H NMR spectra ($\text{DMSO}-d_6$) in the range of 5.4–6.4 ppm at $t =$ (a) 0 and (b) 1 h for the AN/PMMA–Y/CP–I/AIBN/BNI system (75 °C). The reaction condition is given in Table 3.3 (entry 3).

Figure 3.11. Plot of F_{fr} vs. monomer conversion for the AN/PMMA–Y/CP–I/AIBN/BNI system at 75 °C (Table 3.2 (entry 2) and Table 3.3 (entry 3)).

Because of the predominant AFCT, we were able to obtain PMMA–PAN block copolymers in this system. The GPC curves smoothly shifted from the low molecular weight side to the high molecular weight side (Figure 3.12). The first order plot of the monomer concentration was linear (Figure 3.13a). After 7 h, the monomer conversion reached 86%, M_n was 15000, D was 1.82 (Table 3.3 (entry 3)), and 88% of PMMA–Y was consumed (Figure 3.13b), suggesting that a large amount of PMMA–Y became PMMA–PAN block copolymers. PAN–Y was accumulated and turned to decay after 5 h (Figure 3.13c) similarly to the St polymerization.

Figure 3.12. GPC chromatograms (DMF-GPC) for the AN/PMMA–Y/CP–I/AIBN/BNI system (75 °C). The reaction condition is given in Table 3.3 (entry 3).

Figure 3.13. Plots of (a) $\ln([M]_0/[M])$, (b) fraction of PMMA–Y, and (c) fraction of PAN–Y vs. time t for the AN/PMMA–Y/CP–I/AIBN/BNI system (75 °C). The reaction condition is given in Table 3.3 (entry 3).

Block Copolymerizations of Functional Acrylates from PMMA–Y.

We previously reported an RCMP of BA using PMMA–Y to synthesize PMMA–PBA block copolymers. The F_{fr} value is >90% for acrylates (as mentioned above), rationalizing the formation of PMMA–PBA block copolymers. In the present work, we expanded the monomer scope to functional acrylates, i.e., hydrophobic 2-methoxyethyl acrylate (MEA) and amphiphilic poly(ethylene glycol) methyl ether acrylate (PEGA) (molecular weight = 480 g mol⁻¹), both of which are biocompatible acrylate monomers (Figure 3.2). We carried out bulk RCMPs of these monomers (100 or 200 equiv.) with PMMA–Y (1 equiv.), CP–I (1 equiv.), and BNI (8 equiv.) at 110 °C (Table 3.2 (entries 4 and 5)). The relatively high temperature of

110 °C was required for RCMP of acrylates because the secondary carbon-iodine bonds are relatively strong and cleavable at high temperatures with BNI catalyst.¹¹ The GPC curve shifted over time for both MEA (Figure 3.14) and PEGA (Figure 3.15). After 24 h, we obtained polymers with $M_n = 15000$ and $\bar{D} = 1.96$ for MEA (monomer conversion = 72%) and $M_n = 13000$ and $\bar{D} = 1.53$ for PEGA (monomer conversion = 41%). 86% of PMMA–Y was consumed after 24 h in both polymerizations (Figure 3.16b and Figure 3.17b). PME–Y (Figure 3.18) and PPEGA–Y (Figure 3.19) accumulated to nearly the same extent that PMMA–Y was consumed in the first 2–4 h (Figure 3.16c and Figure 3.17c). The F_{fr} value was determined to be ~100% for PME and 83% for PPEGA (Table 3.2 (entries 3 and 4)), showing high efficiencies of AFCT to obtain block copolymers. These results demonstrate the use of PMMA–Y and functional acrylates to have access to block copolymers.

Figure 3.14. GPC chromatograms (THF-GPC) for the MEA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.3 (entry 4).

Figure 3.15. GPC chromatograms (DMF-GPC) for the PEGA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.3 (entry 5).

Figure 3.16. Plots of (a) $\ln([M]_0/[M])$, (b) fraction of PMMA–Y, and (c) fraction of PMEAY vs. time t for the MEA/PMMA–Y/CP–I/BNI system (110 °C) (Table 3.3 (entry 4)).

Figure 3.17. Plots of (a) $\ln([M]_0/[M])$, (b) fraction of PMMA–Y, and (c) fraction of PPEGA–Y vs. time t for the PEGA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.3 (entry 5).

Figure 3.18. ^1H NMR spectra (CDCl₃) in the range of 5.4–6.3 ppm at $t =$ (a) 0 and (b) 4 h for the MEA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.3 (entry 4).

Figure 3.19. ^1H NMR spectra (CDCl₃) in the range of 5.4–6.3 ppm at $t =$ (a) 0 and (b) 4 h for the PEGA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.3 (entry 5).

We attempted to remove PEGA monomer from the block copolymer by reprecipitation into a Et₂O/hexane mixture. However, despite changing the ratio of Et₂O/hexane, we were not able to fully remove the monomer. In the NMR spectra (Figure 3.19), peak *c* from PEGA–Y is not overlapped with any peak of the PEGA monomer. Hence we can determine the concentration of PEGA–Y and the fragmentation from the peak ratio of *c* and *a*.

Use of I₂ and an Azo Compound.

Table 3.4. Polymerizations of St, AN, MEA and PEGA with PMMA–Y ($M_n = 3900$ and $\bar{D} = 1.67$) using azo compound and iodine.

Entry	Monomer	azo	[Monomer] ₀ /[PMMA–Y] ₀ / [I ₂] ₀ /[azo] ₀ /[BNI] ₀ (mM)	<i>T</i> (°C)	<i>t</i> (h)	Conv (%)	M_n^a ($M_{n,theo}^b$)	$\bar{D}^a$	PMMA–Y remaining (%)
1	St	AIBN	8000/40/20/28.8/0 ^c	120	3	93	15000 (23000)	1.73	1
2	AN	V65/AIBN	8000/40/20/(28.8/4)/160 ^d	75	7	81	13000 (12000)	2.30	22
3	MEA	AIBN	8000/40/20/30/320	110	24	93	15000 (28000)	1.78	15
4	PEGA	AIBN	8000/80/40/88/640 ^d	110	24	54	15000 (30000)	1.67	22

^a PMMA-calibrated GPC values. The eluent was tetrahydrofuran (THF) for entries 1 and 3 and dimethylformamide (DMF) for entries 2 and 4. ^b Theoretical M_n calculated with [Monomer]₀, [PMMA–Y]₀, and monomer conversion. ^c With PBZ (60 mM). ^d Diluted in 50 wt% ethylene carbonate (EC) to dissolve the PAN segment for entry 2 and 10 wt% diglyme to dissolve AIBN for entry 4.

Instead of using an isolated alkyl iodide (CP–I), we may use molecular iodine (I₂) and an azo compound (AIBN or 2,2'-azobis(2,4-dimethylvaleronitrile) (V65)) as starting compounds to generate an alkyl iodide in situ in the polymerization. The azo compound (R–N=N–R) generates an alkyl radical (R[•]), which then reacts with I₂ to produce an alkyl iodide (R–I). This I₂/azo method was initially developed in ITP^{6,17,34,35} and subsequently used in RCMP.^{11,36} This method is attractive for practical use, because I₂ and AIBN are inexpensive. In the present work, we used the I₂/azo method for the polymerizations of St, AN, MEA, and PEGA using PMMA–Y. We heated a mixture of monomer (100 or 200 equiv.), PMMA–Y (1 equiv.), I₂ (0.5 equiv.), an azo compound (0.72–1.1 equiv.), and BNI at 75–120 °C (Table 3.4). Because the efficiency of an azo compound to produce free R[•] is not unity, an excess of

the azo compound (0.72–1.1 equiv.) to I_2 (0.5 equiv.) was added to ensure that I_2 was quantitatively converted to R–I. BNI was absent for St (ITP) and present for AN, MEA, and PEGA (RCMP). The azo compound completely decomposed within 1 h at the studied temperatures, during which time $R^\bullet$ would predominantly react with I_2 (rather than the monomer) and R–I accumulated. The monomer conversion reached 54–93% in the studied polymerization time (3–24 h), and a large fraction (78–99%) of PMMA–Y was consumed to generate block copolymers (Table 3.4). The polymerization was controlled in a manner similar to that in the CP–I system (Table 3.3) in all cases, demonstrating the effectiveness of the I_2 /azo approach. Again, this method is robust because of no requirement of the isolation of R–I.

Use of PMMA–Y with Higher Molecular Weight.

Table 3.5. Polymerization of BA with PMMA–Y ($M_n = 12000$ and $\bar{D} = 1.78$) (110 °C).

$[BA]_0/[PMMA-Y]_0/[CP-I]_0/[BNI]_0$ (mM)	t (h)	Conv (%)	M_n^a ($M_{n,theo}^b$)	$\bar{D}^a$
8000/27/27/213	4	11	10000 (16000)	1.94
	8	21	12000 (20000)	1.75
	24	72	27000 (40000)	2.63
	72	97	38000 (49000)	3.43

^a PMMA-calibrated THF-GPC values. ^b Theoretical M_n calculated with $[BA]_0$, $[PMMA-Y]_0$, and monomer conversion.

We also used a PMMA–Y with a higher molecular weight, i.e., $M_n = 12000$ and $\bar{D} = 1.78$, in the BA polymerization. We carried out RCMP of BA (300 equiv.) using PMMA–Y (1 equiv.), CP–I (1 equiv.) and BNI (8 equiv.) at 110 °C (Table 3.5 and Figure 3.20). The

polymerization virtually completed after 72 h (monomer conversion = 97%), yielding a polymer with $M_n = 38000$ and $D = 3.43$ (Table 3.5 and Figure 3.21). Interestingly, despite the higher molecular weight of PMMA–Y, a large amount (85%) of PMMA–Y was consumed to generate a PMMA–PBA block copolymer after 72 h (Figure 3.20b).

Figure 3.20. Plots of (a) $\ln([M]_0/[M])$, (b) fraction of PMMA–Y, and (c) fraction of PBA–Y vs. time t for the BA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.5.

Figure 3.21. GPC chromatograms (THF-GPC) for the BA/PMMA–Y/CP–I/BNI system (110 °C). The reaction condition is given in Table 3.5.

3.3. Conclusions

The F_{fr} of PMMA–Y in the St polymerization strongly depended on temperature and ranged from 13% at 40 °C to approximately 100% at 120 °C. PMMA–Y mainly worked as a macromonomer to generate branched polymers at 40 °C and predominantly worked as a macroinitiator to generate PMMA–PSt block copolymers at 120 °C. Such a selective generation would be interesting. Based on this finding, PMMA–PS block copolymers were synthesized at 120 °C via ITP. The F_{fr} values were also high (80–99%) for AN, MEA, and PEGA. The block copolymers were obtained in RCMP (with BNI catalyst) for AN, MEA, and PEGA. For all studied monomers, not only the isolated CP–I but also the alkyl iodide in situ generated from I_2 and azo compound was effectively used as the initiating dormant species. The in situ method is less expensive and robust and hence can be a practically attractive alternative. The RCMP of BA was extended onto a higher molecular weight

PMMA–Y. Despite a longer PMMA chain, a large amount (85%) of PMMA–Y was consumed to produce PMMA–PBA block copolymers.

3.4. Experimental Section

Materials.

Methyl methacrylate (MMA) (>99%, Mitsubishi Chemical Corporation (MCC), Japan), Methyl acrylate (MA) (>99%, MCC), sodium 2-(methacryloyloxy)ethanesulfonate (>98%, MCC), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) (>98%, Wako Pure Chemical, Japan), 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate (Perocta O) (>90%, NOF Corporation, Japan), cobalt (II) acetate tetrahydrate (>99%, Wako), diphenyl glyoxime (>98%, Tokyo Chemical Industry (TCI), Japan), boron trifluoride diethyl ether complex (>98%, TCI), potassium hydroxide (>85%, Wako), sodium sulfate (>99.5%, TCI), diethyl ether (Et₂O) (>99.5%, TCI), styrene (St) (>99%, TCI), acrylonitrile (AN) (>99%, Kanto Chemical, Japan), 2-methoxyethyl acrylate (MEA) (>98%, TCI), poly(ethylene glycol) methyl ether acrylate (PEGA) (98%, Sigma-Aldrich, US), butyl acrylate (BA) (>99%, TCI), *tert*-butyl peroxybenzoate (PBZ) (98%, NOF), 2,2'-azobis(2,4-dimethylvaleronitrile) (V65) (95%, Wako), 1,1'-azobis(cyclohexane-1-carbonitrile) (V40) (98%, Wako), 2,2'-azobis(2-methylpropionitrile) (AIBN) (98%, Wako), tetrabutylammonium iodide (BNI) (>98%, TCI), iodine (I₂) (>98%, TCI), 2-iodo-2-methylpropionitrile (CP-I) (>95%, TCI), ethylene carbonate (>99%, TCI), diglyme (>99%, TCI), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto), hexane (>99%, International Scientific Pte Ltd., Singapore), tetrahydrofuran (THF) (>99.5%, Kanto), silver trifluoroacetate (AgTFA) (>99.99%, Sigma-Aldrich), and *trans*-2-[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>99%, Sigma-Aldrich) were used as received.

Synthesis of Dispersant for Dispersion Polymerization.

61.6 g of 17% aqueous potassium oxide solution, 19.1 g of MMA, and 19.3 g of deionized water were charged into a reaction vessel equipped with a stirrer, condenser tube, and thermometer. The mixture was stirred at room temperature. After the confirmation of an exothermic peak, the mixture was stirred for additional 4 h. Subsequently, the mixture was cooled to room temperature to obtain an aqueous potassium methacrylate solution.

900 g of deionized water, 60 g of sodium 2-(methacryloyloxy) ethanesulfonate, 10 g of the aforementioned aqueous potassium methacrylate solution, and 12 g of MMA were placed in a reaction vessel equipped with a stirrer, condenser tube and thermometer. The mixture was heated to 50 °C under a nitrogen atmosphere. 0.08 g of V-50 was added into the reaction vessel and the mixture was further heated at 60 °C. Subsequently, MMA was continuously added dropwise for 75 min at a rate of 0.24 g/min using a syringe pump. After holding the reaction mixture at 60 °C for 6 h, the mixture was cooled to room temperature to obtain a dispersant as a transparent aqueous solution with a solid content of approximately 10%.

Synthesis of Cobalt Complex for Dispersion Polymerization.

2.00 g (8.03 mmol) of cobalt (II) acetate tetrahydrate, 3.86 g (16.1 mmol) of diphenyl glyoxime, and 100 mL of diethyl ether deoxygenated by nitrogen bubbling were placed in a reaction vessel equipped with a stirrer. The mixture was kept stirring for 2 h at room temperature under a nitrogen atmosphere.

Next, 20 mL of boron trifluoride diethyl ether complex was added, and the mixture was kept stirring for additional 6 h. The resulting mixture was filtered, and the solid was washed with diethyl ether and then vacuum-dried for 12 h at 20 °C to obtain 5.02 g (7.93 mmol, yield: 99%) of cobalt complex as a brown solid.

Dispersion Polymerization for Synthesis of PMMA–Y.

145 g of deionized water, 0.1 g of sodium sulfate, and 0.26 g of the dispersant synthesized above were placed in a reaction vessel equipped with a stirrer, condenser tube, and thermometer, and the mixture was stirred to obtain a homogeneous aqueous solution. To this solution, 100 g of MMA, 0.005 g of cobalt complex, and 0.1 g of Perocta O were added to obtain an aqueous dispersion, which was subsequently heated to 80 °C under a nitrogen atmosphere. The temperature was held at 80 °C for 4 h and then heated to 92 °C and was held for additional 2 h. The aqueous dispersion was cooled to 40 °C and filtered with a filter cloth. The filtrate was washed with deionized water and dried for 16 h at 40 °C to obtain PMMA-Y as white beads ($M_n = 3,900$).

Dispersion Polymerization for Synthesis of PMMA–Y (higher molecular weight).

145 g of deionized water, 0.1 g of sodium sulfate, and 0.18 g of the dispersant synthesized above were placed in a reaction vessel equipped with a stirrer, condenser tube, and thermometer, and the mixture was stirred to obtain a homogeneous aqueous solution. To this solution, 95 g of MMA, 5 g of MA, 1.6 mg of cobalt complex, and 0.13 g of Perocta O were added to obtain an aqueous dispersion, which was subsequently heated to 80 °C under a nitrogen atmosphere. The temperature was held at 80 °C for 4 h and then heated to 92 °C and was held for additional 2 h. The aqueous dispersion was cooled to 40 °C and filtered with a filter cloth. The filtrate was washed with deionized water and dried for 16 h at 40 °C to obtain PMMA-Y as white beads ($M_n = 12,000$).

Measurement.

For Figures 3.12 and 3.15, the GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å). The eluent was dimethyl

formamide (DMF) at a flow rate of 0.8 mL/min (40 °C). The DMF eluent included LiBr (10 mM). Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s.

For Figures 3.6, 3.14, and 3.21, the GPC analysis was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan). The Shimadzu LC-2030C Plus GPC was equipped with both a Shodex KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 µm; pore size = 1500 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 µm; pore size = 3000 Å). The eluent was tetrahydrofuran (THF) at a flow rate of 0.7 mL/min. Sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard PMMA)s.

Viscosity Analysis.

The viscosity analysis (Figure 3.8) was performed on a Viscotek GPC-TDA 302 (Malvern Panalytical, Malvern, UK) equipped with a TSKgel guard column HXL-H (40 × 6.0 mm), two TSKgel GMHXL (300 × 7.8 mm; bead size = 9 µm) and a TSKgel G2500HXL (300 × 7.8 mm; bead size = 5 µm) (TOSOH, Tokyo, Japan). The eluent was THF at a flow rate of 1.0 mL/min (40 °C). Sample detection and quantification were conducted using triple detector (refractive index, differential pressure and 90 degree light scattering). The column system was calibrated with standard polystyrenes.

NMR.

The NMR spectra were recorded on a Bruker (Germany) BBFO spectrometer (400 MHz) at ambient temperature. CDCl₃ (Cambridge Isotope Laboratories, USA) or DMSO-*d*₆ (Cambridge Isotope Laboratories) was used as a solvent, and the chemical shift was

calibrated using the residual undeuterated solvent or tetramethylsilane (TMS) as the internal standard.

Gradient Polymer Elution Chromatography (GPEC).

The GPEC analysis was performed at 40 °C on a HPLC 1260 Infinity liquid chromatograph (Agilent, Santa Clara, USA) equipped with a TSKgel ODS-100V column (TOSOH) (150 × 4.6 mm; bead size = 5 µm). The eluent was a gradient solvent of acetonitrile/THF from 100/0 to 0/100 in 10 min at a flow rate of 1 mL/min. Sample detection was conducted using a Corona Veo RS detector (Thermo Fisher, Waltham, USA).

MALDI-TOF MS.

The matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL, Tokyo, Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared a polymer solution (PMMA–Y: 10 g/L in THF or polymerization mixture: 10 g/L in THF), a cationization agent solution (AgTFA: 10 g/L in THF), and a matrix solution (DCTB: 60 g/L in THF). The polymer solution, the AgTFA solution, and the DCTB solution were mixed in a ratio of 1/1/4 (v/v/v). The mixed solution was deposited on the target plate spot and dried in the air at room temperature.

General Procedure for Block Copolymerization of St.

In a typical run, a mixture of St (0.833 g, 8.00 mmol), PMMA–Y (0.156 g, 0.04 mmol), CP–I (7.8 mg, 0.04 mmol), and PBZ (conventional radical initiator) (11.65 mg, 0.06 mmol) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated at 120 °C under an argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe,

cooled to room temperature, diluted with THF to a known concentration, and analyzed by GPC.

Procedure for Block Copolymerization of AN.

A mixture of AN (0.318 g, 6.00 mmol), PMMA–Y (0.117 g, 0.03 mmol), CP–I (5.85 mg, 0.03 mmol), AIBN (0.493 mg, 0.003 mmol), BNI (0.443 mg, 0.12 mmol), and ethylene carbonate (50wt%, 0.480 g) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated at 75 °C under an argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, diluted with DMF to a known concentration, and analyzed by GPC.

Procedure for Block Copolymerization of MEA.

A mixture of MEA (1.04 g, 8.00 mmol), PMMA–Y (0.156 g, 0.04 mmol), CP–I (7.8 mg, 0.04 mmol), and BNI (118 mg, 0.32 mmol) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated at 110 °C under an argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, diluted with THF to a known concentration, and analyzed by GPC.

Procedure for Block Copolymerization of PEGA.

A mixture of PEGA (1.92 g, 4.00 mmol), PMMA–Y (0.156 g, 0.04 mmol), CP–I (7.8 mg, 0.04 mmol), and BNI (118 mg, 0.32 mmol) was added to a Schlenk flask and the mixture was bubbled with argon for 10 min. The Schlenk flask was then heated at 110 °C under an argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, diluted with DMF to a known concentration, and analyzed by GPC.

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Chapter 4. Recyclable Solid-Supported Catalysts for Amine- and Quaternary Ammonium Iodide-Catalyzed Living Radical Polymerization

Abstract

Polymer resin particles bearing tertiary amine (R_3N) and quaternary ammonium iodide ($R_4N^+I^-$) catalysts were developed as supported catalysts for organocatalyzed living radical polymerization. The supported catalysts were successfully used to synthesize homopolymers and block copolymers of methyl methacrylate, functional methacrylates and acrylonitrile with low dispersities. The supported catalysts could be easily separated (recovered) from the polymerization solutions by filtration, and were also reused in five polymerization cycles without a noticeable decrease in the catalytic efficiency. The facile preparation of the supported catalysts, the broad monomer scope, and the feasibility of the catalyst reuse and recycle are attractive features.

4.1. Introduction

Covalently immobilized catalysts on solid substrates have widely been used in synthetic chemistry.¹⁻⁴ Such immobilized (supported) heterogeneous catalysts are important in industries, because they facilitate catalyst removal and product purification compared with the corresponding homogeneous catalysts. The reuse and recycling of the supported catalysts offer waste-reducing, cost-saving, and “green” processes.^{5,6}

In the field of polymerization, heterogeneous catalysts have been used for the commercial production of polyethylene and polypropylene using, for example, crystalline magnesium chloride-supported Ziegler-Natta catalysts since the 1970s.⁷ To date, supported

metallic catalysts for olefin polymerizations and metathesis polymerizations have extensively been studied.^{8–11} Supported catalysts have also been utilized in living radical polymerization (LRP) (also known as reversible-deactivation radical polymerization). Transition-metal catalysts such as copper and ruthenium catalysts were immobilized onto silica,^{12–16} crosslinked polymers,^{12,13,17} clay,^{18,19} magnetic particles,^{20,21} and metal–organic frameworks^{22,23} for atom transfer radical polymerization (ATRP). In reversible addition-fragmentation chain transfer (RAFT) polymerization, silica- and fiber-supported organic photocatalysts were recently reported.^{24–26} The use of supported catalysts has offered simplified polymer purification and prevention of catalyst residue contamination and coloration.^{27,28}

Our research group has developed an organocatalyzed LRP using an alkyl iodide (R–I) as an initiator and an organic molecule as a catalyst.^{29–34} The catalysts include amines, iodide anion (I^-), azide anion, and oxyanions. Mechanistically, polymer-iodide dormant species (Polymer–I) coordinates a catalyst via a halogen bonding to form a complex (Polymer–I...catalyst), which reversibly generates a propagating radical (Polymer[•]) (Scheme 4.1). This LRP was termed reversible complexation mediated polymerization (RCMP). RCMP is attractive because it does not require special capping agents or metal catalysts and is amenable to a wide range of monomers and polymer structures, including block copolymers, polymer brushes,^{35,36} and micelles.^{37,38} Homogeneous RCMP was utilized in Chapters 2 and 3 for the synthesis of block copolymers from a stable macroinitiator precursor PMMA–Y. One difficulty we faced was the removal of the catalyst after the polymerization.

Scheme 4.1. Reversible activation in RCMP.

DIAION WA-30 (produced by Mitsubishi Chemical) (Figure 4.1), is a commercially available organic crosslinked polystyrene particle (diameter = 300–900 μm) containing tertiary amino groups and is used as an ion-exchange resin. In this chapter, the use of WA-30 as a solid catalyst for heterogeneous RCMP is demonstrated. The tertiary amino groups on the catalyst could also be functionalized to quaternary ammonium iodide moieties which are also effective RCMP catalysts. The catalysts were used in the homopolymerizations and block copolymerizations of methyl methacrylate (MMA), functional methacrylates, and acrylonitrile (AN), yielding well-defined polymers. The catalysts could be separated (recovered) from the polymerization solutions by centrifugation, and the recycling of the recovered supported catalysts was attained multiple times without significant adverse effects to their catalytic activities. Figure 4.1 shows the studied alkyl iodide initiator, catalyst and monomers. The low toxicity, inexpensiveness, ease of preparation, and reusability of the studied supported catalysts are attractive features.

4.2. Results and Discussion

Alkyl Iodide Initiator

Catalyst

Monomers

Figure 4.1. Structures of alkyl iodide, catalysts, and monomers used in this work.

Polymerizations of MMA.

WA-30 was used in the polymerizations of MMA. Because the catalysts (amines) are fixed to the solid support (heterogeneous system), the overall concentrations of the catalysts (activator and deactivator) in the solution may need to be adjusted differently from those in the corresponding homogeneous system. As in ATRP, the activation of the dormant species to generate Polymer[•] is usually a chemically controlled process, and its overall rate would not largely be affected by the heterogeneous local concentration of the activator. Therefore, we may use a similar overall concentration of the activator to that in the homogeneous system. In contrast, the deactivation of Polymer[•] with a deactivator to generate the dormant species is nearly a diffusion controlled process, and its overall rate would largely be affected by the heterogeneity in the local concentration of the deactivator.³⁹ Therefore, we would need to use a much higher overall concentration of the deactivator than that in the homogeneous system so that Polymer[•] can sufficiently rapidly react with the deactivator. The required overall concentration of the deactivator is a key difference between the homogeneous and supported catalyst systems.

A deactivator in RCMP using amines is the amine...I[•] complex (Scheme 4.2a). Combination of the unstable amine...I[•] radical with another amine...I[•] radical then forms the I₂...amine complex (Scheme 4.2b).⁴⁰⁻⁴² I₂...amine is another deactivator (Scheme 4.2c), and its concentration can be increased by the direct addition of I₂ in the system. Therefore, in the present study, we optimized the deactivator concentration with the addition of I₂, as described below.

Scheme 4.2. (a) Reversible activation in RCMP, (b) Combination of $\bullet\text{I}\cdots\text{amine}$ and (c) Deactivation with $\text{I}_2\cdots\text{amine}$.

Table 4.1. Polymerizations of MMA.^a

Entry	Catalyst (wt% ^b)	[MMA] ₀ /[CP-I] ₀ / [I ₂] ₀ /[AIBN] ₀ (mM)	<i>T</i> (°C)	<i>t</i> (h)	Conv ^c (%)	<i>M</i> _n ^c (<i>M</i> _{n,theo} ^d)	<i>Đ</i> ^c
1	WA-30 (15 wt%, 290 mM)	8000/80/0/0	70	24	14	54000 (1400)	2.07
2	WA-30 (15 wt%, 290 mM)	8000/80/160/0	70	24	10	1600 (1000)	1.28
3	WA-30 (15 wt%, 290 mM)	8000/80/120/80	70	4	84	8800 (8400)	1.23
4	WA-30 (5 wt%, 100 mM)	8000/80/42/80	70	4	88	8600 (8800)	1.22
5	WA-30 (1 wt%, 20 mM)	8000/80/8.4/80	70	4	87	8900 (8700)	1.21
6	QWA-30 (1 wt%, 20 mM)	8000/80/8.4/80	70	4	95	8900 (9500)	1.24
C1	None	8000/80/0/0	70	24	0	-	-
C2	Homogeneous catalyst TEA ^e (290 mM)	8000/80/0/0	70	8	55	12000 (5500)	1.36
C3	None	8000/80/120/80	70	24	0	-	-

^a All reactions carried out with the addition of toluene (20 wt%). ^b wt% with respect to monomer. ^c PMMA-calibrated THF-GPC values. ^d Theoretical *M*_n calculated with [MMA]₀, [CP-I]₀, and monomer conversion. ^e Triethylamine.

Figure 4.2. Plots of (a) $\ln([M]_0/[M])$ vs t and (b) M_n and M_w/M_n vs monomer conversion for the MMA/CP-I/I₂/AIBN/catalyst systems (70 °C). The reaction conditions are given in Table 4.1. The symbols are indicated in the figure.

Table 4.1 (entries 1–6) and Figure 4.2 summarizes the polymerization results of MMA with WA-30. The solvent was toluene (20% toluene and 80% MMA). A solution of toluene, MMA (100 equiv.), CP-I (1 equiv.), and WA-30 (3.6 equiv., 15 wt% of MMA) was heated at 70 °C, and the polymerization reached 14% monomer conversion after 24 h (Table 4.1, entry 1). No polymerization took place without the addition of WA-30 (Table 4.1, entry C1), meaning that the polymerization was induced by WA-30 and CP-I to generate a propagating radical. In the early stages of polymerization (Figure 4.2 (filled circle)), the M_n value was much larger than the theoretical M_n ($M_{n,theo}$) value calculated from $[MMA]_0$, $[CP-I]_0$, and the monomer conversion, and the dispersity ($\mathcal{D}$) was large (>2.0). This result suggests that

insufficient amounts of the deactivator (I_2) were present in the early stage of polymerization, causing the addition of many monomers to $\text{Polymer}^\bullet$ in an uncontrolled manner.

For comparison, Table 4.1 (entry C2) and Figure 4.2 (open circle) show the polymerization with a homogeneous catalyst triethylamine (TEA) at the same activator concentration. TEA gave a 55% monomer conversion after 8 h, leading to a faster polymerization than WA-30 (Table 4.1 (entry 1) and Figure 4.2 (filled circle)). The $\bar{D}$ value was relatively small (1.23–1.36) from an early stage of polymerization, indicating that deactivation was sufficiently high. However the M_n value was still larger than the $M_{n,\text{theo}}$ value even in the homogeneous system. Typically, 40 mM of TEA is employed for RCMP. The amount used in this work (290 mM) is higher by more than 7 times, giving a much larger deviation of the M_n value from the $M_{n,\text{theo}}$ value. This is because the excess amine shifts the equilibrium between Polymer-I and $\text{Polymer}^\bullet$ towards the right (Scheme 4.2a), and the addition of $\text{Polymer}^\bullet$ to many monomer units results in the observed deviation.

The addition of I_2 (Table 4.1 (entry 2) and Figure 4.2 (square)) resulted in the M_n values much closer to the $M_{n,\text{theo}}$ values, and also a reduction in $\bar{D}$ ($= 1.28$) from an early stage of polymerization, suggesting that the generated $\text{Polymer}^\bullet$ was deactivated sufficiently rapidly. In heterogeneous systems, larger overall amounts of the deactivators were required, as mentioned above. The amount of the added I_2 (55% to the activator ($= 160 \text{ mM}/290 \text{ mM}$)) was relatively large for the mentioned reason, and this also decreased the polymerization rate. After 24 h, the monomer conversion reached 10%. The addition of I_2 increases the concentration of the deactivator $I_2\cdots\text{amine}$ (Scheme 4.2c), which lowers the concentration of the propagating radical $[P^\bullet]$ in equation (4.1), where k_a and k_{da} are the rate constants of activation and deactivation respectively. The rate of the polymerization depends on $[P^\bullet]$, and is shown in equation (4.2), where R_p is the rate of polymerization, $[M]$ is the concentration of

monomer, k_p is the rate constant of propagation, and t is time. Therefore the addition of I_2 lowered the rate of polymerization.

$$[P^\bullet] = \frac{k_a}{k_{da}} \frac{[\text{Polymer-I}][\text{Amine}]}{[I_2 \cdots \text{Amine}]} \quad (4.1)$$

$$R_p = -\frac{d[M]}{dt} = k_p [P^\bullet] [M] \quad (4.2)$$

The slow polymerization was overcome by the addition of an azo initiator, *i.e.*, 2,2'-azobis(isobutyronitrile) (AIBN, 80 mM) (Table 4.1 (entry 3) and Figure 4.2 (triangle)). Azo initiators increase $[P^\bullet]$ and are often used to effectively increase the polymerization rate in other living radical polymerizations,⁴⁴ as shown in equation (4.2). The monomer conversion reached 84% in 4 h, and $\bar{D}$ was maintained at a low value of 1.23. The low $\bar{D}$ values were attained only in the presence of the supported catalyst. For comparison, no polymers were obtained when no catalyst was used (Table 4.1, entry C3). Without the catalyst, an excess of I_2 (deactivator) was present in the solution, inhibiting the polymerization.

We were also able to reduce the amount of catalyst from 15 wt% to 5 wt% and 1 wt% (Table 4.1, entries 4 and 5, respectively) with keeping a similar level of the dispersity control. The amount of I_2 used was correspondingly reduced at a constant concentration ratio of the catalyst and I_2 to prevent excessive deactivation of the polymerization. A monomer conversion of 87–88% was attained in 4 h with a $\bar{D}$ value of 1.21–1.22.

The surface of the catalyst was analyzed by SEM after the polymerization (Figure 4.3). The SEM images of WA-30 before and after the polymerization were similar, showing that the macroscopic structure of the resin virtually remained unchanged.

Figure 4.3. SEM images of (a) WA-30, (b) crushed WA-30 before the polymerization (with higher magnification) and (c) crushed WA-30 after the polymerization (with higher magnification). A carbon tape was used to adhere WA-30 particle for SEM analysis.

Synthesis of QWA-30.

The WA-30 catalyst was reacted with 1-iodohexane to quaternize the tertiary amino groups via the Menshutkin reaction, yielding quaternary ammonium iodide functionalized WA-30 particles (QWA-30) (Scheme 4.3). The amount of the quaternary ammonium iodide was estimated to be 2.5 mmol per gram of the obtained QWA-30 from the consumption of 1-iodohexane. The extent of the quaternization would have a gradient from the outermost surface to the inner core of the particle. X-ray photoelectron spectroscopy (XPS) (below) showed that at least the outer most surface (a few nanometers thick) of the particle was almost fully (~90%) quaternized and would work as a catalytic interface.

Scheme 4.3. Synthesis of QWA-30.

Surface Characterization of QWA-30.

X-ray photoelectron spectroscopy (XPS) is a useful technique to analyze the elemental composition of the surface of a material by measuring the energy of the electrons that escape from atoms upon X-ray irradiation. The XPS spectra of the original WA-30 and quaternized QWA-30 particles are shown in Figure 4.4. After the quaternization (Figure 4.4b), the iodide 3d electrons (629 and 618 eV) newly appeared and the nitrogen 1s electron signal shifted from 399 eV (uncharged nitrogen atom (Figure 4.4a)) to 402 eV (positively charged nitrogen atom N^+), confirming the preparation of the quaternized QWA-30 particles.⁴³

Figure 4.4. XPS spectra of (a) WA-30 and (b) QWA-30.

Iodide anions are also efficient RCMP catalysts as previously mentioned. In the case of iodide catalysts, the deactivator is $A^+I_2^{\bullet-}$ (Scheme 4.4a). Two unstable $A^+I_2^{\bullet-}$ radicals can undergo disproportionation into A^+I^- (mono-iodide) and $A^+I_3^-$ (tri-iodide) (Scheme 4.4b).³⁰ $A^+I_3^-$ is another deactivator (Scheme 4.4c). The concentration of the $A^+I_3^-$ deactivator can be increased by the addition of I_2 in the system through a reaction of the activator A^+I^- and I_2 for generating $A^+I_3^-$ (Scheme 4.4d). The polymerization of MMA was successful using the synthesized QWA-30 (Table 4.1, entry 6), yielding a PMMA with $M_n = 8900$ and $\bar{D} = 1.24$. The polymerization rate using the quaternized QWA-30 catalysts were slightly higher than the unquaternized WA-30, with a 95% monomer conversion after 4 h.

Scheme 4.4. (a) Reversible Activation and Deactivation, (b) Disproportionation of $\text{A}^{\oplus} \text{I}_2^{\bullet\ominus}$, (c) Deactivation with $\text{A}^{\oplus} \text{I}_3^{\ominus}$, and (d) Combination of $\text{A}^{\oplus} \text{I}^{\ominus}$ and I_2 in RCMP.

Polymerizations with Recycled Catalysts.

After the polymerizations with WA-30 and QWA-30 catalysts, the color of the catalysts turned to dark brown (Figures 4.5c and 4.5d) as a result of the adsorption of I_2 onto the catalysts by halogen bonding (Scheme 4.5). The I_2 remained strongly bound to the catalysts even after washing in THF. Hence we posited that the catalysts might be recycled in subsequent polymerizations without further addition of I_2 (as demonstrated below).

Scheme 4.5. Interaction of (a) amines NR_3 and (b) quaternary ammonium iodides $\text{NR}_4^+ \text{I}^-$ with I_2 via halogen bonding.

The catalysts WA-30 and QWA-30 were recovered from the polymerization of MMA (Table 4.1 (entries 5 and 6, respectively)), and used for subsequent polymerization cycles. I_2 was added only in the first polymerization cycle, and no additional I_2 was added in the second and subsequent cycles. The polymerization time in all cycles was 4 h. The brown color did not significantly become lighter in the subsequent runs, qualitatively suggesting insignificant loss of I_2 or I_3^- in the catalysts. As Figures 4.5a and 4.5b show, the monomer conversion (88%–99%), M_n value (8900–9700), and D value (1.20–1.42) were similar in the five runs for WA-30 and ten runs for QWA-30, demonstrating the good recyclability of both catalysts. The recyclability is attractive for the reduction in the chemical waste. Between the two catalysts, the quaternized resin QWA-30 more consistently achieved similar polymerizations, with lower D (1.20–1.31) over the 10 cycles compared to unquaternized WA-30 ($D = 1.21$ –1.42).

Figure 4.5. Polymerizations of MMA with the recycled use of (a) WA-30 and (b) QWA-30 catalysts. The reaction conditions are given in entries 5 and 6 in Table 4.1, respectively. Images before polymerization, after the first polymerization run, after the fifth polymerization run and after the tenth polymerization run (QWA-30 only) for (c) WA-30 and (d) QWA-30 catalysts. The polymerization time in all cycles was 4 h.

Polymerizations of Other Monomers.

The polymerizations of other monomers were performed using QWA-30 as it achieved a higher polymerization rate and more consistent recyclability compared to WA-30. QWA-30 was amenable to several functional methacrylates and acrylonitrile (Table 4.2). The monomers include bulky methacrylates such as lauryl methacrylate (LMA) and 2-ethylhexyl methacrylate (EHMA), as well as a hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA) (Figure 4.1). The use of bulkier methacrylates such as LMA and EHMA (Table 4.2, entries 1 and 2) required a greater amount of AIBN due to their lower rate of polymerization, as well as an increase in solvent (toluene) to compensate for the poor solubility of AIBN in both monomers.

Table 4.2. Polymerizations of other monomers using QWA-30.

Entry	QWA-30 ^a	Monomer	In ^b	Solvent ^c	[Monomer] ₀ /[CP-I] ₀ / [I ₂] ₀ /[In ^b] ₀ (mM)	<i>T</i> (°C)	<i>t</i> (h)	Conv (%) ^d	<i>M</i> _n ^e (<i>M</i> _{n,theo} ^f)	<i>D</i> ^e
1	1 wt%, 51 mM	LMA	AIBN	Toluene	8000/80/21.6/160	70	4	96	18000 (24000)	1.26
2	1 wt%, 40 mM	EHMA	AIBN	Toluene	8000/80/16.8/200	70	4	98	12000 (19000)	1.23
3	1 wt%, 35 mM	BzMA	AIBN	Toluene	8000/80/14.8/80	70	4	99	13000 (18000)	1.21
4	2 wt%, 51 mM	HEMA	V65	Ethanol	8000/80/21.6/160	60	1	73	16000 (10000)	1.33
5	13 wt%, 140 mM	AN	AIBN	EC ^g	8000/40/60/60	75	5	72	11000 (7600)	1.39

^a wt% with respect to monomer. ^b Conventional radical initiator. ^c The addition of 40 wt% solvent (monomer/toluene = 6/4 (w/w)) for entries 1 and 2, the addition of 20 wt% solvent (monomer/toluene = 4/1 (w/w)) for entry 3, the addition of 20 wt% solvent (monomer/ethanol = 4/1 (w/w)) for entry 4 and 50 wt% solvent to monomer (monomer/EC = 1/1 (w/w)) for entry 5. ^d Monomer conversions determined from the ¹H NMR peak areas of the remaining monomers. ^e PMMA-calibrated THF-GPC values for entries 1–3. PMMA-calibrated DMF-GPC values for entry 4 and 5. ^f Theoretical *M*_n calculated with [Monomer]₀, [CP-I]₀, and monomer conversion. ^g Ethylene carbonate.

Block Copolymerization.

QWA-30 was used to prepare PMMA-iodide (PMMA-I) macroinitiators using the same conditions in Table 4.1, entry 6, but for shorter polymerization times. The polymerization was deliberately stopped at low molecular weights in order to retain the high chain-end fidelity of PMMA-I. The polymers were purified by reprecipitation twice to remove small molecules such as the monomer and other impurities. The obtained PMMA-I with $M_n = 4500$ and $D = 1.26$ after purification (as a macroinitiator for the block copolymerizations in Table 4.3, entries 1 and 2), for example, was analyzed with ^1H NMR (Figure 4.6) to estimate the iodide-chain-end fidelity.

The OCH_3 protons (a) of the monomer units appeared at 3.55–3.68 ppm. The downfield shifted signal at 3.72–3.76 ppm is assigned to the ω -terminal chain-end OCH_3 unit (a') adjacent to iodine.³⁰ From the peak area of a and a' , as well as the M_n value ($= 4500$) determined with GPC, the fraction of iodine chain end was calculated to be 99% (94–100% with experimental error), showing high chain-end fidelity of the PMMA macroinitiator.

Figure 4.6. ^1H NMR spectrum (CDCl_3) of PMMA-I ($M_n = 4500$ and $\bar{D} = 1.26$ after purification), synthesized using QWA-30.

The catalysts were separated (recovered) from the polymerization solutions by centrifugation and reused in the block polymerizations. Using the PMMA-I macroinitiator and the recycled QWA-30, the block polymerizations of LMA, BzMA and AN yielded low-dispersity block copolymers with $M_n = 17000$ and $\bar{D} \leq 1.45$ (Table 4.3). A large fraction of the PMMA-I macroinitiators extended to block copolymers (Figure 4.7). Through the GPC peak resolution, the block efficiency of PMMA-I was 75% and 95% in the LMA and BzMA block copolymerizations respectively. The results demonstrate the accessibility to hard-hard hydrophobic and hard-soft hydrophobic block copolymers, as well as a block copolymer containing a different family of monomer.

Table 4.3. Block polymerizations with PMMA-I macroinitiator and QWA-30.

Entry	QWA-30	Monomer	Solvent ^a	[Monomer] ₀ /[PMMA-I] ^b ₀ /[AIBN] ₀ (mM)	<i>T</i> (°C)	<i>t</i> (h)	Conv (%) ^c	<i>M</i> _n ^d (<i>M</i> _{n,theo} ^e)	<i>D</i> ^d
1	1 wt%, 51 mM	LMA	Diglyme	8000/80/160	70	4	82	17000 (25000)	1.45
2	1 wt%, 35 mM	BzMA	Toluene	8000/80/80	70	4	99	17000 (22000)	1.23
3	13 wt%, 140 mM	AN	EC ^f	8000/40/60	75	4	90	17000 (14000)	1.42

^a The addition of 36 wt% diglyme (36wt% of diglyme and 64 wt% of monomer and PMMA-I)

for entry 1, 17 wt% toluene (17 wt% of toluene and 83 wt% of monomer and PMMA-I) for

entry 2 and 50 wt% EC (50 wt% EC and 50 wt% monomer and PMMA-I) for entry 3. ^b

PMMA-I (*M*_n = 4500 and *D* = 1.26) for entry 1 and 2 and (*M*_n = 4400 and *D* = 1.14) for entry

3. ^c Monomer conversions determined from the ¹H NMR peak areas of the remaining

monomers. ^d PMMA-calibrated THF-GPC values for entries 1 and 2. PMMA-calibrated

DMF-GPC value for entry 3. ^e Theoretical *M*_n calculated with [Monomer]₀, [PMMA-I]₀, and

monomer conversion. ^f Ethylene carbonate.

Figure 4.7. GPC chromatograms before (dashed lines) and after (solid lines) the block polymerizations (Table 4.3).

4.3. Conclusions

Organic resin particle-supported catalysts were developed for RCMP. The supported catalysts afforded well-defined homopolymers and block copolymers of MMA, functional methacrylates and AN with small $\bar{D}$ values. The supported catalysts were separated from the polymerization solution in simple manners (with centrifugation or filtration) and re-used in further polymerizations for up to five times without apparent decrease in the catalytic efficiency. The facile preparation of the supported catalysts, the broad monomer scope, and the feasibility of the catalyst reuse and recycle are attractive features.

4.4. Experimental Section

Materials.

Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), 2-hydroxyethyl methacrylate (HEMA) (>95%, TCI), lauryl methacrylate (LMA) (>97%, TCI), 2-ethylhexyl methacrylate (EHMA) (99%, TCI), benzyl methacrylate (BzMA) (>98%, TCI), acrylonitrile (AN) (>99%, Kanto Chemical, Japan), 2-iodo-2-methylpropionitrile (CP-I) (>95%, TCI), triethylamine (TEA) (>99%, TCI), iodine (I₂) (>98%, TCI), 1-iodohexane (≥98%, Sigma-Aldrich), toluene (>99%, J. T. Baker, USA), ethylene carbonate (EC) (>99%, TCI), diethylene glycol dimethyl ether (diglyme) (>99.0%, TCI), 2,2'-azobis(2-methylpropionitrile) (AIBN) (98%, Wako Pure Chemical Industries, Japan), 2,2'-azobis(2,4-dimethylvaleronitrile) (V65) (95%, Wako), tetrahydrofuran (THF) (>99.5%, Kanto Chemical), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto Chemical), ethanol (≥99.8%, Fisher Scientific, USA) and hexane (>99%, International Scientific, Singapore) were used as received. Poly(*N,N*-dimethylaminomethyl styrene) porous crosslinked resin (DIAION WA-30, diameter = 300–900 μm) was provided by Mitsubishi Chemical Co., Ltd. (Japan).

NMR.

The NMR spectra were recorded on a Bruker (Germany) BBFO spectrometer (400 MHz) at ambient temperature. CDCl₃, DMSO-*d*₆, methanol-*d*₄ or acetone-*d*₆ (Cambridge Isotope Laboratories, USA), were used as a solvent, and the chemical shift was calibrated using the residual undeuterated solvent or tetramethylsilane (TMS) as the internal standard.

GPC.

The gel permeation chromatography (GPC) analysis using THF as an eluent was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan). The Shimadzu LC-2030C Plus GPC was equipped with both a Shodex KF-804L mixed gel

column (300×8.0 mm; bead size = $7\ \mu\text{m}$; pore size = $20\text{--}200\ \text{\AA}$) and a Shodex LF-804 mixed gel column (300×8.0 mm; bead size = $6\ \mu\text{m}$; pore size = $3000\ \text{\AA}$). The eluent was tetrahydrofuran (THF) at a flow rate of $0.7\ \text{mL/min}$. Sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s.

The GPC analysis using DMF as an eluent was performed on a Shimadzu LC-2030C Plus liquid chromatograph with a Shodex KF-802 (300×8.0 mm; bead size = $6\ \mu\text{m}$; pore size = $150\ \text{\AA}$) and two Shodex LF-804L mixed gel columns (300×8.0 mm; bead size = $7\ \mu\text{m}$; pore size = $1500\ \text{\AA}$) at a flow rate of $0.34\ \text{mL/min}$ ($40\ ^\circ\text{C}$). The DMF eluent included LiBr ($10\ \text{mM}$). Sample detection was conducted using a Shodex differential refractometer RI-101. The column system was calibrated with standard PMMA)s.

Centrifugation.

The centrifugation of the catalysts was carried out with Sorvall ST8 centrifuge (Thermo scientific, USA) at $8000\ \text{rpm}$ for $5\ \text{min}$.

XPS.

The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany).

SEM.

The scanning electron microscopy (SEM) analysis was performed with a JEOL-JSM-7600F microscope (JEOL, Japan).

Preparation of Resin-Supported Catalyst QWA-30.

WA-30 particles (2.0 g), 1-iodohexane (1.21 g, 5.71 mmol), and tetrahydrofuran (THF) (8 mL) were placed in a round bottom flask and refluxed for 16 h. The consumption of 1-iodohexane was determined with ^1H NMR (CDCl_3). Benzene was added as an internal standard to a known concentration and used to quantify the remaining (unreacted) 1-iodohexane. The quaternized resin QWA-30 was collected with a filter paper, washed with THF repeatedly to remove the unreacted 1-iodohexane, and dried under vacuum.

General Polymerization Procedure.

In a typical run, a mixture of a monomer (1.5 g), a supported catalyst, CP-I, an azo initiator (if used), iodine, and a solvent (if used) was heated in a Schlenk flask at the desired temperature under argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF or DMF to a known concentration and analyzed with GPC.

Polymerization of MMA with Recycled Catalysts.

A reaction mixture of MMA (1.4 g, 14 mmol), CP-I (28 mg, 0.14 mmol), WA-30 or QWA-30 catalyst (14 mg, 1 wt% of MMA), I_2 (3.7 mg, 0.014 mmol), AIBN (23 mg, 0.14 mmol), and toluene (0.35 g) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring for 4 h. The mixture was cooled to room temperature and analyzed with GPC. The reaction mixture was diluted with THF (10 mL), and the WA-30 or QWA-30 catalyst was separated from the reaction mixture by centrifugation. The WA-30 or QWA-30 catalyst was washed with THF (with stirring for 5 min) three times, dried in vacuo, and used in the subsequent polymerizations. Subsequent polymerizations were carried out using the same reaction conditions, without the addition of I_2 .

Synthesis of PMMA–I Macroinitiator Using Resin-Supported QWA-30 Catalyst.

A mixture of MMA (0.7 g, 7 mmol), CP–I (13.7 mg, 0.07 mmol), QWA-30 catalyst (7.0 mg, 1 wt% of MMA), I₂ (1.87 mg, 0.0074 mmol), AIBN (11.5 mg, 0.07 mmol), and toluene (0.175 g) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 1 h, the mixture was cooled to room temperature and diluted with THF (8 mL). The QWA-30 catalyst was separated from the reaction mixture by centrifugation. The polymer was reprecipitated from hexane (100 mL) twice to completely remove the monomer and dried in vacuo to give PMMA–I macroinitiator (monomer conversion = 37%, M_n = 4500 and $\bar{D}$ = 1.26 after purification) as a pale yellow solid. The separated (recovered) QWA-30 catalyst was washed with THF (with stirring for 5 min) three times, collected by centrifugation, and dried in vacuo for the use in the subsequent block polymerization.

Block Copolymerizations.

In a typical run using benzyl methacrylate (BzMA) as an example, BzMA (0.7 g, 4 mmol), PMMA–I macroinitiator (0.172 g, 0.04 mmol), recycled QWA-30 (0.007 g, 1 wt% of BzMA), AIBN (6.6 mg, 0.04 mmol), and toluene (0.176 g) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring for 4 h. After cooling to room temperature, an aliquot (0.1 mL) of the solution was analyzed with ¹H NMR to determine the monomer conversion. The rest of the solution was diluted with THF (5 mL). The polymer was reprecipitated from hexane (50 mL), dried in vacuo, and analyzed with GPC.

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Chapter 5. Chain end Functionalization of Polymer-Iodides to Vinyl-Iodide-Terminated Polymers.

Abstract

The facile chain-end transformation of polymers with a terminal iodide group (Polymer-I) was successfully carried out via an organocatalyzed radical addition to phenylacetylene to obtain polymers bearing terminal vinyl iodide groups in high yields. This transformation reaction was also applicable to other functional alkynes, yielding vinyl-iodide-terminated polymers with additional functionality. The polymers studied in this reaction were poly(butyl acrylate) and poly(2-methoxyethyl acrylate) and were synthesized via reversible complexation mediated polymerization (RCMP). The chain-end transformations were comprehensively analyzed via matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). This reaction is attractive for being completely metal-free and simple to perform. The vinyl-iodide-terminated polymers are promising precursors for developing a range of functional polymer materials through transition-metal-catalyzed cross-coupling reactions.

5.1. Introduction

The continued development of RCMP and the extension of its applications are the aims of this Ph.D. thesis. In Chapter 3, we selectively obtained linear and branched copolymers by changing the polymerization temperature, demonstrating control over the polymer architecture. Inspired by this successful result, we targeted chain-end functionalized polymers. In Chapters 2–4, polymers bearing chain-end iodide groups (polymer-iodide) were obtained. Our group has previously conducted the chain-end transformations of polymer-iodide. The

iodide group was successfully converted to other groups such as Si(OEt)₃, SH, OH and N₃, yielding chain-end functionalized polymers.¹⁻³ The transformation was also applied to polymer brushes on solid surfaces, providing patterned polymer brushes with different chain ends.⁴⁻⁵

Vinyl iodides are useful precursors for transition-metal-catalyzed coupling reactions to form vinyl sulfides⁶, vinyl amides⁷, vinyl azides⁸ as well as decarboxylative coupling with carboxylic acids, forming new sp³-sp² bonds.⁹ In polymer chemistry, vinyl iodides have been incorporated into polymer backbones. The solid-phase polymerization of diiodobutadiyne (co-crystallized with a Lewis base via halogen bonding) resulted in the spontaneous formation of conjugated poly(diiiododiacetylene).¹⁰ Another example is the step-growth iodo-yne polymerizations of 1,9-decadiyne and diiodoperfluorohexane, yielding semifluorinated polymers that contained vinyl iodide functionalities on the main chain. The vinyl iodide groups were subsequently modified via cross-coupling reactions to introduce other functionalities.¹¹ However, there has been no report for the synthesis of polymers containing chain-end vinyl iodide groups.

Alkyl iodides (R₁-I) can react with alkynes (CH≡C-R₂) to yield vinyl iodides (R₁-CH=CI-R₂) via iodine atom transfer through a radical addition step (Scheme 5.1a) followed by iodine abstraction by the vinyl radical (Scheme 5.1b).¹²

Scheme 5.1. (a) Alkyl radical addition to alkyne forming the vinyl radical and (b) iodine abstraction by the vinyl radical to form vinyl iodide.

Reversible complexation mediated polymerization (RCMP) employs polymer-iodide (Polymer-I) as the dormant species and a catalyst such as iodide anion (I^-).¹³ The organic salt tetrabutylammonium iodide (BNI) is typically used as a source of I^- . Polymer-I and I^- forms a halogen-bonding complex ($\text{Polymer-I}\cdots\text{I}^-$) that can reversibly generate the propagating radical ($\text{Polymer}^\bullet$) and $\text{I}_2^{\bullet-}$ (Scheme 5.2).

Scheme 5.2. Reversible activation in RCMP.

In this chapter, we report the chain-end transformation of polyacrylate-iodides via the organocatalyzed radical addition to alkynes, obtaining vinyl-iodide-terminated polyacrylates in a facile manner. Mechanistically, Polymer-I and the RCMP catalyst generate $\text{Polymer}^\bullet$ and $\text{I}^\bullet$ (Scheme 5.3a). $\text{Polymer}^\bullet$ adds to an alkyne to form the vinyl radical species Polymer-vinyl $^\bullet$ (Scheme 5.3b). Polymer-vinyl $^\bullet$ is subsequently capped by $\text{I}^\bullet$ to give the chain-end vinyl-

iodide polymer (Scheme 5.3c). Such polymers are promising precursors for cross-coupling reactions to develop a range of functional polymers.

Scheme 5.3. Formation of vinyl-iodide-terminated polymers from the organocatalyzed radical addition to alkynes.

5.2. Results and Discussion

Preparation and Characterization of Polymer-I.

Poly(butyl acrylate) iodide (PBA-I) was synthesized via RCMP by heating a mixture of butyl acrylate (monomer (100 equiv.)), 2-iodo-2-methylpropionitrile (CP-I) (alkyl iodide initiator (1 equiv.)), and tetrabutylammonium iodide (BNI) (catalyst (4 equiv.)) at 110 °C for 6 h. The monomer conversion was 26% (obtained via ^1H NMR). The polymerization was deliberately stopped at low molecular weights to retain the high fidelity of the PBA-I chain-end. The synthesized PBA-I was subsequently purified by reprecipitation twice to remove the monomer, the catalyst and other impurities. The obtained PBA-I ($M_n = 4000$ and dispersity (D) = 1.19 after purification) was analyzed with ^1H NMR (Figure 5.1) to estimate the iodide-chain-end fidelity. The M_n and D values were determined by a gel permeation chromatography (GPC), calibrated with poly(methyl methacrylate) standards.

Figure 5.1. ^1H NMR spectrum (CD_3CN) of PBA-I.

The protons belonging to OCH_2 (d) of the side chains were observed at 3.75–4.2 ppm. The downfield shifted resonance of the ω -terminal CH unit (c') neighboring iodine appeared at 4.3–4.4 ppm. By comparing the area under the resonances c' and d , as well as the M_n value (= 4000) determined with GPC, the percentage of iodide on the polymer chain-end was calculated as 98% (93–100% with experimental error), indicating high chain-end fidelity of PBA-I. As the M_n value (= 4000) was determined by a PMMA-calibrated GPC, it is not the absolute molecular weight, and thus the calculated iodide-chain-end fidelity is viewed as an estimate.

We also prepared a poly(2-methoxyethyl acrylate) iodide (PMEA-I) using the same reaction conditions as that of PBA-I. The monomer conversion obtained was 31% (obtained

via ^1H NMR). The crude mixture was purified using a preparative GPC followed by reprecipitation into hexane to remove the monomer, the catalyst and other impurities to obtain PMEAI ($M_n = 6200$ and $D = 1.25$ after purification).

The purified PMEAI was analyzed with ^1H NMR (Figure 5.2). The ester OCH_2 protons of the side chains (c) were assigned to 4.0–4.3 ppm. The ω -terminal CH unit (b') adjacent to iodine was assigned to the downfield shifted resonance at 4.4–4.5 ppm. From the peak area of c and b' , as well as the M_n value ($= 6200$) determined with GPC, the percentage of iodide on the polymer chain-end was calculated as 88% (83–93% with experimental error), indicating a high chain-end fidelity of PMEAI. Again, the calculated iodide-chain-end fidelity is viewed as an estimate.

Figure 5.2. ^1H NMR spectrum (CDCl_3) of PMEA-I.

The purified PBA-I and PMEA-I were analyzed with matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The theoretical mass of the polymers are calculated as follows:

$$68.05 + 128.0832 \times n + Y + 22.99 \text{ (for PBA-I)} \quad (1)$$

$$68.05 + 130.0625 \times n + Y + 22.99 \text{ (for PMEA-I)} \quad (2)$$

Where 68.05 is the mass of the initiating CP terminal group, 128.0832 is the mass of the BA monomer repeat unit, 130.0625 is the mass of the MEA monomer repeat unit and 22.99 is the mass of the additive cation Na^+ . The degree of polymerization is referred to as n and Y is the mass of the terminal group. The labeled mass numbers refer to the leftmost peak of each species, which correspond to polymers without ^{13}C atoms (containing only ^{12}C atoms).

The MALDI-TOF MS spectra of PBA-I is shown in figure 5.3a. A main series of peaks appeared at 2523.58, for example, with regular intervals of 128.09 (BA unit) (Figure 5.3a). The experimental isotope distribution well matches the theoretical distribution of PBA-I (Figure 5.3b), and is consistent with the expected structure.¹ Three series of minor peaks appeared at 2537.85, 2541.82 and 2595.81. These species are believed to have been formed in the MALDI-TOF MS analysis, with the species at 2595.81 previously being identified as PBA with a lactone ring end group (PBA-Lac) (theoretical mass = 2595.64).^{1,14} The species at 2537.85 and 2541.82 were previously unidentified in literature. These species are now assigned to PBA macromonomer (PBA-ene) (theoretical mass = 2537.64) and PBA with a hydroxyl chain end (PBA-OH) (theoretical mass = 2541.63). The PBA macromonomer could be generated via a backbiting reaction during the analysis, forming a mid-chain radical followed by β -scission.¹⁵ The ¹H NMR analysis of PBA-I did not detect any unsaturated end-groups, thus the macromonomer would most likely be formed during the MALDI-TOF MS analysis. The PBA-OH species would be formed via the reaction between PBA-I and a water molecule (H₂O) during the MALDI-TOF MS analysis. No product of radical-radical termination was observed (theoretical mass = 2592.61). Because of the radical nature of the polymerization, termination did occur. The result indicates that the terminated polymer chains were in negligibly small amounts in this particular case.

The MALDI-TOF MS spectra of PMEA-I is shown in Figure 5.3c. A main series of peaks at 4120.14, for example, with regular intervals of 130.09 (MEA unit) were observed and corresponds to PMEA-I (theoretical mass = 4119.83). Four series of minor peaks also appeared at 4136.31, 4140.36, 4158.30 and 4194.33, which were formed during the MALDI-TOF MS analysis in a manner similar to that of PBA-I. The first species at 4136.31 is assigned to PMEA macromonomer (PMEA-ene) (theoretical mass = 4136.00), the second species at 4140.36 is assigned to PMEA with a hydroxyl chain end (PMEA-OH) (theoretical

mass = 4139.99) and the fourth species at 4194.33 is assigned to PMEA with a lactone ring chain end (PMEA–Lac) (theoretical mass = 4194.00). The third species at 4158.30 remains unclear.

(a) PBA–I

(b) Isotope distribution of PBA–I

Figure 5.3 (continued in next page). MALDI-TOF MS spectra of (a) PBA–I, (b) experimental and theoretical isotope distributions and (c) PMEA–I.

(c) PMEAI

Figure 5.3 (continued from previous page). MALDI-TOF MS spectra of (a) PBA-I, (b) experimental and theoretical isotope distributions and (c) PMEAI-I.

Chain-end Transformation of Polymer-I Using Phenylacetylene.

The transformation of the PBA-I chain-end using phenylacetylene (PA) was studied. A mixture of PBA-I (1 equiv.), PA (10 equiv.) and BNI (1 equiv.) in diglyme as a solvent (50 wt%) was heated for 6 h at 110 °C (Table 5.1, entry 1). Scheme 5.3 (general scheme) and Scheme 5.4 (specific scheme to PBA and PA) shows the supposed mechanism. PBA-I reacts with BNI, generating PBA[•] and I[•] (Scheme 5.4a). PBA[•] then undergoes radical addition of PA to form PBA-PA[•] (Scheme 5.4b). PBA-PA[•] is subsequently capped by I[•], forming the vinyl iodide species PBA-PA-I (Scheme 5.4c). Because the bond strength of vinyl iodides are

much stronger,¹⁶ PBA-PA-I and BNI would hardly react to generate the vinyl radical PBA-PA[•].

Table 5.1. Reactions of Polymer-I with phenylacetylene (PA) at 110 °C.

Entry	Polymer-I ^a	[PA] ₀ /[Polymer-I] ₀ /[BNI] ₀	<i>t</i> (h)	Solvent ^b	Polymer-I Remaining ^c	Polymer-(PA) _n -I ^c				
						n = 1	2	3	4	5
1	PBA-I	10 / 1 / 1	6	50 wt%	8%	84%	7%	-	-	-
2	PBA-I	30 / 1 / 1	6	50 wt%	7%	79%	13%	-	-	-
3	PBA-I	60 / 1 / 1	6	30 wt%	9%	72%	19%	-	-	-
4	PBA-I	100 / 1 / 1	6	None	11%	47%	19%	7%	9%	6%
5	PBA-I	10 / 1 / 2	14	50 wt%	5%	86%	9%	-	-	-
6	PMEA-I	10 / 1 / 2	14	50 wt%	0%	88% ^d	-	-	-	-

^a PBA-I (*M_n* = 4000, *D* = 1.19), PMEA-I (*M_n* = 6200, *D* = 1.25). ^b Diglyme was used as the solvent. ^c Calculated based on the peak intensity ratio in MALDI-TOF MS. ^d 12% formed a currently unidentified product.

Scheme 5.4. Mechanisms in the formation of PBA-PA-I from PBA-I.

The reaction mixture was purified using a preparative GPC to remove the remaining PA, catalyst, and other impurities. The mass yield of the obtained polymer was 88%, meaning that most of the polymer was collected after the purification. Analysis of the obtained polymer was performed by MALDI-TOF MS. In this analysis, we compared the intensity ratio of the peaks in the MALDI-TOF spectra to estimate the ratio of the amount of the species present in the product. The intensity ratio may not be exactly the same as that of the amount of the species but would be a good estimate. We were interested only in the conversion from PBA-I to the PBA-vinyl iodides. Therefore PBA-ene, PBA-OH and PBA-Lac signals were excluded from the calculations. We also assume that the molecular weight of PBA-I does not significantly affect the transformation reaction.

Figure 5.4a shows the MALDI-TOF MS spectra after the reaction. A series of major peaks appeared at 2497.57, as well as a series of minor peaks at 2599.79. The peak at 2497.57 closely matches the theoretical mass (2497.41) of the desired vinyl iodide chain-end species (PBA-PA₁-I) (Figure 5.4b). Another possible structure for the peak at 2497.57 is a species containing six repeating PA units capped with a terminal hydrogen atom (theoretical mass = 2497.50) (PBA-PA₆-H) (Figure 5.4b). The experimental isotope distributions were compared against the theoretical distributions for the two possible structures PBA-PA₁-I and PBA-PA₆-H (Figure 5.4b). The experimental isotope distribution closely matches that of PBA-PA₁-I rather than PBA-PA₆-H, supporting the formation of the vinyl-iodide chain-end species. The peak at 2599.79 was attributed to a PBA containing two PA units capped with iodide (PBA-PA₂-I) (theoretical mass = 2599.46) (Figure 5.4a). Based on the peak intensity ratios, 84% of PBA-I was successfully transformed into PBA-PA₁-I, 7% of PBA-I was transformed into PBA-PA₂-I and 8% of PBA-I remained unreacted (Table 5.1, entry 1). From the polymer mass yield of 88% obtained after purification, the mass yield for PBA-PA₁-I and PBA-PA₂-I would be 74% and 6% respectively.

(a) Reaction of PBA-I with 10 equiv. PA (110 °C, 6 h) (Table 5.1, entry 1)

(b) Isotope distributions

Figure 5.4. MALDI-TOF MS spectra for (a) the reaction of PBA-I with PA (Table 5.1, entry 1) and (b) the isotope distributions of experimental and theoretical structures.

We increased the amount of PA to 30, 60 and 100 equivalent (Table 5.1, entries 2, 3 and 4 respectively). Based on the intensity of the peak ratios, more than 89% of PBA-I reacted with PA and the amount of PBA-I unreacted did not change significantly by the amount of PA (7–11%). Instead, as the concentration of PA increased to 30 and 60 equivalent (Table 5.1, entries 2 and 3), a greater proportion of PBA-PA₂-I was observed. At 100 equivalent of PA used (Table 5.1, entry 4), we also observed PBA containing 3–5 PA units capped with iodide (PBA-PA₃-I, PBA-PA₄-I and PBA-PA₅-I, theoretical mass = 2573.42,

2547.39 and 2521.35 respectively) in the MALDI-TOF spectra (Figure 5.5). The addition of multiple PA units likely occurred before PBA-PA^{*} was capped with the iodide radical I^{*} (Scheme 5.4c). Thus a higher concentration of PA allows for more PA units to be added.

Figure 5.5. MALDI-TOF MS spectra for the reaction of PBA-I and 100 equivalent of PA (Table 5.1, entry 4).

We increased the reaction time and amount of catalyst (BNI) used in the system with 10 equivalent of PA (Table 5.1, entry 5) to completely consume PBA-I. However, still 5% of PBA-I remained unreacted.

The chain-end conversion of PMEA-I was also studied. We heated a mixture of PMEA-I (1 equiv.), PA (10 equiv.) and BNI (2 equiv.) in diglyme as a solvent (50 wt%) for 14 h at 110 °C (Table 5.1, entry 6). The MALDI-TOF MS spectra of PMEA-I after the

reaction is shown in Figure 5.6. No PMEA-I remained and only one series of major peaks at 4222.09 was observed, corresponding to PMEA-PA₁-I. Based on the peak intensity ratios, 88% of PMEA-I was converted to the desired PMEA-PA₁-I. The rest (12%) formed an unidentified species at 4123.18. The peaks at 4140.21 and 4194.20 correspond to PMEA-OH and PMEA-Lac, respectively, which were formed during the MALDI-TOF MS analysis as mentioned above and thus excluded from the calculations.

Figure 5.6. MALDI-TOF MS spectra after the reaction of PMEA-I and PA (Table 5.1, entry 6).

Instead of polyacrylate-iodides (PBA-I and PMEA-I), we also preliminarily tested a polymethacrylate-iodide (PMMA-I) and polystyrene-iodide (PSt-I). However, we did not observe the expected vinyl iodide chain-end polymers. This would most probably be because the generated PMMA[•] and PSt[•] radicals are too stable to react with PA.

Chain-end Transformation of PBA-I Using Other Functional Alkynes.

Instead of PA, the end-group transformation reaction of PBA-I was studied using alkynes containing other functional groups, i.e., 4-ethynylbenzyl alcohol (EBA) with an OH group and 4-ethynyl-trifluorotoluene (TFT) with a super-hydrophobic nature (Table 5.2, entries 1 and 2 respectively). After the reaction of PBA-I with EBA at 110 °C for 14 h (Table 5.2, entry 1), the polymers were analyzed by MALDI-TOF MS (Figure 5.7a). PBA-I was exclusively transformed into the desired PBA-EBA₁-I (92%) (Figure 5.7a), with no other products, and 8% of PBA-I remained. The peaks at 2537.88, 2541.87 and 2595.88 correspond to PBA-ene, PBA-OH, and PBA-Lac, respectively, which were generated during the MALDI-TOF MS analysis, as discussed above. The reaction of PBA-I with TFT at 110 °C (Table 5.2, entry 2 and Figure 5.7b) was also successful. PBA-I was converted to the desired PBA-TFT₁-I (84%) as well as PBA-TFT₂-I (9%), and 7% of PBA-I remained. Therefore, we obtained the vinyl-iodide chain-end PBAs bearing hydroxyl and trifluoromethyl functionalities.

Table 5.2. Reactions of PBA-I with other alkynes at 110 °C.

Entry	Alkyne (X)	[Alkyne] ₀ /[PBA-I] ₀ /[BNI] ₀	<i>t</i> (h)	Solvent ^a	PBA-I	PBA-(X) _n -I ^b	
					remaining ^b	n = 1	2
1	4-ethynylbenzyl	10 / 1 / 2	14	50 wt%	8%	92%	-
	alcohol						
2	4-ethynyltrifluorotoluene	10 / 1 / 2	14	50 wt%	7%	84%	9%

^a Diglyme was used as the solvent. ^b Calculated based on the peak intensity ratio in MALDI-TOF MS.

(a) 10 equiv. of EBA (110 °C, 14 h) (Table 5.2, entry 1)

(b) 10 equiv. of TFT (110 °C, 14 h) (Table 5.2, entry 2)

Figure 5.7. MALDI-TOF MS spectra after the reaction of PBA-I with (a) EBA and (b) TFT (Table 5.2, entries 1 and 2).

5.3. Conclusions

The chain-ends of PBA-I and PMEA-I were transformed via the organocatalyzed radical addition to PA, yielding vinyl-iodide-terminated polymers. The addition of multiple PA units was also observed as the concentration of PA increased. The chain-end transformation reaction was also amenable to functional alkynes, giving vinyl-iodide chain-end PBAs bearing hydroxyl group and trifluoromethyl functionalities. The reaction is easy to

perform, and free from metals. The obtained vinyl-iodide chain-end polymers are promising precursors for cross-coupling reactions to develop functional polymer materials.

5.4. Experimental Section

Materials.

Butyl acrylate (BA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), 2-methoxyethyl acrylate (MEA) (>98%, TCI), (2-iodo-2-methylpropionitrile (CP-I) (>95%, TCI), phenylacetylene (98%, Aldrich), 4-ethynylbenzyl alcohol (97%, Aldrich), 4-ethynyltrifluorotoluene (97%, Aldrich), diethylene glycol dimethyl ether (diglyme) (>99.0%, TCI), tetrahydrofuran (THF) (>99.5%, Kanto Chemical), methanol ($\geq$ 99.8%, VWR, USA), chloroform (>99%, VWR), hexane (>99%, International Scientific, Singapore), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>99%, Aldrich), tetrabutylammonium iodide (BNI) (>98%, TCI) and sodium trifluoroacetate (NaTFA) (>98%, TCI) were used as received.

NMR.

The ^1H NMR analysis was conducted with a Bruker (Germany) BBFO spectrometer (400 MHz) at room temperature. Acetonitrile- d_3 or CDCl_3 (Cambridge Isotope Laboratories, USA) were used as a solvent, and the chemical shift was calibrated using the residual undeuterated solvent or tetramethylsilane (TMS) as the internal standard.

MALDI-TOF MS.

The matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis was performed using a JMS-S3000 SpiralTOF (JEOL, Japan) at an accelerating potential of 20 kV in the positive spiral mode. The polymer solutions (polymer sample: 10 g/L in THF), matrix solution (DCTB: 60 g/L in THF), and cationization agent solution (NaTFA: 10 g/L in THF) were prepared. The polymer solutions, NaTFA solution and DCTB solution were mixed in a 1/1/2 ratio (v/v/v). The mixed solution was deposited on the MALDI plate spot and air-dried at ambient temperature.

GPC.

The gel permeation chromatography (GPC) analysis was performed using a Shimadzu LC-2030C Plus HPLC (Kyoto, Japan) that was equipped with both a Shodex KF-804L column (300×8.0 mm; bead size = $7\ \mu\text{m}$; pore size = $20\text{--}200\ \text{\AA}$) and a Shodex LF-804 column (300×8.0 mm; bead size = $6\ \mu\text{m}$; pore size = $3000\ \text{\AA}$). THF was used as the eluent at a flow rate of $0.7\ \text{mL/min}$. The GPC was calibrated with standard PMMA samples. A Shimadzu refractive index detector RID-20A was used for sample detection.

Synthesis of PBA–I Macroinitiator.

BA (20 g, 156 mmol), CP–I (304 mg, 1.56 mmol) and BNI (2.31 g, 6.24 mmol) was added into a flask capped with a 3-way stopcock. The mixture was bubbled for 10 min with argon, then heated at $110\ ^\circ\text{C}$ in an oil bath with magnetic stirring under an inert atmosphere for 6 h. THF (10 mL) was added to the polymerization mixture and the polymer was precipitated from a methanol/water mixture (7/3 v/v) (200 mL) twice to completely remove the monomer and dried under vacuum overnight to give PBA–I macroinitiator (monomer conversion = 26%, $M_n = 4000$ and $D = 1.19$ after purification) as a pale yellow viscous liquid.

Synthesis of PMEA–I Macroinitiator.

MEA (3 g, 23 mmol), CP–I (45 mg, 0.23 mmol) and BNI (341 mg, 0.92 mmol) was added to a flask capped with a 3-way stopcock and bubbled with argon for 10 min. The mixture was then heated at $110\ ^\circ\text{C}$ for 6 h in an oil bath with magnetic stirring under an inert atmosphere. The polymerization mixture was dissolved in chloroform (10 mL) and the polymer was purified using a preparative GPC and subsequently precipitated into hexane to completely remove the monomer. The polymer was then dried under vacuum to give PMEA–I macroinitiator (monomer conversion = 31%, $M_n = 6200$ and $D = 1.25$ after purification) as a dark brown viscous liquid.

General Reaction Procedure.

In a typical run, a mixture of the alkyne, PBA-I or PMEAI, BNI, and diglyme (if used) was added to a flask capped with a 3-way stopcock and bubbled with argon for 10 min. The mixture was then heated at 110 °C with magnetic stirring under an inert atmosphere for the desired time. The mixture was cooled to room temperature, then chloroform (10 mL) was added. The polymers were purified by preparative GPC and analyzed via MALDI-TOF MS.

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Chapter 6. Conclusions

The motivation of this Ph.D. thesis was the further development of RCMP. This work focused on extending the applications of RCMP, improving its ease of use and its practical application to industry. In Chapter 2, PMMA–PBA block copolymers were synthesized from the macroinitiator precursor PMMA–Y via organocatalyzed LRP using BNI as the catalyst. PMMA–Y was first transformed into PMMA–I via AFCT followed by subsequent block copolymerization with BA monomer in one-pot. This method is advantageous due to the stability of PMMA–Y, and significantly eases the operation compared to the use of isolated PMMA–I macroinitiator. Further investigation of PMMA–Y was carried out in Chapter 3, where the temperature dependence of AFCT and propagation of PMMA–Y in the styrene polymerization was revealed via kinetic studies. The significant finding is the predominant occurrence of fragmentation at 120 °C which allows the formation of PMMA–PSt block copolymers controlled via ITP. Conversely, by reducing the temperature to 40 °C, mainly branched polymers can be obtained. AFCT of PMMA–Y was also predominant with AN, MEA and PEGA. For those monomers, block copolymers were obtained via RCMP using BNI as a catalyst. The RCMP of BA monomer was also performed on PMMA–Y with a higher molecular weight to synthesize PMMA–PBA block copolymers with a longer PMMA segment. For all the studied monomers in Chapter 2 and 3, the inexpensive AIBN/I₂ method to form the alkyl iodide initiator in situ was also effective, which is an attractive alternative compared to the use of isolated CP–I.

In Chapters 2 and 3, BNI was used as the catalyst for homogeneous RCMP. The removal of the catalyst after the polymerization was one difficulty that was encountered. Chapter 4 reported the development of resin-supported catalysts containing amine and quaternary ammonium iodide moieties for heterogeneous RCMP. The supported catalysts were easily prepared and produced low dispersity homopolymers and block copolymers for

several methacrylates and AN monomers. The supported catalysts could be easily removed from the polymerization mixture via simple filtration or centrifugation, which significantly eases the catalyst removal process compared to homogeneous catalysts such as BNI. Furthermore, the separated supported catalysts could be reused in subsequent polymerizations without any loss of catalytic activity. The supported catalysts are attractive for their broad monomer scope and recyclability, which offer waste reduction and cost savings.

The successful control of the polymer architecture was demonstrated in Chapter 3 by changing the polymerization temperature to selectively induce AFCT or propagation, yielding block or branched copolymers respectively. Building on this result, we targeted chain-end functionalized polymers. In Chapters 2–4, polymers bearing chain-end iodide groups were obtained. The iodide group is useful for post-polymerization transformation reactions into other functional groups. In Chapter 5, the chain-end functionalization of polyacrylate-iodides PBA–I and PME–I was carried out via the organocatalyzed radical addition to PA, yielding vinyl-iodide-terminated polymers. When the concentration of PA in the mixture increased, the addition of multiple PA units was observed. Through the use of functional alkynes, vinyl-iodide-terminated polymers bearing hydroxyl and trifluoromethyl functionalities could also be obtained. These polymers are promising precursors for the development of functional polymer materials via cross-coupling reactions. Such applications of the vinyl-iodide-terminated polymers will be interesting to study in the future.