Block copolymer assisted preparation of functional nano-composites

Chaurasia, Alok

2012

Chaurasia, A. (2012). Block copolymer assisted preparation of functional nano-composites.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/48006>

<https://doi.org/10.32657/10356/48006>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**BLOCK COPOLYMER ASSISTED PREPARATION OF
FUNCTIONAL NANO-COMPOSITES**

ALOK CHAURASIA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2012

**BLOCK COPOLYMER ASSISTED
PREPARATION OF FUNCTIONAL NANO-
COMPOSITES**

ALOK CHAURASIA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University in
fulfillment of the requirement for the degree of

Doctor of Philosophy

2012

Abstract

Block copolymers are widely used in the field of nanotechnology for the production of functional nanomaterials and nanocomposites. We report a technique for the synthesis of C_{60} /polymer colloid nanocomposites in aqueous medium from a non-aqueous system *via* complex formation. A tri-block poly(4-vinylpyridine)-*b*-polyethylene-*b*-poly(4-vinylpyridine), P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was complexed with fullerene (C_{60}) in toluene *via* charge transfer complex formation, which resulted in a fullerene assembly in cluster form. A nanocomposite dispersion in aqueous solution could be obtained using an aged solution of the polymer/ C_{60} /toluene by solvent evaporation technique. However, the rate of complexation was found to be slow in toluene and took several months for unmodified fullerene (C_{60}) to complete.

Rate enhancement of the charge transfer complex formation was attempted using fullerene derivative (PCBM) instead of fullerene (C_{60}) in toluene and THF system. The reaction was found to be typically fast in THF compared with toluene system, which allowed us to study the interaction kinetics of the reaction both qualitatively and quantitatively. Our results show that the reaction follows pseudo-first order kinetics and the P4VP units in the copolymer interact with the fullerene derivative more than two order of magnitude faster than does the small molecular model compound tert-butylpyridine. Based on this understanding, studies were carried out to enhance the rate of charge transfer complex formation of underivatized fullerene (C_{60}) with PS-*b*-P4VP. Rapid assembly of C_{60} /PS-*b*-P4VP composite was realized using a mixed solvent. The poor solubility of C_{60} in THF was overcome by first dissolving C_{60} in toluene before adding in THF. The complexation reaction was completed within 10 days in THF

whereas negligible reaction occurs even after one month when toluene used as solvent as observed previously. Significant morphological refining was observed in C₆₀/PS-*b*-P4VP complex after a solvent exchange process when the THF of was exchanged with toluene. The coordinating property of P4VP blocks also allowed to the synthesis of ZnO quantum dots using PS-*b*-P4VP as templates. The nanocomposite of ZnO QDs/PS-*b*-P4VP was obtained *via* a new and facile method using a non toxic ZnO precursor. ZnO QDs in the nanocomposite films were well assembled, densely distributed and of uniform size. The mechanisms and factors that govern the synthesis and assembly have also been studied in details.

Dedicated To
The Service of the Nation

Acknowledgements

I wish to express my deepest gratitude to my supervisor Prof. Hu Xiao and co-supervisor Prof. Gan Leong Huat for their continuous encouragement, perceptive guidance, thoughtful and constructive criticism and kindness during the course of investigation. Their broad knowledge and creative ideas were crucial for the success of this dissertation. I would like to give special thanks to Prof. Gan Leong Huat for correcting the Chapter-I, Chapter-II and Chapter-IV of the thesis.

I would like to express my sincere thanks to thesis committee members, Prof Andrew Clive Grimsdale and Prof. Gan Leong Huat for their guidance and valuable suggestions. I would like to acknowledge Dr. Yu Hui, Dr. Mao Bao Wie, Dr. Li Fei, Liu Ming, Liang Yen Nan, Wang Libo, Samuel Shen Yaodong and Hu Jinhua, for their constant help.

I would like to thank my colleagues in polymer laboratory and it has been really a great pleasure working with them in the laboratory. I am also grateful to MSE technical staffs, especially Mr. Patrick Lai and Mr. Wilson Lim for their technical assistance. I express my sincere thanks to all for their support and constant encouragements.

I would also like to thank specially to my family members and friends for their constant encouragements and motivation.

Table of Contents

Organization of Thesis	1
Chapter-I	2
1. Introduction.....	2
1.1. Introduction.....	3
1.2. Objectives	3
1.3. Literature review	5
1.3.1. Amphiphilic block copolymer	5
1.3.2. Application of block polymer	7
1.3.2a. Bio-application	7
1.3.2b. Nanoparticles synthesis and application.....	7
1.3.3. Fullerene	11
1.3.4. Fullerene and polymer	11
1.3.5. Atom transfer radical polymerization (ATRP)	13
Outline of the thesis:	15

Chapter-II	16
Self-assembled amphiphilic polymer/fullerene (C₆₀) supramolecular composites.....	16
Abstract	17
2.1. Introduction.....	18
2.2. Materials and methods.....	20
2.2.1. Chemicals & Materials	20
2.2.2. Synthesis of PEO macroinitiator	20
2.2.3. Synthesis of triblock copolymer P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈	21
2.2.4. Charge transfer complex formation.....	22
2.2.5. Preparation of aqueous colloidal solution of fullerene/polymer nanocomposite.....	22
2.2.6. <i>In vitro</i> cytotoxicity test.....	22
2.3. Characterization	24
2.3.1. Gel Permeation Chromatography (GPC).....	24
2.3.2. Nuclear Magnetic Resonance (NMR) Spectroscopy.....	24
2.3.3. Fourier Transform Infrared Spectrometer (FTIR).....	24
2.3.4. UV Spectrophotometer	24
2.3.5. Dynamic Light Scattering (DLS)	24

2.3.6. Transmission Electron Microscopy (TEM)	25
2.4. Results and Discussion	26
2.5. Conclusion	37
 Chapter-III	 38
 Dramatic solvent effect on interaction kinetics and self-organization of phenyl-C61- butyric-acid-methyl-ester (PCBM) in a tri-block copolymer	 38
Abstract	39
3.1. Introduction.....	40
3.2. Materials and Method.....	43
3.2.1. Chemicals and materials	43
3.2.2. Synthesis of tri-block copolymer P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈	43
3.2.3. Formation of charge transfer complex	43
3.3. Characterization	45
3.4. Results and Discussion	46
3.4.1. Polymer Synthesis and complexation.....	46
3.4.2. Kinetics of charge transfer complexation	48
3.4.3. Morphology of Micelles	60

3.5. Conclusion	64
-----------------------	----

Chapter-IV	65
-------------------------	-----------

Rate enhancement of charge transfer complexation for self-assembly of underivatized fullerene by electron donating units of block copolymers.....	65
--	-----------

Abstract	66
----------------	----

4.1. Introduction.....	67
------------------------	----

4.2. Materials and Methods	69
----------------------------------	----

4.3. Characterization	70
-----------------------------	----

4.4. Results and discussion.....	71
----------------------------------	----

4.5. Conclusion	78
-----------------------	----

Chapter-V	79
------------------------	-----------

A facile method based on block-copolymer assisted preparation of functional hybrid materials containing ZnO quantum dots	79
---	-----------

Abstract	80
----------------	----

5.1.1. Introduction.....	81
--------------------------	----

5.1.2. Problem Statement	81
--------------------------------	----

5.1.3. Objectives	82
-------------------------	----

5.1.4. Outline of the work.....	82
Overview of chapter-V.....	83
5.2. Literature review	84
5.3. Materials and Method.....	89
5.3.1 Materials	89
5.3.2 Method.....	89
5.4. Characterization	91
5.5. Results and Discussion	92
5.5.1. Block copolymer and micelle	93
5.5.2. Loading of Zn(Ac) ₂ into polymer micelle core	93
5.5.3. Effect of temperature on conversion of Zn(OAc) ₂ into ZnO	96
5.5.4. Effect of time on ZnO QDs synthesis at 200 °C	97
5.5.5. Effect of temperature on morphology of the polymer/Zn(OAc) ₂ film.....	98
5.5.6. Effect of corsslink agent	105
5.5.7. X-ray Diffraction (XRD)	115
5.5.8. UV-Vis absorption	117
5.5.9. Photoluminance (PL) study	119

5.6. Conclusion	120
6. Chapter-VI	122
6.1. Summary and Future Suggestions.....	122
6.2. Summary.....	123
6.2. Future Suggestions	125
References	126
List of publications.....	153
Appendix	155

List of Tables

Table 1.1 Solubility of buckminsterfullerene (C_{60}) in various solvent.	12
Table 3.1. Pseudo first order rate constants k_A (s^{-1}) and the second order rate constants k ($Lmol^{-1} s^{-1}$) of the complexation between $P4VP_8-b-PEO_{105}-b-P4VP_8$ and PCBM in THF at different temperatures determined at $\lambda = 310$ and $\lambda = 329$ nm.	55
Table 3.2. Activation energy and thermodynamic parameters of activation for the complexation of $P4VP_8-b-PEO_{105}-b-P4VP_8$ with PCBM in THF. The values calculated at $\lambda = 310$ and $\lambda = 329$ nm are presented.	56
Table 3.3. Comparison of rate constants for the complex formation between PCBM and $P4VP_8-b-PEO_{105}-b-P4VP_8$ and 4-t-butyl pyridine at $40^\circ C$ (313 K) in THF.	57
Table 3.4. Summary of light scattering data showing the micelle morphology	62
Table 4.1 The DLS data obtained at scattering angle of 90°	74
Table 5.1. Comparison of size of ZnO QDs calculated from various techniques.	118

List of Figures

Figure 1.1. Schematic diagram of formation of micelle in different solvent.	5
Figure 1.2. Metal nanoparticles with different morphology could be obtained depending on nature of reducing agent	9
Figure 1.3. Structures of (a) fullerene (C_{60}); (b) methanofullerene phenyl-C61-butyric-acid-methyl-ester (PCBM).	11
Figure 1.4. Schematic diagram of formation of micelle in different solvent.	15
Figure 1.5. Schematic depiction of the outline of this thesis.....	15
Figure 2.1. Scheme for synthesis of triblock copolymer and charge-transfer complex formation between $P4VP_8-b-PEO_{105}-b-P4VP_8$ and C_{60}	26
Figure 2.2. 1H NMR spectra of tri block $P4VP_8-b-PEO_{105}-b-P4VP_8$ polymer $CDCl_3$	27
Figure 2.3. Colors of the solution for (a) freshly prepared $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) in toluene (b) two months aged $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) (c) $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) in water prepared from two months aged solution by a solvent exchange process.....	28
Figure 2.4. UV-Vis spectra of (i) C_{60} in toluene; (ii) $P4VP_8-b-PEO_{105}-b-P4VP_8$ in toluene (iii) $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) dissolved in toluene at different aging times (up to two months).....	29

Figure 2.5. UV-Vis spectra of P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /C ₆₀ (95/5 w/w) dissolved in toluene (0.5 mg/ml).....	30
Figure 2.6. FT-IR spectra of (a) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /toluene; (b) two months aged solution of P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /C ₆₀ (95/5 w/w) in toluene.....	31
Figure 2.7. UV-Vis spectrum of polymer/C ₆₀ nanocomposite in aqueous solution.....	32
Figure 2.8. Dynamic Light Scattering of (a) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ in toluene; (b) two months aged P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /C ₆₀ (95/5 w/w) in toluene; (c) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /C ₆₀ nanocomposite in aqueous solution.....	33
Figure 2.9. TEM images (a) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ in toluene with iodine stain; (b) Aged P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /C ₆₀ (95/5 w/w) in toluene solution(scale bar 500 nm) without iodine staining; (c) Fullerene cluster from aqueous solution (100 nm); (c1) zoom in form of ‘c’ where fullerene clusters are visible, images were taken without iodine staining.	34
Figure 2.10. <i>In vitro</i> cytotoxicity studies of (B) polymer in water; (C) polymer/C ₆₀ nanocomposite in water.....	36
Figure 3.1. Scheme for preparation of the triblock copolymer and charge transfer complex between P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ and PCBM.	44
Figure 3.2. ¹ H-NMR (700 MHz) study of charge transfer complexation between P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ and PCBM in deuterated THF showing the emergence of sharper shoulder peaks at 6.82 and 8.75 ppm after 4320 minutes (72 hrs) interaction.	47

Figure 3.3. FTIR spectra of (a) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/THF; (b) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with PCBM in THF after complex formation for 4320 minutes (72 hrs); (c) PCBM in THF.48

Figure 3.4. Time resolved UV-Vis spectra following the interaction of P4VP₈-PEO₁₀₅-P4VP₈ and PCBM in THF recorded at different temperatures (a) 25 °C; (b) 40 °C; (c) 50 °C. In all studies, polymer concentration was kept at 1 mg/ml corresponding to a [4VP] of 2.54×10^{-3} M, and PCBM concentration was kept at 3.6×10^{-5} M with [PCBM]/4VP ratio of 1:71. (d) For comparison, a series of spectra monitoring the interaction between a model small molecular pyridine compound, tert-butyl pyridine (6.7×10^{-2} M) and PCBM (3.6×10^{-5} M) were recorded at 40 °C. The spectra of the copolymer/THF solution, P1 and PCBM/THF solution, P2 are also given in (a) for comparison.

.....51

Figure 3.5. (a) Plots of $\ln \frac{A_{\infty} - A_t}{A_{\infty} - A_0}$ versus time for the charge transfer complex formation at 50 °C using absorbance data at different wavelength, i.e., 329 and 310 nm

.....52

Figure 3.5. (b) Arrhenius plots of $\ln k$ verses $1/T$; (c) Eyring plots of $\ln(k/T)$ verses $1/T$.

.....53

Figure 3.6. Time resolved UV-Vis spectra following the interaction between P4VP₈-PEO₁₀₅-*b*-P4VP₈ and PCBM in toluene (a) and between tert-butyl pyridine and PCBM (b) collected over 28 days at 25 °C. The concentrations of copolymer and PCBM were kept

the same as those in Figure 3.4. The spectra of the copolymer/toluene solution, P1 and PCBM/toluene solution, P2 are also given in (a) for comparison.	60
Figure 3.7. TEM images of samples after solvent evaporation: (a) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ from THF solution (b) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /PCBM from a 76 h aged THF, (c) P4VP ₈ -PEO ₁₀₅ -P4VP ₈ in toluene, (d) P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈ /PCBM in toluene solution after 12 days.	63
Figure 4.1. Schematic illustration for the experimental procedure for charge transfer complex formation between PS- <i>b</i> -P4VP and underivatized C ₆₀	70
Figure 4.2. The UV-Vis spectra changes for the interaction of PS- <i>b</i> -P4VP with underivatized fullerene at 25 °C in (a) THF; (b) toluene.	72
Figure 4.3. UV-Vis spectra of (i) PS- <i>b</i> -P4VP in toluene; (ii) complex formation of underivatized fullerene with PS- <i>b</i> -P4VP in THF after 10 days; (iii) after the THF of (ii) was replaced by toluene.	73
Figure 4.4. Size distribution and intensity data of (a) PS- <i>b</i> -P4VP in THF solution; (b) 4 days aged PS- <i>b</i> -P4VP/C ₆₀ in THF; (c) 10 days aged PS- <i>b</i> -P4VP/C ₆₀ in THF; (d) PS- <i>b</i> -P4VP/C ₆₀ in toluene obtained by replacing THF of (c) with toluene.	75
Figure 4.5. TEM images of samples casted on copper grid from (a) PS- <i>b</i> -P4VP in THF solution & stained with iodine; (b) 10 days aged PS- <i>b</i> -P4VP/underivatized fullerene in THF without iodine staining; (c) PS- <i>b</i> -P4VP/underivatized fullerene in toluene obtained by replacing THF of (b) with toluene.	76
Figure 5.1. Schematic depiction of the outline of synthesis & assembly of ZnO QDs. ...	83

Figure 5.2. Scheme for block copolymer assisted synthesis and assembly of ZnO QDs.	90
Figure 5.3. TEM images of PS- <i>b</i> -P4VP ($M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene (2 mg/ml) coated on copper grid stained with iodine.	92
Figure 5.4. Atomic force microscopy (AFM) image of PS- <i>b</i> -P4VP film casted on silicon	93
Figure 5.5. TEM image of PS- <i>b</i> -P4VP/Zn(OAc) ₂ film coated on copper grid without iodine staining.....	94
Figure 5.6. A schematic which presents how the swelling of P4VP core is effected by methanol and consequently facilitates the absorption of zinc acetate.	95
Figure 5.7. UV-Vis spectra for monitoring the formation of ZnO QDs at different temperature.	96
Figure 5.8. Time resolved UV-Vis spectra for monitoring the formation of ZnO QDs with time at 200 °C.	97
Figure 5.9. TEM image of PS- <i>b</i> -P4VP/Zn(OAc) ₂ film coated on copper grid after heat treatment at 180 °C for 30 min. (small black dot is ZnO).....	98
Figure 5.10. TEM images of (a) PS- <i>b</i> -P4VP/ZnO QDs film obtained after heat treatment at 200 °C for 30 min of PS- <i>b</i> -P4VP/Zn(OAc) ₂ film coated on copper grid; (b) zoom in image at a higher magnification; (c) HR-TEM of ZnO QDs with visible fringes.....	99

Figure 5.11. TEM images of (a) as coated PS- <i>b</i> -P4VP/Zn(OAc) ₂ film on copper grid; (b) after heat treatment at 180 °C for 30 min; (c) after heat treatment at 200 °C for 30 min.	100
Figure 5.12. TEM images of (a) PS- <i>b</i> -P4VP/Zn(OAc) ₂ film casted from chloroform solution; (b) self-assembled PS- <i>b</i> -P4VP/ZnO QDs formed after heating of ‘a’; (c) zoom in form of (b) to see clear distribution of ZnO QDs.	102
Figures 5.13. TEM images of (a) P4VP/ZnO QDs film, formed after heat treatment at 200 °C for 30 min of film P4VP/Zn(OAc) ₂ casted from mixture solution of toluene and DMF; (b) zoom in form of to see clear distribution of ZnO QDs.	103
Figures 5.14. TEM images of different morphology of polymer/ZnO QDs films, formed after heat treatment at 200 °C for 30 min of film casted from (a) PS- <i>b</i> -P4VP/Zn(OAc) ₂ in toluene; (b) PS- <i>b</i> -P4VP/Zn(OAc) ₂ in chloroform; (c) P4VP/Zn(OAc) ₂ in mixture solution of toluene and DMF.	104
Figure 5.15. TEM images of PS- <i>b</i> -P4VP/Zn(OAc) ₂ film with crosslink agent 1,4 dibromobutane coated on copper grid before heat treatment, (a) monolayer coated on copper grid; (b) bilayer coated on copper grid; (c) existence of monolayer and bilayer in same sample.....	106
Figure 5.16. TEM image of PS- <i>b</i> -P4VP/ZnO QDs film after heat treatment at 200 °C for 30 min of crosslinked monolayer PS- <i>b</i> -P4VP/Zn(OAc) ₂ film casted on copper grid; (b) HR-TEM image of P4VP domain of PS- <i>b</i> -P4VP/ZnO QDs film	107

Figures 5.17. A schematic diagram represents how the ZnO QDs is formed inside P4VP core of PS- <i>b</i> -P4VP block polymer.....	108
Figure 5.18. TEM image of PS- <i>b</i> -P4VP/ZnO QDs film after heat treatment at 200 °C for 30 min of crosslinked bilayer PS- <i>b</i> -P4VP/Zn(OAc) ₂ film casted on copper grid.	109
Figures 5.19. A schematic model showing how the net work type of structure containing ZnO QDs can be formed based on TEM study. TEM images of polymer/ZnO QDs film, formed after heat treatment at 200 °C for 30 min of film obtained from PS- <i>b</i> -P4VP /Zn(OAc) ₂ (PS- <i>b</i> -P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene using crosslinking agent, (a) monolayer; (b) schematic model for monolayer; (c) bilayer (d) schematic model for bilayer.	111
Figures 5.20. A schematic model showing how the network type of structure containing ZnO QDs can be formed based on TEM study.....	111
Figure 5.21. TEM images of (a) self-assembled PS- <i>b</i> -P4VP/ZnO QDs formed after heat treatment at 200 °C for 30 min of crosslinked PS- <i>b</i> -P4VP/Zn(OAc) ₂ film; (b) & (c) are in zoom in form.	113
Figure 5.22. TEM images of self-assembled PS- <i>b</i> -P4VP/ZnO QDs formed after heat treatment at 200 °C for 30 min of crosslinked PS- <i>b</i> -P4VP/Zn(OAc) ₂ film when, (a) PS- <i>b</i> -P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol; (b) PS- <i>b</i> -P4VP with $M_{PS} = 47,600$ g/mol, $M_{P4VP} = 20,900$ g/mol used as polymer templates.	114
Figure 5.23. XRD spectra of (a) PS- <i>b</i> -P4VP/Zn(OAc) ₂ ; (b) PS- <i>b</i> -P4VP/ZnO without DBB; (c) PS- <i>b</i> -P4VP/ZnO QDs with DBB crosslinker.	116

Figure 5.24. UV-Vis spectra of (a) PS- <i>b</i> -P4VP/Zn(OAc) ₂ ; (b) PS- <i>b</i> -P4VP/ZnO QDs without DBB; (c) PS- <i>b</i> -P4VP/ZnO QDs with DBB crosslinker.	117
Figure 5.25. Photo luminance (PL) emission spectra of (a) PS- <i>b</i> -P4VP/Zn(OAc) ₂ ; (b) PS- <i>b</i> -P4VP/ZnO without DBB; (c) PS- <i>b</i> -P4VP/ZnO QDs with DBB crosslinker.	119
Figures 5.26. TEM images of polymer/ZnO QDs film, formed after heat treatment at 200 °C for 30 min of film casted from (a) PS- <i>b</i> -P4VP/Zn(OAc) ₂ (PS- <i>b</i> -P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene; (b) PS- <i>b</i> -P4VP/Zn(OAc) ₂ (PS- <i>b</i> -P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in chloroform; (c) P4VP/Zn(OAc) ₂ (P4VP with $M_{P4VP} = 9800$ g/mol) in mixture solution of toluene and DMF; (d) monolayer of PS- <i>b</i> -P4VP/Zn(OAc) ₂ (PS- <i>b</i> -P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene using crosslinking agent; (e) monolayer of PS- <i>b</i> -P4VP/Zn(OAc) ₂ (PS- <i>b</i> -P4VP with $M_{PS} = 47,600$ g/mol, $M_{P4VP} = 20,900$ g/mol) in toluene using crosslinking agent; (f) bilayer of PS- <i>b</i> -P4VP/Zn(OAc) ₂ (PS- <i>b</i> -P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene using crosslinking agent.	121

List of Abbreviations

ATRP	Atom Transfer Radical Polymerization
AFM	Atomic Force Microscopy
CRP	Controlled Radical Polymerization
CuCl	Copper(I) chloride
DBB	1,4 dibromobutane
DMA	2-(dimethylamino)ethyl-methacrylate
DP	Degree of Polymerization
DLS	Dynamic Light Scattering
EDAX	Energy dispersive analysis of X-ray
FT-IR	Fourier transform infrared spectroscopy
GPC	Gel Permeation Chromatography
HMTETA	Hexamethyl-triethylene-tetramine
SEC	Size Exclusion Chromatography
LCST	Lower Critical Solution Temperature
Me6TREN	Tris(2-dimethylaminoethyl)-amine
NMR	Nuclear Magnetic Resonance
PCBM	[6,6]-phenyl C61 butyric acid methyl ester
PS	Polystyrene
PEG	Poly (ethylene glycol)
P4VP	Poly-(4- vinyl Pyridine)
PEO	Poly-(ethylene Oxide)

PDEA	Poly-(N,N-diethyl-acrylamide)
PDI	Polydispersity Index
PL	Photoluminescence
PMDETA	N,N,N',N'',N'''-pentamethyldiethylenetriamine
QDs	Quantum dots
RAFT	Reversible addition-fragmentation chain transfer
SAED	Selected area electron diffraction
TEM	Transmission electron microscope
HR-TEM	High resolution- Transmission electron microscope
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-visible
VP	Vinylpyridine
XRD	X-ray diffraction
ZnO	Zinc oxide
Zn(Ac) ₂	Zinc acetate dihydrate

Organization of Thesis

This thesis comprises of 6 chapters. In chapter 1, an introduction, objectives and literature review containing organization of fullerenes, fullerene derivatives and zinc oxide quantum dots are presented.

In chapters 2, 3 & 4, a specific literature review for each chapter concerning assembly of fullerenes and fullerene derivatives is presented.

Chapter 2 describes a technique for the synthesis of well-defined C₆₀/polymer colloid nanoparticles in aqueous solution through non-aqueous media. A tri-block copolymer containing a polyethylene oxide (PEO) central block and two 4-vinyl pyridine (4VP) end blocks, poly(4-vinylpyridine)-*b*-polyethylene-*b*-poly(4-vinylpyridine), P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with fullerene (C₆₀) are discussed.

Chapter 3 presents studies of interaction kinetics and supramolecular structure of charge transfer complex of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with a fullerene derivative methanofullerene phenyl-C₆₁-butyric-acid-methyl-ester (PCBM).

The enhancement of rate of charge-transfer complexation for self-assembly of underivatized fullerene by electron donating units of block copolymer is presented in the chapter 4. The rate enhance of complexation of unmodified fullerene with polystyrene-*block*-poly(4-vinylpyridine), PS-*b*-P4VP is discussed.

Chapter 5 begins with a literature review for the synthesis and assembly of ZnO quantum dots (QDs). The main focus of this chapter is to develop the simple synthesis method of ZnO QDs, tuning the assembly of ZnO QDs using factors such as temperature, crosslinking agent, solvent, and block copolymer in a rational approach.

The summary and recommendations for future research are presented in Chapter 6.

Chapter-I

Introduction

1.1 Introduction

In recent years, polymer research has moved rapidly towards an area known as advanced polymer materials. These are polymers which possess special properties, many of which are responsive to change in environment like temperature, pH and solvent. Some have ability to form complex with various transition metals and other compounds such as fullerene and fullerene derivatives. These polymeric materials are basic platforms for the formation of various hybrid nanomaterials. The polymeric materials can act as interfaces between the nanoscale “soft” materials and “hard” materials with interesting features.

A well-known example of this class of polymer is poly (4-vinylpyridine) (P4VP). This polymer has the possibility to form complexes with transition metals and fullerenes.

1.2 Objectives

This research work aims to build up a novel system for the self assembly of fullerene or fullerene derivatives and zinc oxide using block copolymers.

The research reported in this thesis consists of the following areas:

- i) Synthesis and characterizations of block copolymer containing one of the common block P4VP using atom transfer radical polymerization (ATRP) technique.
- ii) Developing systems for the assembly of fullerenes and other potential materials using block copolymers.
- iii) Investigate the factors that govern the assembly behavior of fullerene or fullerene derivatives and zinc oxide quantum dots such as the effect of solvent and block copolymers.

iv) Standardization and characterization of the self assembly of these materials.

v) Preparation of polymeric films with the incorporation of fullerene or PCBM and metal oxide for potential applications in the fields of sensors and optics.

1.3. Literature review

The term advanced materials refers to a class of materials which have unique properties. This includes materials which have the ability to show significant changes in their properties with changing factors such as pH, solvent, electric field and magnetic field. Some of these materials have the ability to form complexes with various transition metals, fullerene and fullerene derivatives. These unique features have brought considerable interest for researchers.

1.3.1 Amphiphilic block copolymer

Amphiphilic block copolymers consist of distinct hydrophilic and hydrophobic segments that are able to form micelles in appropriate solvents. The formation of micelle depends on the nature of block, solvent and concentration (Figure 1.1). The size and shape of micelles depend on the chemical structure of block, molecular weight of each block, number of aggregation and nature of solvent.¹⁻⁴

Figure 1.1. Schematic diagram of formation of micelle in different solvent.

Recent progresses in synthetic techniques have lead to the successful synthesis of a wide range of block copolymers containing different types of core and corona blocks with desired properties. Micelles of different shapes and sizes can be obtained. The aggregates can be in the form of rods, spheres or vesicles depending on various factors including the type of solvent and aggregation number.⁵⁻¹³

1.3.2 Application of block polymer

Amphiphilic block copolymers are multipurpose useful materials. In recent years block copolymers have found wide application in many areas. These are also be used as vehicles for controlling as well as targeting the release of vector agents, both hydrophobic and hydrophilic systems.^{14, 15} Thus, these are exploited for applications in drug delivery,¹⁶⁻²⁰ tissue engineering, cosmetic, water treatment and industrial waste treatment.¹

1.3.2a Bio-application

PEG is found to be nontoxic and accepted by the Food and Drug Administration (FDA or USFDA) for use in different pharmaceutical formulations, foods and cosmetics. Most PEGs are removed from the body unchanged with rate which is inversely proportional to its molecular weight. PEGs are available with a wide range of end-functions which makes its widely use in biomedical related research, like drug delivery, gene delivery, tissue engineering scaffolds, surface fuctionalization, and many other applications.^{21, 22} It is worth to mention that PEGs are also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight

1.3.2b Nanoparticles synthesis and application

The synthesis of metal or metal oxide nanoparticles in block copolymer micelles has brought substantial interest as a result of their unique properties. Block copolymer micelles filled with nanoparticles have shown special catalytic,²³⁻²⁷ magnetic, electrical,^{28,}²⁹ and optical³⁰ properties.

For block copolymers, the selectivity towards the core-forming block is important because of a physico-chemical interaction between the polymer core and the metal precursor that accelerate the metal incorporation into the micelle. A polymer block containing particular functional groups forming the micellar core can be loaded with some specific metal compounds. The micelles can often serve as a nano-reactor for nanoparticles formation. It may also play a role in stabilizing the nanoparticles as the core forming polymer block that can be considered to exist in a quasi-solid state (as the core forming block is insoluble in the selective solvent).²⁴

Block copolymers are used as colloidal stabilizers to synthesize metallo-nanoparticle with controlled shape and size. They can provide an environment that can be used to prevent corrosion and leakage of heavy metals. They can also protect catalytic nanoparticles from deactivation.^{5, 26, 31}

Using this concept, block copolymer micelles containing a polystyrene core and a functional corona have been used to produce gold nanoparticles.³² Gold (Au)-labeled micelles have been incorporated using di-blocks of poly(2-vinylpyridine) (P2VP)²⁴ / poly(4-vinylpyridine) (P4VP)³³ and poly(ethylene oxide) (PEO) in water. The size of gold nano-particles obtained is dependent on the nature and number of unit of the two blocks.

For example, the size of gold nanoparticle is 1 to 4 nm for P2VP₁₃₅-*b*-PEO₃₅₀ whereas gold nanoparticles formed from P4VP₂₈-*b*-PEO₄₅ ranged in size from 5 to 10 nm. The advantage of gold-labeled micelles with poly(ethylene oxide) PEO corona is that they allow for their preparation in water, an environmental friendly medium. Zubarev et al. reported a new approach for better control of the interfacial assembly of gold (Au) nanoparticles in self-assembled nanostructures of block copolymers, starting from the gold nanoparticles which are covalently attached to V-shaped heteroarm chains.³⁴ The supramolecular self-assembly of heteroarm star polymers directs the gold nanoparticles precisely at the core-shell interfaces of micelles.³⁴ Park and co-workers investigated the assembly of CdS or CdSe/ZnS quantum dots in vesicles or nanorods of PAA-based block copolymers.³⁵ The application of block polymer also reported for nanolithography for the development of biological performance of mineral oil, in biological and pharmaceutical applications.³⁶⁻³⁹ The synthesis of metal or semiconductor nanoparticles in the cores of amphiphilic block copolymer micelles in organic solvents was reported by many research groups.^{5, 40, 41} Using block copolymer micelle core as nano reactors allows the synthesis of mono and bimetallic nanoparticles. The size of the nanoparticles, among other factors, depends on the particular reducing conditions as depicted on Figure 1.2. Different morphology of nanoparticles significantly change the catalytic properties of such systems, even though the size may be similar. The crosslinking of block copolymer micelles provides an additional degree of stabilization to nanoparticles and allows the modification of micelle morphology.⁴²⁻⁴⁴ The possibility of using nanospheres as nanoreactors for inorganic nanoparticles was demonstrated by the formation of iron oxide magnetic particles⁴⁴ and catalytic Pd nanoparticles.⁴³ The spatial distribution of nanoparticles in

block copolymers was also investigated by many researchers.^{1, 5, 45} The selective separation of nanoparticles among blocks was achieved as a result of the presence of functional groups in a selected block.^{24, 33}

Figure 1.2. Metal nanoparticles with different morphology could be obtained depending on nature of reducing agent.⁴³

A large number of amphiphilic block copolymers forming micelles with a functionalized core in an organic medium are available but when aqueous solutions are favored, the choice of block copolymers is very limited. Here, nanoparticle formation is normally more complicated as the pH of the medium should be taken into consideration. A few examples of such block copolymers include poly(ethylene oxide)-*block*-poly(2-vinylpyridine)(PEO-*b*-P2VP), polybutadiene-*block*-poly(ethylene oxide) (PB-*b*-PEO), polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO), and poly-[methoxyhexa(ethylene glycol) methacrylate]-*block*-[2-(diethylamino)ethyl methacrylate] (PHEGMA-*b*-PDEAEMA). P2VP and PDEAEMA are examples of pH sensitive block as their core forming capability depends on pH.³⁶ For example, at pH below 5, PEO-*b*-P2VP forms a molecular solution in water, whereas a further decrease of pH, the PEO-*b*-P2VP forms micellar solution. No micellar decomposition took place during incorporation of metal compounds or metal nanoparticle into micelle solution due to interaction with metal species.⁴⁶ Morfit et al. reported the formation of spherical assemblies of CdS containing block copolymer using reverse micelles in aqueous solution.⁴⁷ These stable assemblies were created by the slow addition of water into mixtures of reverse micelles formed by polystyrene-*b*-poly(acrylic acid) diblock chains. This resulted in micelles containing quantum-confined CdS nanoparticles. This method allows the relocation of CdS nanoparticles formed in the micelle cores in organic medium to aqueous medium without the loss of stability or nanoparticle aggregation.⁴⁷

The choice of P4VP as the core-forming block in many block copolymers is due to the coordinating property of 4VP with a wide range of metal ions.⁴⁸

1.3.3. Fullerene

Fullerenes, a family of carbon allotropes, were discovered in 1985 by Robert Curl, Harold Kroto and Richard Smalley. Spherical fullerenes are also called buckyballs. The structure of fullerene (C_{60}) and methanofullerene phenyl-C₆₁-butyric-acid-methyl-ester (PCBM) are shown in Figure 1.3.

Figure 1.3. Structures of (a) fullerene (C_{60}); (b) methanofullerene phenyl-C₆₁-butyric-acid-methyl-ester (PCBM).

Fullerene (C_{60}) has attracted continuous attention since its discovery due to its exceptional physical and chemical properties. Fullerene-containing materials have shown wide and promising applications in the field of superconductors, ferro-magnets, lubrications, photoconductors, and catalysts.⁴⁹⁻⁵¹

1.3.4. Fullerene and polymer

Despite their great promise, the poor solubility and processibility of fullerenes greatly limit their practical applications. The solubility of fullerene C_{60} in some selected solvents are listed in Table 1.1 in order of decreasing solubility.⁵²

Table 1.1 Solubility of buckminsterfullerene (C₆₀) in various solvent.

Solvents	Solubility (mg/ml)
1-Chloronaphthalene	51.0
1-Methlnaphthalene	33.0
1,2-Dichlorobenzene	24.0
1,2,4-Trimethylbenzene	18.0
Tetrahydronaphthalene	16.0
Carbon disulfide	8.0
1,2,3-Tribromopropane	8.0
Toluene	3.0
Benzene	1.5
Cyclohexane	1.2
Carbon tetrachloride	0.4
n-Hexane	0.046
Tetrahydrofuran	0.006
Methanol	4.0×10^{-4}
Water	1.3×10^{-11}

Various derivatives of fullerenes have been synthesized in order to improve the solubility, control the assembly and provide further functionalities.^{53, 54} Efforts have been made on the self-assembly of fullerenes by connecting to specific blocks of block copolymers using covalent interactions⁵⁵⁻⁵⁸ or by using complementary physical interactions, such as acid-base interactions and hydrogen bonding.⁵⁹

Fullerene (C_{60}) containing polymeric materials, fullerene-endcapped telechelic polymers,^{54, 60, 61} have been extensively studied so that the position of fullerene moieties can be precisely known.^{58, 62, 63} Generally, in C_{60} -terminated polymers formed with fullerene in the core are less well-defined. These are found in polymers like poly(ethylene oxide) (PEO),⁶⁴ poly(acrylic acid) (PAA),⁶⁵ poly(methyl methacrylate) (PMMA),⁶⁶ and poly[methacrylic acid]-block-poly [2 (dimethylamino)ethyl methacrylate] (PMAA-*b*-PDMAEMA).⁶⁷

It is thus highly desirable to tune the specific arrangement of fullerene moieties within a polymer matrix (e.g. fullerene nanowires, nanotubes, and nanofilms) in a more elaborate manner to widen its practical applications in the fields of hybrid solar cells, molecular medicines and superconductors. Using polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP), Ikkala and co-workers fabricated C_{60} -containing nanostructures *via* the combination of block copolymer self assembly and charge-transfer complex formation between fullerenes and P4VP segments.⁶⁸ This process took several months.

1.3.5. Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP)^{60, 69} is one of the most successful controlled radical polymerization (CRP) techniques. The method has been developed and proposed by researcher group of Matyjaszewski. The technique is simple and inexpensive,⁶⁶ is able to polymerize a wide range of monomers including various styrenes, acrylates and methacrylates in addition other monomers, such as acrylonitrile, vinylpyridine and dienes. Simple alkyl halides are used as a initiators where as simple transition metals (iron, copper) as catalysts in this process. These catalysts can be used in very low concentration

compared to other controlled polymerization systems. ATRP is able to control the polymerization by generating radicals which can grow and reversibly neutralized to form dormant species. Reactivation of the dormant species is needed to start polymerization again. In this process, polymer chain grows slowly but steadily with well-defined end group which is usually an alkyl halide. A Schematic diagram for atom transfer radical polymerization is shown in Figure 1.4. The initiator is generally a simple, commercially available, alkyl halide. The catalyst is a transition metal which complexed with one or more ligands during the process. It is does not necessary to use catalyst in a one-to-one ratio with the initiator .Catalyst can be used in much smaller amounts depends on the requirement.⁷⁰

Figure 1.4. A Schematic diagram for atom transfer radical polymerization.

ATRP can be operated in bulk solution or even in a heterogeneous system such as suspension or emulsion and mini-emulsion. Various solvents including toluene, acetone, DMSO, DMF, water and carbon dioxide have been used for different monomers.⁷¹ By using ATRP many novel and previously inaccessible materials have been prepared. The list includes not only macromolecules with precisely controlled compositions and architectures but also many new hybrids in which well-defined organic polymers are covalently attached to inorganic materials or to natural products.⁷²

Outline of the thesis:

The outline of the thesis is shown in Figure 1.5.

Figure 1.5. Schematic depiction of the outline of this thesis.

Chapter-II

Self-assembled amphiphilic polymer/fullerene (C₆₀) supramolecular composites

Abstract

A technique for the synthesis of well-defined C₆₀/polymer colloid nanocomposites in aqueous medium from a non-aqueous system via complex formation is described. A bio-compatible tri-block poly(4-vinylpyridine)-*b*-poly(ethylene oxide)-*b*-poly(4-vinylpyridine), P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was synthesized by atom transfer radical polymerization. The block copolymer formed a complex with fullerene (C₆₀) in toluene which resulted fullerene assembly in cluster form. A nanocomposite dispersion in aqueous solution could be obtained using an aged solution of the polymer/C₆₀ in toluene by solvent evaporation technique. The complex formation of fullerene with the polymer plays a significant role in controlling the PDI and size of polymer/C₆₀ micelles in toluene solution. The complex formation was confirmed by UV-Vis and FTIR spectroscopy. The particle size and morphology of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈, P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ mixture were studied by dynamic light scattering (DLS) and transmission electron microscopy (TEM). In cytotoxicity tests, both pure polymer and the resulting polymer/C₆₀ composite in water showed more than 90% cells-viability at 1 mg/ml concentration.

2.1. Introduction

Organization of fullerene (C_{60}) and its derivatives into nanostructures within polymer systems has potential applications in solar cells and biomedicine.⁷³⁻⁷⁶ For example, interesting polymer solar cells results were reported using a blend of fullerene derivative and a block copolymer of poly(4-vinyl pyridine) and poly(3-hexyl thiophene) (P3HT-*b*-P4VP).⁷⁷ It was also found that fullerene in aqueous solution can generate singlet oxygen under photo-irradiation which has implications in the studies of biomedical and environmental science.^{76, 78} One of the biologically most relevant features of C_{60} is the ability to function as a “free radical sponge” and quench various free radicals more efficiently than conventional antioxidants.⁷⁹ Fullerene has widespread applications ranging from drug-delivery and tissue-scaffolding systems to consumer products,⁸⁰ and it has been explored in the area of biological chemistry, such as enzyme inhibition, antiviral activity, DNA cleavage and photodynamic therapy.⁸¹ However, many of C_{60} potential applications have been seriously hampered^{62, 82} by its extremely low solubility in water. Derivatization of the fullerene molecule with various functional groups and other solubilization procedures such as surfactants or long chain polymers^{83, 84} through covalent interactions^{55-57, 60} may change the properties of C_{60} . It was reported that 1O_2 quantum yield decreases with decreasing double bonds in the fullerene molecule due to modification.^{85, 86} Generally, introduction of any substituent into the fullerene core can diminish these properties.⁸⁵⁻⁸⁷ A more effective and promising approach is to organize fullerene by specific non-covalent interactions with amphiphilic block copolymers through charge transfer complexation between fullerenes and block copolymers. Ikkala and co-workers fabricated functionally unmodified C_{60} -containing nanostructures *via* a

combination of PS-*b*-P4VP block copolymer self-assembly and charge-transfer complexation between fullerenes and P4VP segments in organic solvent.⁶⁸ However, synthesis of water-soluble adducts of this spherical carbon allotrope (potential biological applications) became a particularly challenging topic. So, to enhance the processibility and water solubility of the materials, self-assembly systems of pristine C₆₀ with block copolymers have been explored. For example, the water-soluble C₆₀/PS-*b*-PEO composites obtained through a tedious process, exhibited a wide distribution of particle sizes.⁸⁸ However, supramolecular aggregates with a more uniform size distribution could be obtained. This was done through the aggregation of C₆₀ with PS-*b*-PDMAEMA in water using dialysis process, where fullerene preferably goes into the PS region due to hydrophobic interactions.⁸⁹ However, in most cases, incorporation of fullerenes into water-soluble supramolecular structures using surfactants or other modifying agent results in the fullerene core being completely covered by the modifying agent. This reduces the possibility of contact between water soluble oxygen and fullerenes, thereby inhibit some of the desired prosperities such as ability to quench singlet oxygen (¹O₂). Clearly, the preparation of well structure-defined aggregates from C60 with biocompatible polymers in aqueous medium remains a challenge to overcome.

The present study focuses on the development of a simple method which will allow the assembly of fullerene with an amphiphilic block copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ in aqueous and organic media. The choice of P4VP block is due to its more hydrophilic nature compared to PS which will be more accessible to dissolved oxygen.

The P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ amphiphilic block copolymer was synthesized using atom transfer radical polymerization.^{33, 90}

2.2. Materials and methods

2.2.1. Chemicals & Materials

The hydroxy-end-capped PEO [degree of polymerization (DP) 105; PDI 1.08] was purchased from Aldrich. 4-Vinylpyridine (VP) (99%) was purified by stirring over CaH_2 , and distilled under vacuum. 2-Bromoisobutyl bromide, triethylamine, CuCl (99.99%), N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA 95%), and fullerene (99.5%) were purchased from Aldrich and used without further purification.

2.2.2. Synthesis of PEO macroinitiator

Hydroxy-terminated PEO (4.98 gm) was added to a three-neck round-bottom flask and dissolved in 250 ml of dry toluene. To remove trace amounts of water from PEO, 40-50 ml of toluene was distilled from the reaction mixture by azeotropic distillation. The solution was cooled to 0 °C by an ice bath and triethylamine was added. Under continuous stirring, 2-bromoisobutyl bromide (1.5 times of -OH by the mole ratio) was added dropwise using a pressure-equalizer funnel over 1 hr. The reaction mixture was kept under constant stirring for 24 h at room temperature, and the triethylamine hydrobromide salt was then removed by filtration. The solution was concentrated by rotary evaporation prior to precipitation in 20-fold excess of cold diethyl-ether. The polymer was then filtered, dried under vacuum. The yield was 92.5% by weight. ^1H NMR in CDCl_3 (ppm): 4.35 (*t*) (- $\text{OCH}_2\text{CH}_2\text{-OC=O}$), 3.66 (*s*) (- $\text{OCH}_2\text{CH}_2\text{-}$)_{*n*}, 1.97(*s*) (- CH_3).

2.2.3. Synthesis of triblock copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈.

A Schlenk flask was connected to the vacuum line, the moisture was removed by repeated application of vacuum and nitrogen filling. Under nitrogen environment, Br-terminated PEO macroinitiator and CuCl were charged into the flask that was tightly sealed with a rubber septum. Using a nitrogen washed syringe, deoxygenated DMF and monomer (volume ratio of DMF : 4-vinylpyridine 10:1) were introduced into the flask, and the mixture was stirred at room temperature for 15 min until it became homogeneous. The reaction mixture was degassed using three freeze-thraw cycles. Once the mixture approached room temperature, degassed ligand (PMDETA) was introduced using a nitrogen-purged syringe. The flask was placed in a thermostated oil bath kept at 50 °C. The reaction mixture became dark green and turned progressively more viscous, indicating the progress of polymerization. The polymerization was terminated after 18 hrs by the addition of tetrahydrofuran (THF). The catalyst was removed by passing the reaction mixture through a basic alumina column followed by Na⁺ ion exchange resin to remove trace amount of Cu ions. The polymer solution was concentrated by rotary evaporation and subsequently recovered by drop wise addition to precipitation in excess amounts of cold diethyl ether, where the un-reacted vinyl pyridine monomer and other contaminants were removed. The polymer was filtered and dried in a vacuum oven at room temperature to yield a light brown colored powder. The yield of the polymer was about 90%.

2.2.4. Charge transfer complex formation

The polymer was dissolved in toluene (1 mg/ml) and stirred for 24 h. Fullerene was separately dissolved in toluene with concentration of 1 mg/ml. The color of the solution was purple. The fullerene solution (1 ml) was then added to 19 ml of polymer stock solution, keeping polymer and fullerene ratio of 95:5 (w/w). The initial color of solution was purple but with time it gradually turned into brown indicating complex formation. The formation of the charge transfer complex as a function of time was monitored by UV-Vis spectrophotometry.

2.2.5. Preparation of aqueous colloidal solution of fullerene/polymer nanocomposite

The aqueous colloidal solution of fullerene/polymer nanocomposite was obtained by pouring 10 ml two-month aged solutions of toluene into 100 ml of water. Toluene was allowed to evaporate at 80 °C for 6 hrs and the final volume of fullerene/polymer composite in aqueous solution was kept as 10 ml. No precipitation was observed.

2.2.6. *In vitro* cytotoxicity test

In vitro cytotoxicity test was performed to study the biocompatibility of the polymer, polymer/C₆₀ nanocomposite in aqueous solution. For cytotoxicity test, cell culture experiments were carried out using L929 mouse fibroblasts which was obtained from American Type Culture Collection (ATCC). Cells were grown in Dulbecco's modified Eagle's Medium (DMEM) supplemented with 10% heat inactivated Fetal Bovine Serum (FBS) (Lonza) and 1% Penicillin-Streptomycin-Glutamine (Antibiotic) (Gibco) maintained at 37 °C in 5% CO₂ and 95% relative humidity. Cell cytotoxicity test was

performed using the Promega CellTiter 96[®] AQueous One Solution Cell Proliferation Assay (MTS). This is a colorimetric method and the solution contains a tetrazolium compound [3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H tetrazolium (MTS) and an electron-coupling reagent (phenazine ethosulfate, PES). The compound is bio-reduced by living cells into a colored formazan product that is soluble in tissue culture medium. The quantity of formazan product is measured at 490 nm at which the intensity of absorbance is directly proportional to the number of living cells in culture.⁹¹⁻⁹³ Cells were seeded at a density of 2×10^4 cells/well in 96 well plates. After 24 hr, culture medium was replaced by 200 μ l serial dilutions of the polymer solutions and the cells were incubated for 24 hr. Polymer solutions were prepared in serum supplemented DMEM and sterilized by filtration (0.2 μ m). MTS assay was done for four different concentrations; 0.1 mg/ml, 0.25 mg/ml, 0.5 mg/ml and 1 mg/ml. At the end of incubation time period (24 hr), polymer solutions were aspirated and replaced with 100 μ l fresh DMEM, to which 20 μ l CellTiter 96[®] AQueous One Solution was added. The cells were then incubated for 4 hr at 37 °C in 5% CO₂ incubator. Then the absorbance was measured at 490 nm in a microplate reader (TECAN, Tecan Group Ltd., Switzerland). The cell viability (%) related to control wells containing cell culture medium without polymer was calculated by $[A]_{\text{test}} / [A]_{\text{control}} \times 100$ equation. Each sample was tested in triplicates.

2.3. Characterization

2.3.1. Gel Permeation Chromatography (GPC).

An Agilent 1100 series GPC system equipped with a liquid chromatography pump, DMF column, and refractive index detector was used to determinate the molecular weights and molecular weight distributions. The column was calibrated with the narrow molecular weight polystyrene standards. The eluent was HPLC grade DMF at a flow rate of 1.0 ml/min.

2.3.2. Nuclear Magnetic Resonance (NMR) Spectroscopy.

The ^1H NMR spectrum for the block copolymer in CDCl_3 was recorded using a Bruker DRX400 instrument at 25 °C.

2.3.3. Fourier Transform Infrared Spectrometer (FTIR)

Perkin Elmer system 2000 was used for FTIR analysis.

2.3.4. UV Spectrophotometer

UV2501PC Pharmaspec (Shimadzu) spectrophotometer was used to monitor the complex formation.

2.3.5. Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) was performed using Nano Zetasize. The aggregation behavior of $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8/\text{toluene}$, $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8/\text{C}_{60}$ in toluene and aqueous were studied by dynamic light scattering using Zetasizer Nano ZS and ZS90 (Malvern).

2.3.6. Transmission Electron Microscopy (TEM)

The supramolecular aggregates of clusters were observed using a JEOL JEM-2010 transmission electron microscope operating at an accelerating voltage of 200 kV. TEM specimens were prepared by dropping one or two drops of the solution onto carbon-coated 400-mesh copper grids pre-coated with Formvar.

2.4. Results and Discussion

The block copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was prepared *via* atom transfer radical polymerization (ATRP) as outlined in Figure 2.1.

Figure 2.1. Scheme for synthesis of triblock copolymer and charge-transfer complex formation between P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and C₆₀.

PEO was reacted with 2-bromoisobutyryl bromide to yield a Br-terminated PEO macroinitiator with PDI of 1.14. 4-Vinyl pyridine was copolymerized with the macroinitiator in presence of CuCl/PMDETA catalyst in DMF at 50 °C.

The tri-block copolymer obtained has a PDI of 1.21. ¹H-NMR spectrum of the copolymer is shown in Figure 2.2 with the following peak assignment:

8.32, 6.36 (for *ortho* and *meta* H of 4VP), 3.61 ($-\text{CH}_2$, PEO), 3.33 ($\alpha\text{-CH}_3$, PEO), 1.42-2.33 (CH_2 and CH , 4VP), 0.97 (C-CH_3 , PEO).

Figure 2.2. ^1H NMR spectra of tri block $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8$ polymer CDCl_3 .

The average degree of polymerization of the P4VP blocks of tri-block $\text{P4VP-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}$ was determined by ^1H NMR. In the resulting block copolymer the molecular weight of the P4VP block was found to be 1681, *i.e.*, the degree of polymerization of two 4-VP blocks was 16. The molar composition of $\text{P4VP-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}$ copolymer was determined from the relative intensities at 3.66 ppm ($-\text{CH}_2\text{CH}_2\text{O}$ of the PEO block) and 8.38 or 6.45 ppm ($-\text{2H}$ of *ortho* or *meta* H of the P4VP block). Since both chain-ends propagated under similar conditions during polymerization, a chemical structure of $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8$ was obtained based on the degree of polymerization and the number-average molecular weight (M_n).

Fullerene (C_{60}) dissolves readily in toluene, which leads to a purple colour solution.

Fullerene solution in toluene (1 ml) was then added to 19 ml of polymer stock solution (1 mg/ml), giving a polymer: fullerene ratio of 95:5 by weight. The initial color of solution was purple but with time it gradually turned into brown indicating complex formation as shown in Figure 2.3.

Figure 2.3. Colors of the solution for (a) freshly prepared $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) in toluene (b) two months aged $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) (c) $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) in water prepared from two months aged solution by a solvent exchange process.

The color change was similar to that for the solution of C_{60} in pyridine. This agrees with the formation of charge-transfer complexes between the electron donating pyridine solvent and the electron-accepting fullerenes.^{94, 95} The changes in the visible spectrum are shown in Figure 2.4.

The solution shows a broad and weak absorption band ranging from 410 to 650 nm. The absorbance in the region increases with aging.

Figure 2.4. UV-Vis spectra of (i) C₆₀ in toluene; (ii) P4VP₈-b-PEO₁₀₅-b-P4VP₈ in toluene (iii) P4VP₈-b-PEO₁₀₅-b-P4VP₈/C₆₀ (95/5 w/w) dissolved in toluene at different aging times (up to two months).

Due to high concentration of fullerene in the solution of P4VP₈-b-PEO₁₀₅-b-P4VP₈/C₆₀ (95/5 w/w) the characteristic absorption peak of fullerene at ~332 nm was not observed. The change in absorbance for the characteristics peak at ~ 332 nm is clearly shown in

Figure 2.5 when the polymer/C₆₀ solution concentration was reduced by 50%.

Figure 2.5. UV-Vis spectra of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) dissolved in toluene (0.5 mg/ml).

The spectral change for Figure 2.4. (iii) is attributed to the formation of a charge transfer complex.^{94, 95} FTIR spectroscopy provides further evidence for the complex formation. Upon aging of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) in toluene, the pyridine peak at 1603 cm⁻¹ is slowly shifted to 1618 cm⁻¹ as shown in Figure 2.6. The shifting of most characteristic peak due to interaction of P4VP near 1600 cm⁻¹ for C=N stretching indicates that a slight electron transfer took place from 4-vinylpyridine to C₆₀.

Figure 2.6. FT-IR spectra of (a) P4VP₈-b-PEO₁₀₅-b-P4VP₈/toluene; (b) two months aged solution of P4VP₈-b-PEO₁₀₅-b-P4VP₈/C₆₀ (95/5 w/w) in toluene.

The UV-Vis spectrum of polymer/C₆₀ nanocomposite in aqueous solution shows a broad peak of fullerene at about 340 nm indicating the presence of fullerene in aqueous solution as shown in Figure 2.7.

Figure 2.7. UV-Vis spectrum of polymer/C₆₀ nanocomposite in aqueous solution.

The aggregation behavior of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ block copolymers was studied by dynamic light scattering using Zetasizer Nano ZS and ZS90 (Malvern). The apparent hydrodynamic radius (R_h) can be calculated using the Stokes-Einstein equation (2.1):

$$R_h = \frac{kT}{6\pi\eta D} \quad 2.1$$

where k is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and D is the diffusion coefficient. The DLS was conducted at a scattering angle of 90°.

The polymer in toluene solution (1 mg/ml) showed bimodal peaks with mean diameters of ~24.4 nm and ~199 nm respectively. (Figure 2.8 (a)). The PDI was 0.534. The particle size ranges from 10 to 400 nm. However, in the presence of C₆₀ the polymer solution aggregates into one type of particle with mean diameter of 28.2 nm (Figure 2.9 (b)) with PDI 0.205. The particle size varies from 10 to 100 nm. The change in the aggregation behavior is clearly due to the C₆₀ complex formation.

Figure 2.8. Dynamic Light Scattering of (a) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ in toluene; (b) two months aged P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) in toluene; (c) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ nanocomposite in aqueous solution.

Change of modality of the P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ from bimodal to unimodal is the effect complexation of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with C₆₀. P4VP-C₆₀ moieties are more compatible with toluene than P4VP. (Figure 2.8(b)).

However, the higher solubility of PEO and P4VP blocks in aqueous is the one of the reason for change in size and distribution of $C_{60}/P4VP_8-b-PEO_{105}-b-P4VP_8$ nanocomposite after solvent exchange (Figure 2.8(c)). TEM micrographs are shown in Figure 2.9. Figure 2.9.(a) shows the micelle consisting of a compact P4VP core and PEO chains as the corona. This is because of different solubility of PEO and P4VP segments in toluene, PEO is soluble whereas P4VP has very poor solubility in toluene, THF and deionised water⁹⁶⁻⁹⁹

Figure 2.9. TEM images (a) $P4VP_8-b-PEO_{105}-b-P4VP_8$ in toluene with iodine stain; (b) Aged $P4VP_8-b-PEO_{105}-b-P4VP_8/C_{60}$ (95/5 w/w) in toluene solution(scale bar 500 nm)

without iodine staining; (c) Fullerene cluster from aqueous solution (100 nm); (c1) zoom in form of 'c' where fullerene clusters are visible, images were taken without iodine staining.

Whereas the polymer/fullerene composite in toluene and aqueous are shown in Figure 2.9.(b) & (c) respectively without iodine staining. The non-iodine staining was to avoid confusion between P4VP and fullerene which shows up clearly in the fullerene aggregates. The particle size from TEM studies is in good agreement with the light scattering data for the P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ polymer and C₆₀ complexes. From TEM it was determined that the C₆₀ clusters were aggregated with a size of ~30 nm. In light scattering studies, the polymer/C₆₀ nanocomposite micelle in aqueous solution shows the bimodal distribution with mean diameters of ~30 nm and ~110 nm. One of the reasons for change in mean diameter of C₆₀/P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ nanocomposite is the higher solubility of PEO blocks in aqueous. This agrees reasonably with the TEM images. The TEM images confirm the formation of fullerene cluster in both processes. The results confirm that the micelle in solution consists of P4VP in the core and the PEO in the corona. The fullerenes are located in the core of the polymer aggregates.

To evaluate the possibility of pure polymer and polymer/C₆₀ nanocomposite in aqueous solution for bio-application, *in vitro* cytotoxicity studies were performed by MTS assay, This is a colorimetric test, based on the selective ability of viable cells to reduce the tetrazolium component of MTS into purple colored formazan crystals. MTS assay was done for four different concentrations viz; 0.1 mg/ml, 0.25 mg/ml, 0.5 mg/ml and 1 mg/ml. The results (Figure 2.10) show that there is no significant cytotoxicity of the four

different concentrations of pure polymer and polymer/C₆₀ nanocomposite. It was found that more than 90% cells are viable in all the different concentrations for both the cases.

Figure 2.10. *In vitro* cytotoxicity studies of (B) polymer in water; (C) polymer/C₆₀ nanocomposite in water.

2.5. Conclusion

This study shows that P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ systems can lead to the formation of self-assembled structures. The C₆₀ complexation process has significant effect on the aggregation behaviour. Upon aging of the solution charge transfer complex between vinyl pyridine unit and C₆₀ was formed, which lead to the formation of self-assembled fullerene cluste. These results were supported by UV-Vis, TEM and DLS study. The formation of biocompatible P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ nanocomposite in water may have potential application in biomedicine, cosmetic (as singlet oxygen generator) or other useful applications. In summary, organic soluble and water-soluble, structurally well-defined C₆₀/polymer nanocomposites were achieved through the self-assembly of pristine C₆₀ with polymer. However, the rate of complex formation was found to be slow.

Chapter-III

**Dramatic solvent effect on interaction
kinetics and self-organization of phenyl-
C61-butyric-acid-methyl-ester (PCBM) in
a tri-block copolymer**

Abstract

We report a quantitative study on the interactions of a tri-block copolymer containing a polyethylene oxide (PEO) central block and two 4-vinyl pyridine (4VP) end blocks with a fullerene derivative methanofullerene phenyl-C₆₁-butyric-acid-methyl-ester (PCBM). While no obvious interaction can be detected between the copolymer and PCBM in toluene, there is, however, a well-defined charge transfer complex formation between the copolymer and PCBM in THF solution, which allows the interaction kinetics to be, studied both qualitatively and quantitatively. Under the experimental conditions, the interaction was found to follow the pseudo-first order kinetics. The rate constants were measured at different temperatures and kinetic and thermodynamic parameters of reaction were determined. Results also showed that the 4VP units in the block copolymer interacts with the fullerene derivative more than two orders of magnitude faster than does a small molecular model compound, tert-butyl pyridine. There seems to be an interplay between charge complexation kinetics and self-assembled supramolecular micellar structures of the copolymer/PCBM system. The findings should provide useful insight in the design and formation of nano-scale domains of fullerene and derivatives in polymer blend systems.

3.1. Introduction

Fullerenes and its derivatives have attracted considerable attention in recent years due to their unique electronic, superconducting, biochemical, electrochemical, photochemical and photophysical properties.^{75, 100-109} Fullerenes are used as functional nano-materials in the forms of nanowires, nanoclusters and thin films for wide range of applications. Recently, it is found that fullerene clusters in aqueous solution can generate singlet oxygen under photo-irradiation which has implications in the studies of biomedical and environmental science.⁸⁹ The study of the assembly of fullerene and its derivatives has also attracted increasing attention because of their potential in polymer bulk heterojunction solar cells as the electron acceptors.^{74, 110} Therefore, it is highly interesting to study the fullerene assembly behavior in the presence of polymers and the formation mechanisms of various fullerene nanostructures. Unlike the unmodified fullerenes, the applications of fullerene derivatives are no longer limited by poor solubility and processability,^{62, 111-116} although understanding and controlling of their clustering nano-scale morphologies are of paramount importance.¹¹⁵ Hence, intensive efforts have been directed towards overcoming these difficulties. One of the approaches is to organize fullerene and its derivative molecules by utilizing their specific interactions with amphiphilic copolymers. Block copolymers with fullerene derivatives are among the building blocks studied for functional nano-structured materials. Tailoring of the polymer blocks and architectures allows control of the micro, nano-scale structures, which lead to modification of the phase transitions for various applications.^{68, 90, 116-119} Another rational way is to introduce covalently linked functional groups, surfactants or long chain polymers to fullerene.^{82-84, 88}

In summary, there are mainly three kind of interactions which were used to ‘connect’ fullerenes with specific blocks of block copolymers, i.e., covalent interactions,^{55-57, 60, 66, 120} acid-base interactions, hydrogen bonding and charge transfer complexation.^{58, 59, 67, 112, 121, 122} Based on covalent interaction, pH and temperature responsive water soluble [60]fullerene-containing poly[2-(dimethylamino)-ethyl methacrylate] (C_{60} -*b*-PDMAEMA) and triblock copolymer poly(2-(dimethylamino) ethyl methacrylate)-block-poly(ethylene oxide)- block-poly(2-(dimethylamino)ethyl methacrylate) capped with C_{60} at both ends (C_{60} -DMAEMA₆₀-*b*-EO₁₀₅-*b*-DMAEMA₆₀- C_{60}) have been reported.^{67, 90} The acid-base interaction was exemplified in the supramolecular aggregates arising from the interaction between host block copolymers of styrene-*b*-(4-vinylpyridine) (PS-*b*-P4VP) and a guest [60]fullerene carboxylic acid which selectively bonds to the basic pyridine groups resulting in a self-assembled structure.⁵⁹ Yet another interaction is the formation of charge transfer complexes through electron donor–acceptor interactions.^{121, 122} Self-assembled structure of unmodified fullerenes with PS-*block*-P4VP block copolymers via charge-transfer complexation in xylene has been reported.⁶⁸ In particular, polymer solar cells were fabricated by taking the advantages of the charge transfer interaction of fullerene and a poly(3-hexyl thiophene-*b*-4-vinyl pyridine) (P3HT-*b*-P4VP) block copolymer.⁷⁷ However, the reported studies concerning fullerene and block copolymer interactions have focused on the morphology of fullerene because of its importance in applications, notably in solar energy harvesting and photo-biochemistry. Although it is recognized that the final domain morphologies of fullerene are inevitably affected if not governed by its interaction, e.g., charge transfer complexation, with the polymer systems, there is no quantitative study on the interaction kinetics between copolymers and

fullerene derivatives. It is therefore highly desirable to investigate the kinetics and mechanisms of such an important interaction. Kinetics study is essential in the process of understanding how the interaction affects the self-assembled structures of the copolymer/fullerene hybrids. In this work, we analyze the interaction kinetics of a fullerene derivative and a block copolymer containing 4-vinyl pyridine blocks. Solvent and temperature dependency of the interaction kinetics are discussed quantitatively and the changes in supramolecular self-assembly due to fullerene-copolymer interaction were investigated. Furthermore, studies using small molecular model pyridine compound allow better understanding of the phenomena observed in the copolymer.

3.2. Materials and Method

3.2.1. Chemicals and materials

The hydroxy-end-capped PEO [degree of polymerization (DP), 105; PDI, 1.08] were purchased from Aldrich. 4-Vinyl pyridine (VP) (Aldrich, 99%) was purified by stirring over CaH_2 , and distilled under vacuum. 2-Bromoisobutyryl bromide, triethylamine, CuCl (99.99%), N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA 95%), PCBM (>99.5%) were purchased from Aldrich and used without further purification. Analytical grade toluene (99.8%) and tetrahydrofuran (THF, 99.9%) were used without further purification.

3.2.2. Synthesis of tri-block copolymer $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8$

The block copolymer $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8$ was prepared via atom transfer radical polymerization (ATRP) as described in Figure 3.1. PEO was reacted with 2-bromoisobutyryl bromide to prepare a Br-terminated PEO macroinitiator with PDI of 1.14. 4-Vinyl pyridine was copolymerized with the macroinitiator in the presence of CuCl /PMDETA catalyst in DMF at 50°C . The tri-block copolymer obtained has a PDI of 1.21. The synthesis of block copolymer was described in previous chapter.

3.2.3. Formation of charge transfer complex

It is known that fullerene may form donor-acceptor charge transfer complexes with pyridine in the copolymers.⁶⁸ 1 mg/ml copolymer $\text{P4VP}_8\text{-}b\text{-PEO}_{105}\text{-}b\text{-P4VP}_8$ solution in toluene or THF was prepared by stirring the required amount of copolymer into the solvent for 24 hrs. Separately, PCBM was dissolved in toluene or THF to prepare a 1

mg/ml solution. Toluene and THF were used because of their ability to dissolve the copolymer and PCBM. The initial color of toluene/PCBM solution was purple while THF/PCBM was light brown. Required amount of toluene/PCBM solution was mixed with 20 ml of toluene/copolymer solution, the required amount of THF/PCBM solution was added to 20 ml of the THF/copolymer solution, in order to maintain a consistent molar ratio of [copolymer]:[PCBM] at 4.5:1, which corresponds to a [4VP]:[PCBM] of about 70:1. Freshly prepared solution mixtures were used for kinetic studies. The color of the solution gradually turned dark brown for THF/PCBM/copolymer and for Toluene/PCBM/copolymer system it is gradually changed to light brown color. The copolymer concentration and the corresponding 4VP concentration are $1.59 \times 10^{-4} \text{ mol L}^{-1}$ and $2.548 \times 10^{-3} \text{ mol L}^{-1}$ respectively.

Figure 3.1. Scheme for preparation of the triblock copolymer and charge transfer complex between P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and PCBM.

3.3. Characterization

An Agilent 1100 series GPC system equipped with a liquid chromatography pump, DMF column, and refractive index detector was used to determine the molecular weight and molecular weight distributions. The column was calibrated with polystyrene standards. The eluent was HPLC grade DMF at a flow rate of 1.0 ml/min. ^1H NMR spectrum for the block copolymer in CDCl_3 (1 mg/ml) was recorded using a Bruker DRX400 instrument at 25 °C. FTIR spectra were recorded on a Perkin Elmer FTIR system 2000 using 32 number of scans. A Shimadzu UV spectrophotometer, UV2501PC, was used to monitor the complex formation with time. The supramolecular aggregates of clusters were observed using a JEOL JEM-2010 transmission electron microscope operating at an accelerating voltage of 200 kV. TEM specimens were prepared by dropping one or two drops of the solution onto carbon-coated 400-mesh copper grids pre-coated with Formvar.

3.4. Results and Discussion

3.4.1. Polymer Synthesis and complexation

The block copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was prepared via atom transfer radical polymerization (ATRP) as described in Figure 3.1 PEO was reacted with 2-bromoisobutryl bromide to prepare a Br-terminated PEO macroinitiator with PDI of 1.14. 4-Vinyl pyridine was copolymerized with the macroinitiator in the presence of CuCl /PMDETA catalyst in DMF at 50 °C as described in previous chapter. ¹H NMR spectra provide evidence for the charge transfer interaction. Figure 3.2 compares the NMR spectra of PCBM, copolymer and a PCBM/copolymer hybrid in THF solution. An emergence of sharper shoulder peaks in vinylpyridine region, δ (ppm): 8.32, 6.36 (for *ortho* and *meta* H of 4VP) was seen after ageing of the mixed solution of PCBM and the copolymer. This is consistent with a de-shielding effect due to the shift of electron from nitrogen of pyridine to PCBM which allows the *ortho* and *meta* H of 4VP to resonate at lower magnetic fields.⁹⁴

Figure 3.2. ^1H -NMR (700 MHz) study of charge transfer complexation between P4VP_8 - b - PEO_{105} - b - P4VP_8 and PCBM in deuterated THF showing the emergence of sharper shoulder peaks at 6.82 and 8.75 ppm after 4320 minutes (72 hrs) interaction.

Figure 3.3 shows the FTIR spectra of the copolymer, PCBM and copolymer/PCBM hybrid in THF, which also clearly indicates the charge transfer interaction between copolymer and the fullerene derivative. Upon mixing of P4VP_8 - b - PEO_{105} - b - P4VP_8 with PCBM, in addition to the expected pyridine peak at 1603 cm^{-1} , another peak appeared at 1633 cm^{-1} . The 1633 cm^{-1} band is believed to be due to the pyridine ring after electron transfer to the fullerene took place.^{123, 124}

Figure 3.3. FTIR spectra of (a) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/THF; (b) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with PCBM in THF after complex formation for 4320 minutes (72 hrs); (c) PCBM in THF.

3.4.2. Kinetics of charge transfer complexation

Perhaps one of the simplest and yet effective ways of studying the charge transfer complex formation is via monitoring the changes of the UV-Vis spectra during the interaction between PCBM and P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈. Figures 3.4.a to 3.4.c show the time-resolved UV-Vis absorption spectra of the PCBM and copolymer mixture in THF at different temperatures, 25, 40 and 50 °C.

Figure 3.4. Time resolved UV-Vis spectra following the interaction of P4VP₈-PEO₁₀₅-PCBM in THF recorded at different temperatures (a) 25 °C; (b) 40 °C;

(c) 50 °C. In all studies, polymer concentration was kept at 1 mg/ml corresponding to a [4VP] of 2.54×10^{-3} M, and PCBM concentration was kept at 3.6×10^{-5} M with [PCBM]/4VP ratio of 1:71. (d) For comparison, a series of spectra monitoring the interaction between a model small molecular pyridine compound, tert-butyl pyridine (6.7×10^{-2} M) and PCBM (3.6×10^{-5} M) were recorded at 40 °C. The spectra of the copolymer/THF solution, P1 and PCBM/THF solution, P2 are also given in (a) for comparison.

In Figure 3.4.(a), the initial spectrum after mixing solutions of PCBM/THF and copolymer/THF shows a distinct peak at 330 nm, assignable to the absorption of the fullerene derivative, overlapped on a background of the copolymer and the solvent. The intensity of this peak reduces gradually with increasing time of interaction or aging of the solution mixture, as can be seen in the time-resolved absorption spectra in Figures 3.4.(a)-3.4.(c). Furthermore, two isobestic points were observed at about 321 and 346 nm in the time-resolved spectra indicating formation of well-defined charge transfer complex between the copolymer and PCBM. An enlarged portion of the spectra is given in the inset of Figure 3.4.(b), which provide a clearer view of the isobestic point. Kinetics of the interaction can be quantitatively analyzed by following the changes in absorbance in the spectra as a function of time. The reaction rate was analyzed using the absorbance at two wavelengths i.e., 310 nm and 329 nm which are located at each side of an isobestic point respectively. The first-order rate constant, k_A , can be determined using the equation (1).¹²⁵

$$\ln \frac{A_{\infty} - A_t}{A_{\infty} - A_o} = -k_A t \quad (3.1)$$

where t is time, A_0 , A_t , and A_∞ are the initial absorbance, absorbance at time t , and absorbance at infinite time respectively. Similar study was carried out at 25 °C., 30 °C. 40 °C. and 50 °C. As an example, the plot of $\ln \frac{A_\infty - A_t}{A_\infty - A_0}$ versus time for the complexation at 50 °C is shown in Figure 3.5. (a), and the rate constants k_A can be determined from the gradient of the linear plots.

Figure 3.5. (a) Plots of $\ln \frac{A_\infty - A_t}{A_\infty - A_0}$ versus time for the charge transfer complex formation

at 50 °C using absorbance data at different wavelength, i.e., 329 and 310 nm.

Figure 3.5. (b) Arrhenius plots of $\ln k$ versus $1/T$; (c) Eyring plots of $\ln(k/T)$ versus $1/T$.

By using the same method, rate constants at different temperatures were determined.

Table 3.1 shows that the k_A values obtained using the absorbance data at the two different wavelengths i.e., 329 and 310 nm are in good agreement and the k_A value increases with temperature. Since the 4VP in copolymer is in large excess in comparison to the PCBM concentration used in this study, the k_A so obtained is the apparent pseudo first-order reaction rate. Division of k_A by the molar concentration of the 4VP units in the copolymer converts it to the corresponding second order rate constant k (Table 3.1). Based on equations 2 and 3, the Arrhenius plots of $\ln(k)$ versus $1/T$ and Eyring plots of $\ln(k/T)$ versus $1/T$ were generated using data in Table 3.1. Both show linear relationships as seen in Figures 3.5.(b) and 3.5.(c).

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln(A) \quad \text{Arrhenius equation (3.2)}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R} \quad \text{Eyring equation (3.3)}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3.4)$$

where T is temperature, E_a the activation energy, R the universal gas constant, $\Delta H^\ddagger$ enthalpy of activation (J mol^{-1}), $\Delta S^\ddagger$ entropy of activation ($\text{J K}^{-1} \text{mol}^{-1}$), h the Planck constant, k_B the Boltzmann's constant and $\Delta G^\ddagger$ the Gibbs free energy of activation (J mol^{-1}).

Table 3.1. Pseudo first order rate constants k_A (s^{-1}) and the second order rate constants k ($Lmol^{-1}s^{-1}$) of the complexation between P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and PCBM in THF at different temperatures determined at $\lambda = 310$ and $\lambda = 329$ nm.

$\lambda = 310$ nm

T (K)	1/ T×10 ³ (1/K)	k_A (s^{-1})	$k = k_A/[4VP]$ ($Lmol^{-1}s^{-1}$)	lnk	ln(k/T)
298	3.36	6.97×10^{-6}	2.74×10^{-3}	-5.90	-11.60
303	3.30	1.24×10^{-5}	4.87×10^{-3}	-5.32	-11.04
313	3.19	3.57×10^{-5}	1.41×10^{-2}	-4.26	-10.01
323	3.10	9.50×10^{-5}	3.73×10^{-2}	-3.29	-9.07

$\lambda = 329$ nm

T (K)	1/ T×10 ³ (1/K)	k_A (s^{-1})	$k = k_A/[4VP]$ ($Lmol^{-1}s^{-1}$)	lnk	ln(k/T)
298	3.36	6.90×10^{-6}	2.71×10^{-3}	-5.91	-11.60
303	3.30	1.12×10^{-5}	4.39×10^{-3}	-5.43	-11.14
313	3.19	4.31×10^{-5}	1.69×10^{-2}	-4.08	-9.83
323	3.10	7.80×10^{-5}	3.06×10^{-2}	-3.49	-9.26

Table 3.2 tabulates the values of E_a , obtained from the Arrhenius plots, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ from the Eyring plots, and $\Delta G^\ddagger$ calculated using equation 4 at 295 K.

Table 3.2. Activation energy and thermodynamic parameters of activation for the complexation of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with PCBM in THF. The values calculated at $\lambda = 310$ and $\lambda = 329$ nm are presented.

λ (nm)	E_a (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)*
310	83.5	81.0	-22.1	87.6
329	81.0	78.4	-30.4	87.4

* $\Delta G^\ddagger$ data are obtained at 298 K.

It can be seen that very similar values are obtained using absorbance data at the two selected wavelengths although $\Delta S^\ddagger$ seems to have a slightly larger discrepancy. However, such discrepancy is not unexpected due to the small value of $\Delta S^\ddagger$. The $\Delta S^\ddagger$ data are in fact reasonable in this case. The entropy of activation $\Delta S^\ddagger$ was found to be a relatively small and negative value of -22 J K⁻¹mol⁻¹. Its negative signage means that the transition state of the complexation has a lower degree of freedom than the initial reactants, the copolymer and PCBM. This is consistent with the expected 'gaining of ordering' through charge transfer complex formation between the 4VP units in the copolymer and PCBM. The small entropy change in this case also indicates that the conditions are favourable towards forming the transition state. The enthalpy of activation, $\Delta H^\ddagger$ (83.5 kJ mol⁻¹) shows the barrier energy of the charge complex interaction similar to

that described by the activation energy, E_a (81 kJmol⁻¹). The positive value of Gibbs free energy of activation, $\Delta G^\ddagger$ (87.6 kJ mol⁻¹) indicates that the formation of the transition state is not necessarily spontaneous and may occur under specific conditions.

A parallel study was conducted to compare the rate of complexation between P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and PCBM, and between a small molecular model pyridine compound, 4-*tert*-butyl pyridine and PCBM. The time-resolved UV-Vis absorption spectra collected at 40 °C are shown in Figure 3.4 (d). Similarly the pseudo-first order rate constant was determined from the linear kinetics plots using equation 3.1. Table 3.3 compares the rate constants of complex formation of *tert*-butyl pyridine with PCBM and that of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ with PCBM.

Table 3.3. Comparison of rate constants for the complex formation between PCBM and P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and 4-*t*-butyl pyridine at 40 °C (313 K) in THF.

λ (nm)	PCBM and P4VP ₈ -PEO ₁₀₅ -P4VP ₈	PCBM and 4- <i>t</i> -butyl pyridine	k ratio
310	1.41×10^{-2}	9.4×10^{-5}	1:151
329	1.69×10^{-2}	8.38×10^{-5}	1:170

It is noted that the block copolymer forms charge complexes with the fullerene derivative more than 150 times faster than does the small molecular pyridine model compound.

This large difference in rate constants is due to differences in the reaction environments of pyridine units at the molecular level. In the block copolymer, the 4VP units are compartmented within the self-assembled micelles (The morphology of which will be

further discussed later), while the 4-tert-butyl pyridine molecules are randomly and more sparsely distributed in the THF solvent. Therefore, the probability of interaction with PCBM should be higher in the micelles which can be considered as ‘nano-reactors’ for the charge transfer complex formation.

Interestingly, this complexation between P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and PCBM is not observed when toluene was used as the solvent instead of THF. Figure 3.6.(a) shows the time-resolved UV-Vis spectra monitoring the interaction of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and PCBM in toluene.

It can be seen that there is little change in the absorption spectra over an extended period of time even after 28 days. No isobestic point appeared in the time-resolved absorption spectra. Therefore, we were not able to carry out quantitative kinetic analysis for the complexation of PCBM with the copolymer in toluene. In order to understand this further, time-resolved spectra are also recorded to monitor the complex interaction of tert-butyl pyridine and PCBM in toluene and are shown in Figure 6.(b). Similarly, only minute spectral change was detected after 28 days, indicating that interaction between tert-butyl pyridine and PCBM is also extremely slow.

Figure 3.6. Time resolved UV-Vis spectra following the interaction between P4VP₈-b-PEO₁₀₅-b-P4VP₈ and PCBM in toluene (a) and between tert-butyl pyridine and PCBM (b) collected over 28 days at 25 °C. The concentrations of copolymer and PCBM were kept

the same as those in Figure 3.4. The spectra of the copolymer/toluene solution, P1 and PCBM/toluene solution, P2 are also given in (a) for comparison.

Therefore, we believe that the lack of interaction between PCBM and P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ in toluene is due primarily to a solvent effect because toluene is expected to have a much stronger affiliation with fullerene due to its more hydrophobic nature and presence of π conjugated aromatic structure in toluene in comparison to THF.^{94, 95} Therefore, toluene, which is the solvent and in large excess, might have hindered the charge complexation between PCBM and either the copolymer or the model small molecular pyridine compound. As a result, the interaction of PCBM and pyridine moieties, either 4VP in the copolymer or tert-butyl pyridine model compound, is substantially slower in toluene, whilst well-defined complexes are formed in THF at a faster rate.

3.4.3. Morphology of Micelles

The morphology and micellization behavior of the copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was studied using light scattering. The apparent hydrodynamic radius (R_h) was determined from dynamic light scattering (DLS) analysis and calculated using the Stokes-Einstein equation 3.5,

$$R_h = \frac{k_B T}{6\pi\eta D} \quad (3.5)$$

where k_B is the Boltzmann's constant, η the solvent viscosity, and D the diffusion coefficient. The DLS experiment was conducted at a scattering angle of 90°. Static light

scattering was also conducted to determine the radius of gyration R_g . Table 3.4 summarizes the light scattering data. Results show that the average hydrodynamic diameter (D_h) of micelles of the copolymer in THF (1 mg/ml) is 98.1 nm and only a single scattering peak was observed. DLS reveals that the micelle size gradually reduces upon aging and complexation between P4VP with PCBM. The D_h value eventually reduced to and stabilized at 62.2 nm after 76 hrs of aging of the copolymer/PCBM solution in THF. In solution, the triblock polymer is believed to assemble into flower type micelles containing PEO and P4VP as the corona and core respectively⁹⁸, and the values of R_g/R_h between 1.1 and 1.3 corroborate with this micelle structure.¹²⁶ The significant decrease of copolymer micelle size may be attributed to the interaction of P4VP with PCBM which reduced the segmental motion of P4VP blocks in the micelles in the core. One reason for the decreasing micelle diameter is the enhanced inter-chain interaction in the micelle when the 4VP units from two or more copolymer chains interact with the fullerene derivative simultaneously. This may give rise to a more compact micelle structure. DLS data also show that the polydispersity index (PDI) of the micelles size remained virtually the same at about 0.30 throughout the solution aging process during which the complexation occurs, indicating good micelle stability.

However, the assembly behavior of the copolymer is very different when toluene is used as the solvent. Although micellization took place, DLS analysis indicates that the micelles have a bi-modal size distribution with average D_h values of 194 and 20.7 nm respectively (Table 3.4).

Table 3.4. Summary of light scattering data showing the micelle morphology

System	D _h (nm)	PDI
Freshly Prepared Copolymer/PCBM/THF	96.0	0.31
Copolymer/PCBM/THF after long time ageing (145 hours)	62.1	0.30
Freshly Prepared Copolymer/PCBM/Toluene	194 (70.4%) ^a 20.4 (29.6%) ^a	0.52
Copolymer/PCBM/Toluene after long time ageing (12 days)	190 (73.7%) ^a 23.4 (26.3%) ^a	0.49

^a The sizes of the bi-modal distributed micelles are tabulated and their corresponding percentages are given in parentheses.

Hence, a wide polydispersity is resulted. Furthermore, in the presence of PCBM, the micelles showed no obvious change in size and the bi-modal distribution characteristics was maintained after 12 days ageing of the solution mixture. This finding is consistent with the observation in the UV-Vis spectroscopic study discussed earlier and both data support the explanation given in the previous section on the solvent effect, that is, the complexation between the copolymer and PCBM in toluene is too slow to cause changes in micelle structure in the time scale investigated in this work. Direct observation of morphology was also carried out using electron microscopy. TEM images shown in Figure 3.7 corroborate with the light scattering results. Figures 3.7.(a) and 3.7.(b) confirm that, in THF, the micelles have a single modal distribution with significant size reduction after the complexation of copolymer and PCBM, while Figures 3.7.(c) and 3.7.(d) clearly

show a bi-modal micelle size distribution characteristics and no size reduction upon ageing of the solution.

Figure 3.7. TEM images of samples after solvent evaporation: (a) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ from THF solution (b) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/PCBM from a 76 h aged THF, (c) P4VP₈-PEO₁₀₅-P4VP₈ in toluene, (d) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/PCBM in toluene solution after 12 days.

3.5. Conclusion

Quantitative analysis of kinetics of charge transfer complexation between the triblock copolymer P4VP₈-PEO₁₀₅-P4VP₈ and fullerene derivative PCBM was carried out. The complexation interaction follows a pseudo first order kinetics. Interaction constants were determined using time-resolved absorption spectroscopy at different temperatures in THF. Activation energy and parameters of thermodynamic of activations were obtained. The comparative study of the interaction between a small molecular model pyridine compounds allows further understanding of the influence of supermolecular assembly of the copolymer on the complexation kinetics. On the other hand, morphological study using light scattering and transmission electron microscopy reveals that the supermolecular assembly is significantly affected by the complex formation. There is a contraction of micelle size of the copolymer upon complexation with PCBM. This is due to reduction of P4VP chain mobility after complexation with PCBM and enhanced interchain interaction among the P4VP blocks since a fullerene derivative could have change transfer interactions with more than one P4VP blocks simultaneously. The kinetics of the complexation was found to be sensitive to solvent. While the kinetics of interaction between the copolymer and PCBM can be analyzed quantitatively in THF, their interaction is so slow in toluene that no meaningful kinetics analysis was able to be performed under the conditions studied. A clear understanding of the interplay between molecular assembly, complexation and solvent effect should serve as a guide in designing nano-structured fullerene derivatives in polymer systems.

Chapter-IV

**Rate enhancement of charge transfer
complexation for self-assembly of
underivatized fullerene by electron
donating units of block copolymers**

Abstract

Here, we report a technique for the rate enhancement of complex formation with tunable morphology of unmodified fullerene utilizing the electron-accepting property of underivatized fullerene (C_{60}) & the electron-donating property of the pyridine groups in a polystyrene-*block*-poly(4-vinylpyridine), PS-*b*-P4VP. The kinetics of complex formation of C_{60} /PS-*b*-P4VP in THF and toluene were studied by UV-Vis spectrophotometry. The poor solubility of underivatized fullerene in THF system was overcome by adding small amount of C_{60} in toluene solution. The rate of complex formation was increased in THF solution and the reaction completed within 10 days whereas in pure toluene solution, there was negligible reaction even after one month. Significant morphological differences were observed when the THF solvent of 10 days aged C_{60} /PS-*b*-P4VP in THF was replaced by toluene. The structures of PS-*b*-P4VP and C_{60} /PS-*b*-P4VP aggregates in thin films were studied by TEM. The micellar aggregates in solution were studied by DLS.

4.1. Introduction

Fullerenes are widely used as functional nanomaterials in the form of nanowires, nanoclusters and thin films for their potential application in the fields of sensor, optics, and electronics. Chemical modification of fullerene has been done to improve solubility, controlled assembly, and to provide further functionalities.^{49, 50, 127} In an effort to control the aggregation and to achieve functional properties in electron acceptors of polymer bulk hetero-junction solar cells, fullerenes have been combined with block copolymer.^{73-75, 104} Therefore, it is highly interesting to understand fullerene assembly behavior in the presence of polymers. Controlled clustering nano-scale morphologies of fullerene in polymer systems are of paramount importance.^{73-75, 77, 89, 104, 110} Block copolymers are useful building blocks for functional nano-structured materials and can be tuned into different micro and nano-scale structures with proper design and manipulation.^{90, 116-119} One of the successful ways to organize fullerene in polymers is to introduce covalent link to fullerene either directly on fullerene moiety or by functionalizing the fullerene.^{82-84, 88} Shinkai and co-workers reported supramolecular aggregates of fullerene through the aggregation of C₆₀ derivatives containing a carboxylic group, with PS-*b*-P4VP in an organic solvent.⁵⁹ While this enables rather precise control in morphology, the covalent modification of fullerene may also cause undesirable changes in the properties of the fullerene.^{85, 86} A more effective and promising approach is to organize underivatized fullerene by utilizing specific non-covalent interactions with block copolymers. One of the most convenient ways to organize fullerene and derivatives into nanostructures is by using the charge transfer complexation between fullerene and block copolymers. Recently, interesting results on polymer solar cells were obtained from a blend of a

fullerene derivative and a block copolymer poly(4-vinyl pyridine) of poly(3-hexyl thiophene) (P3HT-*b*-P4VP).⁷⁷ In another article, well-defined fullerene nanoclusters were synthesized in aqueous solutions via a block copolymer assisted self-organization.⁸⁹ However, the rate of fullerene organization can be very slow and it was reported that several months was needed to complete the self-assembly of underivatized fullerene nanostructures within a model block copolymer PS-*b*-P4VP.⁶⁸ Recently, we reported the quantitative study on the interactions of a tri-block copolymer containing a polyethylene oxide (PEO) central block and two 4-vinyl pyridine (4VP) end blocks with a fullerene derivative methanofullerene phenyl-C61-butyric-acid-methyl-ester (PCBM). The rate of complex formation was highly enhanced in THF solution.¹²⁸ However, the poor solubility of the underivatized fullerene in THF (0.006 mg/ml) remains a main hurdle to its application. In the present work, we show a particularly facile method to increase the rate of complexation and self-assembling process of underivatized C₆₀ with PS-*b*-P4VP block copolymers by improving the solubility of underivatized C₆₀ in THF. This can be achieved by adding C₆₀/toluene solution into polymer/THF system. Solvent exchange has been done by replacing THF of 10 days aged C₆₀/PS-*b*-P4VP in THF solution with toluene using solvent evaporation technique. The morphological changes were monitored by TEM in film and DLS in solution.

4.2. Materials and Methods

PS-*block*-P4VP with 47,600 and 20,900 g/mol of PS and P4VP blocks respectively with polydispersity of (M_w/M_n) 1.14 was obtained from Polymer Source Inc. Fullerene (99.5%) was purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) (99.9%), and toluene (>99.8%, Fluka) were used as received.

The procedure for sample preparation is as follows. Micellar solution of PS-*block*-P4VP in THF and toluene (1 mg/ml) were prepared. Fullerene was separately dissolved (1 mg/ml) in toluene. The color of the solution was purple. The fullerene solution was then added to 19.5 ml of polymer-THF (1 mg/ml) stock solution, keeping polymer and fullerene weight ratio at 97.5:2.5. No precipitation was observed, indicating that underivatized fullerene was well mixed in the THF. The formation of charge transfer complex was monitored by UV-Vis spectrophotometry as a function of time. A similar experiment was carried out in toluene to compare the rate of complexation in THF. Solvent exchange has been carried out using 10 days aged fullerene/PS-*b*-P4VP in THF with toluene using solvent evaporation technique at 80 °C for 6 hrs. The experimental procedure for charge-transfer complexation between PS-*b*-P4VP and underivatized fullerene is presented in Figure 4.1.

Figure 4.1. Schematic illustration for the experimental procedure for charge transfer complex formation between PS-*b*-P4VP and underivatized C₆₀.

4.3. Characterization

A Shimadzu UV spectrophotometer, UV2501PC, was used to monitor the complex formation as a function of time. Zetasizer Nano ZS and ZS90 (Malvern) were used to perform dynamic light scattering (DLS) experiments. The aggregation behavior of PS-*b*-P4VP/THF and PS-*b*-P4VP/C₆₀ in THF and toluene solutions were analyzed by dynamic light scattering. The supramolecular aggregates of clusters were studied by a JEOL JEM-2010 transmission electron microscope, operating at an accelerating voltage of 200 kV. TEM specimens were prepared by dropping one or two drops of solution onto carbon-coated 400-mesh copper grid.

4.4. Results and discussion

One of the simplest but effective ways of studying the charge complex formation is via monitoring the changes of the UV-Vis spectra during the interaction between underivatized fullerene and PS-*b*-P4VP. Figures 4.2 (a) shows the UV-Vis absorption spectra of the C₆₀ and copolymer mixture in THF at 25 °C at different time intervals.

The initial spectrum after mixing C₆₀/PS-*b*-P4VP in THF shows a distinct peak at 330 nm, and its absorbance reduces gradually with increasing time of interaction (Figure 4.2 (a)). Furthermore, isosbestic points at about 345 & 320 nm were observed along with an increase in absorbance in the region 345-550 nm. These observations support the formation of charge-transfer complexes between the electron donating pyridine solvent and the electron-accepting fullerenes.^{94, 95}

The UV-Vis spectra in Figure 4.2 (a) also shows that complexation process in THF system took just about 10 days to complete whereas in toluene system the change in UV-Vis spectra is negligible even after one month (Figure 4.2 (b)). The lack of interaction between fullerene and PS-*b*-P4VP in toluene is primarily a solvent effect because toluene is expected to have a much stronger affinity with fullerene due to its hydrophobic nature and the presence of a π conjugated aromatic structure of toluene.^{94, 95} Therefore, toluene could have hindered the charge complexation between fullerene and block copolymer. As a result, the interaction of fullerene and pyridine moieties in the block copolymer was significantly slower in toluene as stated previously

Figure 4.2. The UV-Vis spectra changes for the interaction of PS-*b*-P4VP with underivatized fullerene at 25 °C in (a) THF; (b) toluene.

In another experiment solvent exchange was carried out with a 10 day aged C_{60} /PS-*b*-P4VP in THF with toluene, utilizing the solvent evaporation technique.

Figure 4.3 (iii) shows the final UV-Vis spectrum in toluene after solvent exchanged from THF. This spectrum is similar to that obtained after several months of reaction time in pure toluene solution without the solvent exchange with THF.¹²⁹

Figure 4.3. UV-Vis spectra of (i) PS-*b*-P4VP in toluene; (ii) complex formation of underivatized fullerene with PS-*b*-P4VP in THF after 10 days; (iii) after the THF of (ii) was replaced by toluene.

The morphology of the system could be influenced by the type of solvent. It was reported that the aggregates in toluene is more uniform.¹²⁹ The aggregation behavior of PS-*b*-P4VP block copolymers was studied by dynamic light scattering. The apparent hydrodynamic radius (R_h) can be calculated by Stokes-Einstein equation (4.1),

$$R_h = \frac{kT}{6\pi\eta D} \quad (4.1)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and D is the diffusion coefficient.

Table 4.1. The DLS data obtained at scattering angle of 90° .

	PS-<i>b</i>-P4VP (a)	C₆₀/PS-<i>b</i>-P4VP in THF after 4 days (b)	C₆₀/PS-<i>b</i>-P4VP in THF after 10 days (c)	C₆₀/PS-<i>b</i>-P4VP in toluene (obtained by solvent exchange process) (d)
Nature	Bimodal	Bimodal	Unimodal	Unimodal
Mean diameter (nm)	82.2 (41.2%) ^a 11.8 (58.8%) ^a	50.1 (93.9%) ^a 9.9 (6.1%) ^a	66.9 (100%) ^a	72.0 (100%) ^a
PDI	0.517	0.285	0.165	0.074

^a The sizes of distributed micelles and the corresponding percentages are given in parentheses.

The PS-*b*-P4VP/THF solution (1 mg/ml) shows bimodal peaks with an overall PDI of 0.517. One peak has a mean diameter of ~82.2 nm (41.2%) where the micelles size ranges from 50 to 120 nm. The other peak has a diameter of 11.6 nm (58.8%) (Figure 4.4 (a)). For the solution of C₆₀/PS-*b*-P4VP in THF (Figure 4.4 (b)) after four days the bimodal peaks have the mean diameters of 50.1 nm (93.9%) and 9.9 nm (6.1%) with PDI to 0.285. In 10 days (Figure 4.4 (c)), it becomes unimodal with a size of 66.9 nm (100%) of 0.165 PDI.

The results show that the micelle size gradually changes from bimodal to unimodal with improved PDI upon aging due to complexation between P4VP of PS-*b*-P4VP and C₆₀.

Figure 4.4. Size distribution and intensity data of (a) PS-*b*-P4VP in THF solution; (b) 4 days aged PS-*b*-P4VP/C₆₀ in THF; (c) 10 days aged PS-*b*-P4VP/C₆₀ in THF; (d) PS-*b*-P4VP/C₆₀ in toluene obtained by replacing THF of (c) with toluene.

The mean diameter of micelle eventually stabilized at 66.9 nm after 10 days of aging of the C₆₀/PS-*b*-P4VP solution in THF.

However, when the solvent exchange process was utilized to obtain a complex of C₆₀/PS-*b*-P4VP in toluene (Figure 4.4 (d)), the aggregates formed were more uniform with low

PDI (0.074) and an average size of 72.1 nm (100%). This indicates that C_{60} influences the aggregation behavior of $C_{60}/PS-b-P4VP$ via complexation.

The TEM micrographs show the changes in morphology of the aggregates.

Figure 4.5. TEM images of samples cast on copper grid from (a) $PS-b-P4VP$ in THF solution & stained with iodine; (b) 10 days aged $PS-b-P4VP$ /underivatized fullerene in THF without iodine staining; (c) $PS-b-P4VP$ /underivatized fullerene in toluene obtained by replacing THF of (b) with toluene.

Figure 4.5 (b) shows the TEM image of 10 days-aged $C_{60}/PS-b-P4VP$ in THF cast on copper grid without iodine staining. It shows a well-defined assembled structure where the fullerene is in the P4VP domain. This morphological change is due to the effect of

weak interaction between P4VP and C_{60} , making P4VP core more solid and rigid, and less soluble in THF. Therefore a larger difference in solubility between PS block and P4VP block results in well-defined structure but the difference in solubility or swelling ability between PS block and P4VP block by THF without complexation is less. Figure 4.5 (c) of $C_{60}/PS-b-P4VP$ in toluene (obtained by solvent exchange process) shows higher uniformity of the well-defined structure in comparison with that obtained in THF. Since there is larger difference in solubility between PS and P4VP block than THF, complexation of $C_{60}/PS-b-P4VP$ in toluene becomes predominant, resulting in a more well-defined structure.

In summary, the rate of complexation shows dramatically enhanced in THF and the reaction completed in about 10 days, whereas the same system in toluene shows negligible changes even after one month.

4.5. Conclusion

It had been demonstrated that the assembly of underivatized fullerene with block copolymer could be achieved by using specific non-covalent interaction (i.e. charge transfer complex) at faster rate. Charge transfer interaction of C_{60} with PS-*b*-P4VP was dependent on the solvent system used. The complexation reaction was very much faster in THF compared to that in toluene, in which the reaction took more than several months to complete. The poor solubility of fullerene in THF system was overcome by adding a small amount of C_{60} /toluene solution. However, the solvent system used in the reaction also influenced the morphological structure of the complex. The morphological structure of the C_{60} /PS-*b*-P4VP prepared from the solvent exchange technique in toluene was more uniform compared to the complex prepared in THF. This study has demonstrated that the formation of well defined structures could be obtained in a much shorter time through a solvent exchange approach. With careful manipulation, the morphology of the materials obtained from the C_{60} /PS-*b*-P4VP system, could also be fine tuned to a certain extent.

Chapter-V

A facile method based on block-copolymer assisted preparation of functional hybrid materials containing ZnO quantum dots

Abstract

In this study we attempted a simple, one-step direct synthesis of ZnO Quantum Dots (QDs) by a new ***Open-Lock-Decompose (OLD)*** mechanism. Using the mechanism, we were successful in producing well assembled, narrowly distributed ZnO QDs of size 4.5 ± 1 nm with tunable morphology. The method is suitable for large-scale fabrication of ZnO QDs composites. Non-toxic zinc acetate dihydrate was used as a ZnO precursor. The co-ordinating property of poly(4-vinylpyridine) (P4VP) block towards Zn^{2+} ion was used as an assembly tool from solution phase polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) micelles in toluene. The resulting hybrid material containing ZnO QDs could be obtained on various substrates in a straightforward manner after heating at 200 °C for 30 min. The final product was characterized by XRD, TEM, UV-Vis and PL. In this chapter the mechanism of ZnO QDs synthesis and effect of different factors *e.g.* temperature and time on the synthesis has been discussed. The effect of other factors such as nature of polymer, cross linking agent, block length of polymer and type of solvent on the assembly of ZnO QDs were also studied.

5.1.1. Introduction

Zinc oxide (ZnO) is a non-toxic semiconductor having a wide range of potential applications in the field of catalysis, energy, sensors, laser and biomedicine. In particular, its tunable band gap (3.3 eV) and exciton dissociation energy make it one of the best candidate for various devices. Recently, outstanding device performance were reported on using ZnO nanocrystals or quantum dots (QDs) in polymer hybrid solar cells, transparent thin film transistors and UV-light emitting diodes.

5.1.2. Problem Statement

Various methods were reported for the synthesis of ZnO QDs, including precipitation, hydrothermal or solvothermal and sol gel process. The QDs obtained are usually dispersed into a polymer matrix for many applications. A number of studies have been reported on the preparation polymer-ZnO nanocomposites by directly incorporating pre-synthesized ZnO nanoparticle into a polymer matrix, mainly by mechanical blending or solvent processing.

However, this approach is complicated and tedious because it requires pre-synthesis of QDs and then dispersion into a polymer system. Achieving a high level of dispersion and homogeneity is still a challenge and usually requires tedious surface functionalization.

It is highly desirable to have a facile synthetic method that is also able to organize the quantum dots into specific well-defined structures and morphologies. This can lead to unique and useful electronic, optical, and magnetic properties for future device applications of ZnO quantum dots.

5.1.3. Objectives

The research work of this chapter aims to build up a novel system for synthesis and assembly of ZnO QDs using block copolymers.

The research reported in this chapter consists of the following areas:

- i) Developing simple novel systems for preparation of polymer/ZnO QDs hybrid materials using functional block copolymers.
- ii) Investigate the factors that govern the synthesis of ZnO QDs such as the effect of temperature and time.
- iii) Investigate the factors that govern the assembly of ZnO QDs such as nature of polymer, cross linking agent, block length of polymer and type of solvent.
- iv) Characterization the polymer/ZnO QDs composite films.

5.1.4. Outline of the work

Schematic depiction of the outline of synthesis & assembly of ZnO QDs in polymer films is given in Figure 5.1.

Overview of chapter-V **Figure 5.1.** Schematic depiction of the outline of synthesis & assembly of ZnO QDs.

5.2. Literature review

Zinc oxide (ZnO) is a non-toxic semiconductor having a wide range of potential applications in the field of catalysis, energy, sensors, laser and biomedicine.¹³⁰⁻¹³⁴ In particular, its large direct band gap (~3.3 eV) and large exciton dissociation energy (~60 meV) at room temperature make it one of the best candidates for various devices. Advantages associated with a large band gap include higher breakdown voltages, ability to perform at large electric fields, lower electronic noise, high-temperature and high-power operation. ZnO has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnO. Recently, outstanding device performances were reported on using ZnO nanocrystals or quantum dots (QDs)^{130, 135-137} For example, the use of ZnO nanoparticles as a photoactive layer in polymer hybrid solar cells to improve the efficiency of hybrid solar cells has been reported. Hybrid solar cells (with 2%-efficient) consists of poly(3-hexylthiophene) as the donor and ZnO as the acceptor in the nanometer range has been reported.¹³² ZnO nanoparticles are also drawing substantial interest for its possible application in transparent thin film transistors. Fabrication of transparent thin film transistors with preferred orientation (002 plan) of ZnO nanoparticles has been reported.¹³³ There are also report of ZnO application in UV-light emitting.^{138, 139} Recently use of ZnO as an electron injection layer for red, green, and blue light-emitting diodes (LEDs) based on core-shell CdSe/ZnS quantum dots (QDs) has been reported. The deposition of ZnO nanocrystals from isopropanol allows fabricating multilayer QD-LEDs that include both hole and electron transport layers by simple solution processing. The

role of ZnO nanocrystals is to improve the electron injection in the light-emitting QDs layer.¹⁴⁰

ZnO QDs have advantages over other metal chalcogenides QDs such as CdS, CdSe and CdTe in terms of its long-term environmental stability, bio-compatibility, non-toxicity and low cost. Recently use of ZnO nanoparticles in the field of medical research is advancing and emerged as a promising candidate in clinical and biomedical areas like photodynamic cancer therapy and bio-imaging.^{141, 142} It was reported that UV irradiation could improve the inhibition ability of cancer cells proliferation when ZnO nanoparticles were used. This effect can be considerably controlled by the varying size of the ZnO nanoparticles. It was also found that cytotoxicity of anticancer agents on cancer cells was evidently enhanced when ZnO nanoparticles were combined with an anticancer drug (daunorubicin), indicating that ZnO nanoparticles could play an important role in drug delivery.

Thus nano-sized ZnO particles are thus potential materials for future device due to their unique properties. Organization of QDs into specific structures is needed to get well control to obtain unique and useful electronic and optical properties.¹⁴³

So far, various physical or chemical synthetic approaches have been developed to produce ZnO nanoparticles. There are some physical process such as, ion implantation,¹⁴⁴ metal-organic chemical-vapor deposition (MOCVD),¹⁴⁵ RF magnetron sputtering,¹⁴⁶ flame spray pyrolysis¹⁴⁷ and vapor phase transport process¹⁴⁸ for ZnO nanoparticles synthesis. Among the different wet chemical methods, the most successful approach to obtain quantum-sized ZnO in dispersion has been the sol-gel route.¹⁴⁹⁻¹⁵² The problem in the sol-gel process lies in the stability of the sol. There is the possibility of precipitation

or gelation during its storage and application which very much depends on the nature of the solvent, the amount of water, the kind and amount of acid, and the temperature. All these factors produce poorer repeatability of the method. Colloidal ZnO nanocrystals which are obtained from sol-gel method have a tendency to aggregate or undergo Ostwald ripening due to their high surface energy.¹⁵³

Precipitation and hydrothermal decomposition process are also used to synthesis of ZnO nanoparticles besides sol-gel method.¹⁵⁴⁻¹⁵⁶ To obtain ZnO nanoparticles may need to go through several steps; either hydrolysis, precipitation, separation or evaporation. Those steps may result in particle agglomeration with low yields.^{154, 157-163}

However, the QDs obtained are usually dispersed into a polymer matrix for many device applications.^{130, 164, 165} A number of studies have been reported on the preparation of polymer-ZnO nanocomposites by incorporating pre-synthesized ZnO nanoparticles into a polymer matrix, mainly by mechanical or solvent blending.^{166, 167} However, it is difficult to achieve a homogeneous dispersion of the nanoparticles due to agglomeration. Generally this approach is complicated and tedious because it requires pre-synthesis of QDs and then dispersed into a polymer system. Achieving high level of dispersion and homogeneity is still a challenge and usually requires tedious surface functionalization.¹⁶⁶

The direct synthesis of ZnO nanoparticles by reacting with solution-phase oxygen anions (O^{2-}) from Zn^{2+} in solution is not supposed to occur because oxygen anions (O^{2-}) in solution are thought not to form and oxygen exists in the form of hydroxide ion (OH^-). The oxidation of organometallic zinc in solution with oxygen can form ZnO directly but the oxidation process is may not well controlled in these cases.¹⁶⁸⁻¹⁷¹

Organization of nanocrystals has been demonstrated by taking the advantage of block copolymer self-assembly. The poly(styrene)-*b*-poly(2-vinyl-pyridine) (PS-*b*-P2VP) diblock copolymer was widely utilized as template for synthesis of hexagonally arranged gold nanoparticles of controlled size.^{172, 173} Non-spherical gold¹⁷⁴ and cobalt²⁸ nanoparticles have been prepared using poly(styrene)-block-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer. However, synthesis of nanoparticle of various metal oxides, e.g. TiO₂¹⁷⁵, SiO₂¹⁷⁶ and Fe₂O₃¹⁷⁷ with the help of various diblock copolymers has been reported. An attempt has been made to prepare organized ZnO nanoparticles using a Zn(CH₂CH₃)₂ precursor in a PS-*b*-P2VP block copolymer. However the procedures are difficulty partly due to the highly reactive and moisture sensitive nature of the precursor, which was traditionally used for MOCVD (metal organic chemical vapor deposition).¹⁷¹ Yoo et al reported synthesis of ZnO nano-arrays using oxygen plasma treatment of a PS-*b*-P4VP/zinc chloride film cast from toluene. ZnO nanoparticles with considerable particle sizes of about 16 nm in diameter were obtained. The photoluminescent property of the particles was investigated, but the chemical composition was not determined.¹⁷⁸ Pál et al also tried to prepare hexagonally aligned zinc oxide nanoparticles using a similar approach. However, zinc silicate (Zn₂SiO₄) was obtained instead of ZnO.¹⁷⁹

All the reported methods are complex processes requires sophisticated equipment and economically prohibitive as high cost materials are usually required, which decides they are not suitable for large-scale fabrication with a relatively low cost. It is highly desirable to have a facile synthetic method that is able to organize the quantum dot into specific well-defined structure and morphology. This should open up new possibilities for electronic and photonic devices using ZnO quantum dots.

In this study, we report a copolymer template assisted facile and versatile single step method for the preparation of ZnO QDs/polymer hybrids with high loading of ZnO QDs using commonly available precursor (up to 25 wt% ZnO QDs loading is achieved, see appendix for TGA analysis).

5.3. Materials and Method

5.3.1 Materials

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP), $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol, $M_w/M_n = 1.04$) was obtained from Polymer Source Inc. Zinc acetate dihydrate, $Zn(O_2CCH_3)_2(H_2O)_2$, 1,4-dibromobutane (DBB), Toluene (99.9 %) and anhydrous methanol (99.8%) were obtained from Aldrich and used as received.

5.3.2 Method

PS-*b*-P4VP block polymer was dissolved in toluene at room temperature (2 mg/ml) for 24 hrs. Spherical micelles of a PS corona and a P4VP core were formed at this concentration because PS block is selective for toluene.⁹⁷ Zinc acetate dihydrate $[Zn(OAc)_2]$ was separately dissolved in methanol. Required amount of $Zn(OAc)_2$ /methanol (20 mg/ml) solution was added to solution of PS-*b*-P4VP to keep the mole ratio of 4VP: $Zn(OAc)_2$ as 1:0.8 in final solution. The final mixture was aged for 48 hrs, so that $Zn(OAc)_2$ can enter in core of micelle with the help of swelling effect caused by methanol. The whole solution was divided into two parts. One part was used for film casting without adding any cross-linker whereas to the 2nd part was added a crosslinking agent, 1,4 dibromobutane (DBB) (4VP:DBB = 2:1) to cross-link the selective core of the micelles at room temperature for 24 h.¹⁸⁰ The solution was drop cast on substrates and subjected to heat treatment for different durations at different temperatures.

In Figure 5.2. a schematic diagram of method for preparation of block copolymer assisted ZnO/polymer composite is shown below.

Figure 5.2. Scheme for block copolymer assisted synthesis and assembly of ZnO QDs.

5.4. Characterization

UV-Vis absorption and Photoluminescence (PL) spectra of the nanocrystals were obtained using a Shimadzu UV2501PC spectrophotometer and a Shimadzu RF-5301 PC fluorometer, respectively. The excitation wavelength for PL is 330 nm. All the optical measurements were performed at room temperature under ambient conditions.

Transmission electron microscopy (TEM) studies were carried out by using a JEOL 2010 microscope fitted with a LaB6 filament using an acceleration voltage of 200 kV. TEM samples were prepared by placing one or two drops of the solution onto carbon-coated copper grids.

Thin film X-ray Diffraction (XRD) studies were carried out in a Rigaku DMAX 2200 using Cu K α radiation ($\lambda=0.1542$ nm) operating at 40 kV and 40 mA. The scanning rate of 2° min^{-1} with 2θ ranging from 20° to 80° was used.

Atomic force microscopy (AFM) was performed with a Nanoscope III from Digital Instruments operating in the tapping model of scan rate 1.795 Hz using Silicon probes. Samples for the AFM experiments were prepared by spin casting of solution on silicon.

5.5. Results and Discussion

5.5.1. Block copolymer and micelle

PS-*b*-P4VP di-block copolymers are composed of polystyrene (PS) and poly(4-vinylpyridine) (P4VP) blocks. PS-*b*-P4VP block copolymers form nanometer-sized micelles in toluene consisting of a soluble corona of PS blocks and an insoluble P4VP core. TEM sample was prepared from polymer/toluene solution and stained with iodine. Figure 5.3 is showing the TEM image of PS-*b*-P4VP micelles with a moderate-range order. P4VP core is directly visualized as the dark region as the sample was stained with iodine which is selective for P4VP.

Figure 5.3. TEM images of PS-*b*-P4VP ($M_{\text{PS}} = 11,800$ g/mol, $M_{\text{P4VP}} = 15,000$ g/mol) in toluene (2 mg/ml) coated on copper grid stained with iodine.

These micelles can be coated onto substrates to form a self-assembled nanostructure. This can serve as a structured template of nanoparticles. Figure 5.4 is showing a self assembled nanostructure spin cast from micellar solution of PS-*b*-P4VP/toluene on silicon.

Figure 5.4. Atomic force microscopy (AFM) image of PS-*b*-P4VP film cast on silicon

5.5.2. Loading of Zn(Ac)₂ into polymer micelle core

Incorporation of ZnO precursor inside the core in a micellar block copolymer solution is needed for synthesis of ZnO in the core areas of the ordered micelles film. Zn(OAc)₂ which is not toxic and inexpensive was selected as a ZnO precursor. Zn(OAc)₂ is insoluble in toluene. So, selection of solvent for dissolution of Zn(OAc)₂ in polymer/toluene solution was very important. Methanol was selected as solvent because toluene and methanol are miscible to each other. This facilitated the Zn(OAc)₂ dissolving in the polymer/toluene solution. Methanol also has ability to swell the P4VP block of a PS-*b*-P4VP block copolymer,¹⁸¹ consequently facilitating the absorption of Zn(OAc)₂ into P4VP core. So methanol is playing a dual role in this work.

P4VP was selected as the core-forming block, as it allows easy coordination with a wide range of metal ions through its electron donating ability of pyridine ring. Thus P4VP has a tendency to co-ordinate with Zn^{2+} ions, used as the assembly tool from solution phase PS-*b*-P4VP micelles in toluene. So swelling effect of methanol and co-ordinating tendency of P4VP block with Zn^{2+} facilitate the absorption of zinc acetate selectively to the P4VP cores of PS-*b*-P4VP block polymeric micelles in toluene.

A TEM image of $\text{Zn}(\text{OAc})_2/\text{PS-}b\text{-P4VP}$ film without iodine staining is shown in Figure 5.5, which indicates that $\text{Zn}(\text{OAc})_2$ precursor selectively loaded into the P4VP core which is visualized as the dark region with micelle having a moderate-range hexagonal order. The dark contrast appeared in the image due to absorption of zinc acetate selectively into P4VP core of PS-*b*-P4VP micelle as P4VP has affinity towards metal ions.

Figure 5.5. TEM image of PS-*b*-P4VP/ $\text{Zn}(\text{OAc})_2$ film coated on copper grid without iodine staining.

Figure 5.6 schematically presents how the swelling of P4VP core is effected by methanol and consequently facilitates the absorption of zinc acetate.

Figure 5.6. A schematic which presents how the swelling of P4VP core is effected by methanol and consequently facilitates the absorption of zinc acetate.

The solution of polymer/Zn(OAc)₂ was drop cast on quartz which subjected to heat treatment. UV-Vis spectroscopy measurement was used to see the effect of heat treatment for different times and temperatures on ZnO synthesis.

5.5.3. Effect of temperature on conversion of $\text{Zn}(\text{OAc})_2$ into ZnO

The conversion of $\text{Zn}(\text{OAc})_2$ into ZnO in $\text{Zn}(\text{OAc})_2$ /polymer film was monitored by UV-Vis spectroscopy. The polymer/ $\text{Zn}(\text{OAc})_2$ film on quartz was subjected to four different temperatures i.e., 140 °C, 160 °C, 180 °C and 200 °C for 30 min. The effect of temperature is shown in Figure 5.7. It was found that the conversion of $\text{Zn}(\text{OAc})_2$ into ZnO started at about 200 °C. It is well known that when zinc acetate is heated in air, it start to decompose at about 190 °C. The change of UV-Vis absorbance in 390-355 nm region is due to ZnO^{182} whereas absorbance at ~260 nm arises from the polymer. The size of ZnO particles was calculated from UV-Vis analysis and found to be 6.5 ± 1 nm which confirmed ZnO particles as ZnO quantum dots (QDs). The calculation regarding ZnO particle size is discussed later.

Figure 5.7. UV-Vis spectra for monitoring the formation of ZnO QDs at different temperature.

5.5.4. Effect of time on ZnO QDs synthesis at 200 °C

The effect of time on ZnO QDs synthesis at 200 °C was also monitored using UV-Vis spectroscopy. The results are shown in Figure 5.8. It can be seen that detectable ZnO QDs formation at 200 °C started after 15 min. Therefore heat treatment duration was set as 200 °C for 30 min throughout this report unless otherwise stated.

Figure 5.8. Time resolved UV-Vis spectra for monitoring the formation of ZnO QDs with time at 200 °C.

5.5.5. Effect of temperature on morphology of the polymer/Zn(OAc)₂ film

TEM study has been carried out to observe the morphological changes occur in nanocomposite film during heating process. In this case, TEM samples were prepared from the solution of polymer/Zn(OAc)₂ by drop casting on copper grid. The copper grid

was subjected to heat treatment for 180 °C and 200 °C for 30 min respectively. TEM image in Figure 5.9 shows that the micellar structure was largely maintained when the film was treated at 180 °C for 30 min. However, due to heating at 180 °C which is above T_g for both PS (100 °C) and P4VP (140-160 °C) the micellar structure stands to lose its spatial order accompanied by partial micellar fusion as seen in the as prepared polymer/Zn(OAc)₂ film (Figure 5.5). It was also noted that a small number of ZnO QDs started to form, which were undetected in UV-Vis study due to low conversion at this temperature.

Figure 5.9. TEM image of PS-*b*-P4VP/Zn(OAc)₂ film coated on copper grid after heat treatment at 180 °C for 30 min. (small black dot is ZnO)

When the sample was treated at 200 °C for 30 min, as shown in Figure 5.10 (a), the hexagonal micellar structure was completely destroyed due to extensive fusion of P4VP domain at this high temperature to form some worm-like domains. Similar annealing induced morphology change was reported in pure PS-*b*-P4VP¹⁸³ and other block copolymers.^{184, 185} In these worms, Figure 5.10 (b) shows the formation of well-dispersed ZnO QDs preferentially in the P4VP domain. The QDs dispersed copolymer evolved into

a random network morphology, where QDs are located in P4VP domains while the PS domain is largely free of QDs.

Figure 5.10. TEM images of (a) PS-*b*-P4VP/ZnO QDs film obtained after heat treatment at 200 °C for 30 min of PS-*b*-P4VP/Zn(OAc)₂ film coated on copper grid; (b) zoom in image at a higher magnification; (c) HR-TEM of ZnO QDs with visible fringes.

Figure 5.11 summarizes graphically how the heating temperature is controlling the ZnO particle formation and the morphology of the polymer/ZnO film. Figure 5.11 (b) can be considered as transient state for formation of ZnO QDs and morphological change of polymeric film introduced by preprocessing due to heating effect.

Figure 5.11. TEM images of (a) as coated PS-*b*-P4VP/Zn(OAc)₂ film on copper grid; (b) after heat treatment at 180 °C for 30 min; (c) after heat treatment at 200 °C for 30 min.

Solvent effects can be introduced in a rational way to tune the morphology of ZnO QDs containing block copolymer film. In this case we used chloroform as a solvent instead of toluene using the same procedure for synthesis of ZnO QDs in toluene. It is reported that PS-*b*-P4VP polymer film appeared as a lamellar form when chloroform was used as solvent.¹⁸⁶ In this case same block copolymer i.e., PS-*b*-P4VP ($M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol, $M_w/M_n = 1.04$) was used. It is very clear from Figures 5.12 (a) that PS-*b*-P4VP/Zn(OAc)₂ in chloroform shows a structure which is no longer existed as lamellar structure. It is believed this is due to the swelling effect of methanol. However, upon heating the PS-*b*-P4VP/Zn(OAc)₂ film cast from chloroform solution at 200 °C for 30 min ZnO QDs were formed. ZnO QDs were uniformly distributed in P4VP region of PS-*b*-P4VP as seen in Figures 5.12 (b) & (c).

Figure 5.12. TEM images of (a) PS-*b*-P4VP/Zn(OAc)₂ film cast from chloroform solution; (b) self-assembled PS-*b*-P4VP/ZnO QDs formed after heating of 'a'; (c) zoom in form of (b) to see clear distribution of ZnO QDs.

Tuning of the morphology of polymer/ZnO film was also done using homo polymer instead of block copolymer. P4VP homo polymer of $M_{\text{P4VP}} = 9,800$ g/mol was used to achieve well distributed ZnO QDs with size of ~ 5 nm throughout almost all places. Here, mixture of toluene and DMF (toluene:DMF 95:5 by volume) solvent was used due to poor solubility of P4VP in toluene. The given morphology, Figure 5.13, was occurred after heating of P4VP/Zn(OAc)₂ film cast from mixture solution of toluene and DMF at 200 °C for 30 min from. It is clear that highly dense, well distributed ZnO QDs were formed.

Figures 5.13. TEM images of (a) P4VP/ZnO QDs film, formed after heat treatment at 200 °C for 30 min of film P4VP/Zn(OAc)₂ cast from mixture solution of toluene and DMF; (b) zoom in form of to see clear distribution of ZnO QDs.

Figure 5.14 summarizes graphically how the final morphology of polymer/ZnO QDs film can be tuned using different solvent or different type of polymer.

Figures 5.14. TEM images of different morphology of polymer/ZnO QDs films, formed after heat treatment at 200 °C for 30 min of film cast from (a) PS-*b*-P4VP/Zn(OAc)₂ in toluene; (b) PS-*b*-P4VP/Zn(OAc)₂ in chloroform; (c) P4VP/Zn(OAc)₂ in mixture solution of toluene and DMF.

5.5.6. Effect of crosslinking agent

It was reported that selective crosslinking of block copolymer could prevent structural change during solvent annealing.¹⁸³ In this study, we adopted this concept to produce nano-hybrids with tunable structure.

1,4 di-bromobutane (DBB) was used as a crosslinking agent which selectively crosslinked the P4VP core.^{183, 187, 188} This brought better thermal stability of PS-*b*-P4VP templates. Figure 5.15 shows TEM images of PS-*b*-P4VP/Zn(OAc)₂ film with crosslink agent (DBB) coated on copper grid before heat treatment. Figure 5.15 (a) shows a monolayer micelle assembly of PS-*b*-P4VP/Zn(OAc)₂. Monolayer was prepared by placing a copper grid on filter paper and applying one drop of solution on it. Figure 5.15 (b) shows the TEM image of a bilayer micelle assembly. The bilayer assembly was prepared by dropping a second drop of solution on the prepared monolayer film of PS-*b*-P4VP/Zn(OAc)₂. Figure 5.15 (c) shows TEM image where both bilayer and monolayer structures co-existing in the same sample. The upper part of the image is clearly monolayer whereas lower part is bilayer.

Figure 5.15. TEM images of PS-*b*-P4VP/Zn(OAc)₂ film with crosslinking agent 1,4 dibromobutane coated on copper grid before heat treatment, (a) monolayer coated on copper grid; (b) bilayer coated on copper grid; (c) existence of monolayer and bilayer in same sample.

TEM characterization has been done to study the stability of morphology of PS-*b*-P4VP/ZnO QDs film (Figure 5.16) after heat treatment at 200 °C for 30 min of crosslinked PS-*b*-P4VP/Zn(OAc)₂ film. It is clear that crosslinking has enabled the retention of morphology of monolayer precursor (Figure 5.15 (a)) film without hampering

the synthesis of ZnO QDs (5.16 (a)). The ZnO QDs preferentially lie in P4VP core of the polymer as expected. Figure 5.16 (b) gives a high resolution TEM image of the ZnO QDs in the P4VP domains. The ZnO QDs were closely packed within the P4VP domains. It showed that the inter-planar distance of fringes was 0.26 nm, which is in good agreement with the (002) plane of wurtzite ZnO.^{189, 190} A detailed study of the XRD have been discussed later.

Figure 5.16. TEM image of PS-*b*-P4VP/ZnO QDs film after heat treatment at 200 °C for 30 min of crosslinked monolayer PS-*b*-P4VP/Zn(OAc)₂ film cast on copper grid; (b) HR-TEM image of P4VP domain of PS-*b*-P4VP/ZnO QDs film .

Figure 5.17 gives a schematic process showing how ZnO QDs is formed inside P4VP core of PS-*b*-P4VP block polymer, which can be used to explain the monolayer morphologies seen in Figure 5.15 (a) and 5.16 (a).

Figures 5.17. A schematic diagram represents how the ZnO QDs is formed inside P4VP core of PS-*b*-P4VP block polymer.

However, when a bilayered PS-*b*-P4VP/Zn(OAc)₂ was heated at 200 °C for 30 min, an inverse type of morphology is formed (Figure 5.18). The QDs dispersed P4VP appears as an interconnected network whereas PS forms discrete domains, encircled by P4VP. This thermal induced inversion has not been reported in previous studies of block copolymer assembly, although “core-shell” inversion is more commonly seen by manipulation of solvent systems or pH values.¹⁹¹⁻¹⁹³ This was due to a unique re-organization of the

blocks at 200 °C. It is clear that a network of ZnO QDs nicely embedded in P4VP region. The mechanism of formation network type structure is given Figure 5.19.

Figure 5.18. TEM image of PS-*b*-P4VP/ZnO QDs film after heat treatment at 200 °C for 30 min of crosslinked bilayer PS-*b*-P4VP/Zn(OAc)₂ film cast on copper grid.

Figure 5.19 schematically presents a model how the order type of structure containing ZnO QDs can be formed based on TEM study. Retention of the assembled micellar monolayer morphology (Figure 5.19 (a)) is accomplished to some extent due to the interaction of the assembled micellar monolayer with the solid surface of the substrate on which micellar monolayer is coated (Figure 5.15 (a)) whereas the maximum force of retention of the assembled micelle monolayer structure arises from crosslinking effect. However, for bilayer (Figure 5.15 (b)) we believed that an inverse type structure is due to an inter layer fusion (Figure 5.19 (c)) This is because, the top micellar layer of the bilayer attached to the top surface of the bottom polymeric micellar layer is less stable compared

to solid surface. This results in inter-layer fusion during heating. Figure 19 (b) and Figure 19.(d) represents schematic model for monlayer and bilayer respectively.

Zn(OAc)₂ or ZnO QDs

Figures 5.19. A schematic model showing how the net work type of structure containing ZnO QDs can be formed based on TEM study. TEM images of polymer/ZnO QDs film, formed after heat treatment at 200 °C for 30 min of film obtained from PS-*b*-P4VP /Zn(OAc)₂ (PS-*b*-P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene

using crosslinking agent, (a) monolayer; (b) schematic model for monolayer; (c) bilayer (d) schematic model for bilayer.

Figure 5.20 shows a dynamic schematic model for a better understanding on how the morphology of micellar monolayer and bilayer of PS-*b*-P4VP/Zn(OAc)₂ with crosslink upon heating leads to the TEM images as Figures 5.20. (a) and Figures 5.20. (b) respectively.

Figures 5.20. A schematic model showing how the network type of structure containing ZnO QDs can be formed based on TEM study.

One of the major anticipated challenges in future semiconductors based nano-electronics is the goal to place well assembly semiconducting materials between the nano-gap electrodes of devices. Here, we report techniques for the assembly of semiconducting ZnO QDs into different pocket-size with tuneable distance. In this work, a different PS-*b*-P4VP (with $M_{PS} = 47,600$ g/mol, $M_{P4VP} = 20,900$ g/mol, $M_w/M_n = 1.14$) as polymer was used as the templates for synthesis ZnO QDs and toluene as the solvent. In Figure 5.21, TEM images clearly show that the P4VP domain is filled with ZnO QDs. The distance between the P4VP domains can be controlled using length of polystyrene (PS) block of PS-*b*-P4VP whereas the size of the P4VP domains can be tuned by controlling length of poly(4-Vinylpyridine) (P4VP) of PS-*b*-P4VP block copolymer. So choice of the block length of block copolymer may help to tune the distance between ZnO QDs filled domains as well as the size of the domains.

Figure 5.21. TEM images of (a) self-assembled PS-*b*-P4VP/ZnO QDs formed after heat treatment at 200 °C for 30 min of crosslinked PS-*b*-P4VP/Zn(OAc)₂ film; (b) & (c) are in zoom in form.

Figure 5.22 summarizes graphically how the choice of the block length of block copolymer PS-*b*-P4VP may help to tune the distance between ZnO QDs filled domains as well as size of the domains in the final morphology of polymer/ZnO QDs film.

Figure 5.22. TEM images of self-assembled PS-*b*-P4VP/ZnO QDs formed after heat treatment at 200 °C for 30 min of crosslinked PS-*b*-P4VP/Zn(OAc)₂ film when, (a) PS-*b*-P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol; (b) PS-*b*-P4VP with $M_{PS} = 47,600$ g/mol, $M_{P4VP} = 20,900$ g/mol used as polymer templates.

The method used in this work for preparation of nanoparticle composite is very simple but unique and can be termed as ***Open-Lock-Decompose (OLD)*** mechanism. (“***Open***”- indicates opening of P4VP core by methanol swelling which facilitates the absorption of precursor of zinc oxide; “***Lock***”- indicates locking of the precursor loaded P4VP core *via* crosslinking which stabilizes the morphology during heat treatment; “***Decompose***”- indicates thermal induced in situ conversion of Zn(OAc)₂ into ZnO QDs).

5.5.7. X-ray Diffraction (XRD)

In Figure 5.23, curves (a), (b) and (c) are the wide angle XRD patterns of PS-*b*-P4VP/Zn(OAc)₂, PS-*b*-P4VP/ZnO QDs without and with crosslinking respectively. It confirms the formation of wurtzite ZnO crystals upon heating of PS-*b*-P4VP/Zn(OAc)₂ film. The diffraction patterns (curves (b) and (c)) show three major diffraction peaks corresponding to (100), (002) and (101) planes for ZnO. It is worth mentioning that the diffraction patterns show that peak (002) at 2θ 34.4° has the highest intensity in comparison to (100) and (101). Comparing with the standard JCPDS (JCPDS No. 800075) diffraction pattern of powder wurtzite ZnO, the high intensity of (002) peak for ZnO QDs of PS-*b*-P4VP/ZnO QDs films means that they have a certain degree of preferred orientation of (002). Such orientation is reported to be favorable for high mobility transistor in spin coated ZnO thin films.¹³³ From Figure 5.23, it is clear that XRD peaks are broad for curves (b) and (c). This is due to small size of crystal as it is well-known that XRD peak becomes widened at decreasing crystal size. The crystallite size D , was determined using the Debye Scherrer formula as given below:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad 5.1$$

where $K = 0.9$, is the shape factor, $\lambda = 1.5408 \text{ \AA}$, θ is the diffraction peak angle (Bragg Angle) in degrees, and β (radians) denotes the full width at half-maximum.

Applying the full-width at half-maximum (FWHM) of the peak at 2θ 34.4° to the Scherrer formula gave an average crystal size of ~ 5.1 nm for both ZnO QDs synthesized using crosslinking or without crosslinks.

It appears that addition of a cross linking agent does not have any notable effect on controlling size or orientation of ZnO QDs. Crystal size of ZnO thin film calculated from XRD is in a good agreement with TEM results.

Figure 5.23. XRD spectra of (a) PS-*b*-P4VP/Zn(OAc)₂; (b) PS-*b*-P4VP/ZnO without DBB; (c) PS-*b*-P4VP/ZnO QDs with DBB crosslinker.

5.5.8. UV-Vis absorption

In Figure 5.24, curves (a), (b) and (c) are the UV-Vis absorption spectrum of PS-*b*-P4VP/Zn(OAc)₂, PS-*b*-P4VP/ZnO QDs without and with crosslinking respectively. It clearly shows that DBB crosslinking does not have a noticeable effect on the UV-Vis absorption property of ZnO QDs. It can be concluded that the role of 1,4 dibromobutane (DBB) in this process is solely to enhance stability of the film's morphologies.

Figure 5.24. UV-Vis spectra of (a) PS-*b*-P4VP/Zn(OAc)₂; (b) PS-*b*-P4VP/ZnO QDs without DBB; (c) PS-*b*-P4VP/ZnO QDs with DBB crosslinker.

A comparison of the size of ZnO particle calculated from TEM image analysis, XRD analysis (Scherrer formula) and UV-Vis analysis have been done which are tabulated in Table 5.1. Diameter was calculated from UV-Vis absorption spectra according to the method of Meulenkaamp¹⁵⁴, using equation 5.2.

$$1240/\lambda_{1/2} = a + b/D^2 - c/D \quad 5.2$$

Where the value for $a = 3.301$, $b = 294.07$, and $c = -1.09$ were obtained from Meulenkamp's paper¹⁵⁴ where $\lambda_{1/2}$ is in nm and diameter D in Å. The above equation proposed based on an experimental relationship between the average diameter (D) and the absorption shoulder ($\lambda_{1/2}$) of the ZnO QDs, where $\lambda_{1/2}$ is wavelength at which the absorption is 50% of the excitonic peak or shoulder and D is the particle diameter of the QDs. A mean diameter of ZnO QDs is 6.5 nm obtained according to equation 5.2. Although there are limitations with this equation which prevent accurate measurement of D ¹⁹⁴. The slight difference of QDs size estimated from UV-Vis study and TEM or XRD analysis is not unexpected.^{194, 195}

Table 5.1. Comparison of size of ZnO QDs calculated from various techniques.

Molar ratio ZnO:4-VP	(a) $\lambda_{1/2}$ (UV/Vis) Film (nm)	(b) Diameter of QDs (TEM) (nm)	(c) Diameter of QDs (UV/Vis) (nm)	(d) Diameter of QDs (XRD) (nm)	(e) Bandgap (eV)
0.8:1	366±2	~ (4.5±1)	~(6.5±1)	~5.1	~3.37±0.02

(a) $\lambda_{1/2}$ is obtained from UV–Vis absorption measurements; (b) Mean Diameter of ZnO QDs from TEM; (c) Size of ZnO QDs from UV-Vis using Meulenkamp method; (d) Size of ZnO QDs from XRD analysis using 002 peak (Scherrer formula); (e) Bandgaps calculated as onsets of the UV–Vis absorption spectra.

5.5.9. Photoluminance (PL) study

Photoluminance (PL) emission spectra of the ZnO QDs are given in Figure 5.24. The PL curves (b) and (c) in Figure 5.25 shows that major emission occurred at 390 nm and 550 nm when ZnO QDs containing film were excited with wavelength of 330 nm. No emission (Figure 5.25 a) for PS-*b*-P4VP/Zn(OAc) film whereas similar emission spectra for ZnO QDs synthesized with or without crosslink agent (1,4 DBB) are observed. The PL of ZnO QDS in this range is commonly ascribed to crystal (surface) defects.^{196, 197} These defects create intra-bandgap energy levels from which recombination occurs.

Figure 5.25. Photo luminance (PL) emission spectra of (a) PS-*b*-P4VP/Zn(OAc)₂; (b) PS-*b*-P4VP/ZnO without DBB; (c) PS-*b*-P4VP/ZnO QDs with DBB crosslinker.

5.6. Conclusion

According to our best knowledge this work is the most successful attempt to synthesis and direct ZnO QDs in a structured block copolymer template. This process is clean, ligand and additive free with possible favourable crystal orientation for device applications. It is also facile, single-step method. Crosslinking is an essential step to fix the assembled hexagonal morphology preventing it from changing into worm-like or even random morphology during the thermal conversion of $\text{Zn}(\text{OAc})_2$ to ZnO. The selection of solvent, polymer, block length of the block copolymer and the architecture of layered assembly are crucial factors besides the use of crosslink agent, for tuning of film morphology of the ZnO QDs/polymer composites. The use of suitable polar solvent such as methanol for the precursor also plays an important role because it has an advantage of ensuring high and selective loading of the precursor into the assembly of P4VP blocks due to a swelling mechanism. Up to 25 wt% ZnO QD loading is achieved. The ZnO QDs obtained have size of 4.5 ± 1 nm and well-dispersed in the polymer with tunable morphology according to TEM analysis as summarized in Figure 5.26.

Figures 5.26. TEM images of polymer/ZnO QDs film, formed after heat treatment at 200 °C for 30 min of film cast from (a) PS-*b*-P4VP/ $\text{Zn}(\text{OAc})_2$ (PS-*b*-P4VP with $M_{\text{PS}} = 11,800$

g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene; (b) PS-*b*-P4VP/Zn(OAc)₂ (PS-*b*-P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in chloroform; (c) P4VP/Zn(OAc)₂ (P4VP with $M_{P4VP} = 9800$ g/mol) in mixture solution of toluene and DMF; (d) monolayer of PS-*b*-P4VP/Zn(OAc)₂ (PS-*b*-P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene using crosslinking agent; (e) monolayer of PS-*b*-P4VP/Zn(OAc)₂ (PS-*b*-P4VP with $M_{PS} = 47,600$ g/mol, $M_{P4VP} = 20,900$ g/mol) in toluene using crosslinking agent; (f) bilayer of PS-*b*-P4VP/Zn(OAc)₂ (PS-*b*-P4VP with $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol) in toluene using crosslinking agent.

The method can be applied for large-scale fabrication of well-dispersed QDs in different polymers.

In conclusion, we successfully demonstrated a new simple single-step method for synthesis and assembly of ZnO QDs in different morphologies. It can provide a unique and versatile opportunity for functional nanocomposites fabrication. Thus, the methodology demonstrated in this study can be a good example of simple, cost effective way of preparing functional nanocomposites using polymers with dual functions as templates and as matrices.

Chapter-VI

Summary and future suggestions

6.1. Summary

In these studies, we were able to synthesize functional polymer nanocomposite film with using fullerene derivatives and ZnO QDs in block copolymers.

The major conclusions of this work are as follows

Underivatized fullerene (C_{60}) is found to form complexes with triblock copolymer $P4VP_8$ - PEO_{105} - $P4VP_8$ in toluene using weak charge transfer interaction. The rate of charge transfer complexation formation was found to be very slow in toluene.

Charge transfer complexation between the triblock copolymer $P4VP_8$ - PEO_{105} - $P4VP_8$ and fullerene derivative PCBM was carried out in toluene and THF solvents. Quantitative analysis showed the kinetics of charge transfer complexation between the triblock copolymer $P4VP_8$ - PEO_{105} - $P4VP_8$ and fullerene derivative PCBM to be highly sensitive to solvent. While the kinetics of interaction between the copolymer and PCBM can be analyzed quantitatively in THF, their interaction is so slow in toluene that no meaningful kinetics analysis could be performed under the conditions studied. Comparative study of the interaction between a small molecular model pyridine compound allows further understanding of the influence of supermolecular assembly of the copolymer on the complexation kinetics. On the other hand, morphological study using light scattering reveals that the supermolecular assembly is significantly affected by the complex formation.

New strategy had been adopted for the assembly of underivatized fullerene with block copolymer with tunable morphology. It could be achieved in two steps. The complexation reaction was very much faster in THF compared to that in toluene, in which the reaction

took more than several months to complete. The poor solubility of fullerene in THF system was overcome by adding a small amount of C₆₀/toluene solution. However, the solvent system used in the reaction also influenced the morphological structure of the complex. The morphological structure of the C₆₀/PS-*b*-P4VP prepared from the solvent exchange technique in toluene was more uniform compared to the complex prepared in THF. This study has demonstrated that the formation of well defined structures could be obtained in a much shorter time through a solvent exchange approach. With careful manipulation, the morphology of the materials obtained from the C₆₀/PS-*b*-P4VP system, could also be fine tuned to a certain extent.

A clear understanding of the interplay among molecular assembly, complexation kinetics and solvent effect should serve as a guide in designing nano-structured fullerene derivatives in polymer systems.

We successfully demonstrated a new simple single-step method for synthesis and assembly of ZnO QDs in different morphologies. According to our best knowledge this work is the most successful attempt to synthesis and direct ZnO QDs in a structured block copolymer template. This process is clean, ligand and additive free with possible favourable crystal orientation for device applications. It is also a facile, single-step method. Crosslinking is an essential step to fix the assembled hexagonal morphology preventing it from changing into worm-like or even random morphology during the thermal conversion of Zn(OAc)₂ to ZnO. The selection of solvent, polymer, block length of the block copolymer and the architecture of layered assembly are crucial factors besides the use of crosslink agent, for tuning of film morphology of the ZnO QDs/polymer composites. The method can be applied for large-scale fabrication of well-

dispersed QDs in different polymers. Thus, the methodology demonstrated in this study can be a good example of simple, cost effective, way of preparing functional nanocomposites using polymers with dual functions as templates and as matrices. It can provide a unique and versatile opportunity for functional nanocomposites fabrication.

6.2. Future Suggestions

The next phase of the study will mainly focus on the device fabrication to find out possible potential application in electronics or optical devices.

Other useful formulations of functional nanocomposite films will also be investigated as summarized below,

- i) Further increase the loading of underivatized fullerene in block copolymer assemblies. More experiments will be needed to improve the loading amount of underivatized fullerene.
- ii) Incorporation of both fullerene and ZnO QDs together in a polymeric film and study of the effective loading with changing the ratio of ZnO QDs, fullerene and polymer on morphological behavior and other functional properties.
- iii) Preparation of ZnO QDs in different polymers and study their UV-shielding characteristics.
- iv) Device fabrication using ZnO QDs/polymer nanocomposites.

References

1. Hadjichristidis, N.; Pispas, S.; Floudas, G., *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*. Wiley-Interscience: 2002.
2. Raez, J.; Tomba, J. P.; Manners, I.; Winnik, M. A., A Reversible Tube-to-Rod Transition in a Block Copolymer Micelle. *Journal of the American Chemical Society* **2003**, 125, (32), 9546-9547.
3. Yan, X.; Liu, F.; Li, Z.; Liu, G., Poly(acrylic acid)-Lined Nanotubes of Poly(butyl methacrylate)-block-poly(2-cinnamoyloxyethyl methacrylate). *Macromolecules* **2001**, 34, (26), 9112-9116.
4. Cao, L.; Manners, I.; Winnik, M. A., Influence of the Interplay of Crystallization and Chain Stretching on Micellar Morphologies: Solution Self-Assembly of Coil - Crystalline Poly(isoprene-block-ferrocenylsilane). *Macromolecules* **2002**, 35, (22), 8258-8260.
5. Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M., Synthesis and characterization of noble metal colloids in block copolymer micelles. *Advanced Materials* **1995**, 7, (12), 1000-1005.
6. Zhang, L.; Eisenberg, A., Multiple Morphologies of "Crew-Cut" Aggregates of Polystyrene-b-poly(acrylic acid) Block Copolymers. *Science* **1995**, 268, (5218), 1728-1731.
7. Shen, H.; Zhang, L.; Eisenberg, A., Multiple pH-Induced Morphological Changes in Aggregates of Polystyrene-block-poly(4-vinylpyridine) in DMF/H₂O Mixtures. *Journal of the American Chemical Society* **1999**, 121, (12), 2728-2740.

-
8. Zhang, Q.; Remsen, E. E.; Wooley, K. L., Shell Cross-Linked Nanoparticles Containing Hydrolytically Degradable, Crystalline Core Domains. *Journal of the American Chemical Society* **2000**, 122, (15), 3642-3651.
 9. Alexandridis, P.; Lindman, B. E., *Amphiphilic block copolymers: self-assembly and applications*. Elsevier Science B.V Amsterdam, 2000.
 10. Discher, D. E.; Eisenberg, A., Polymer Vesicles. *Science* **2002**, 297, (5583), 967-973.
 11. Jain, S.; Bates, F. S., On the Origins of Morphological Complexity in Block Copolymer Surfactants. *Science* **2003**, 300, (5618), 460-464.
 12. Wang, X.-S.; Arsenault, A.; Ozin, G. A.; Winnik, M. A.; Manners, I., Shell Cross-Linked Cylinders of Polyisoprene-*b*-ferrocenyldimethylsilane: Formation of Magnetic Ceramic Replicas and Microfluidic Channel Alignment and Patterning. *Journal of the American Chemical Society* **2003**, 125, (42), 12686-12687.
 13. Liu, G.; Yan, X.; Li, Z.; Zhou, J.; Duncan, S., End Coupling of Block Copolymer Nanotubes to Nanospheres. *Journal of the American Chemical Society* **2003**, 125, (46), 14039-14045.
 14. Gref, R.; Minamitake, Y.; Peracchia, M. T.; Trubetskoy, V.; Torchilin, V.; Langer, R., Biodegradable long-circulating polymeric nanospheres. *Science* **1994**, 263, (5153), 1600-1603.
 15. Allen, C.; Maysinger, D.; Eisenberg, A., Nano-engineering block copolymer aggregates for drug delivery. *Colloids and Surfaces B: Biointerfaces* **1999**, 16, (1-4), 3-27.

-
16. Qiu, L.; Wu, X.; Jin, Y., Doxorubicin-Loaded Polymeric Micelles Based on Amphiphilic Polyphosphazenes with Poly(N -isopropylacrylamide-co- N , N -dimethylacrylamide) and Ethyl Glycinate as Side Groups: Synthesis, Preparation and In Vitro Evaluation *Pharmaceutical Research* **2009**, 26, (4), 946-957.
 17. Lavasanifar, A.; Samuel, J.; Kwon, G. S., Poly(ethylene oxide)-block-poly(-amino acid) micelles for drug delivery. *Advanced Drug Delivery Reviews* **2002**, 54, (2), 169-190.
 18. Jones, M.-C.; Ranger, M.; Leroux, J.-C., pH-sensitive unimolecular polymeric micelles: synthesis of a novel drug carrier. *Bioconjugate Chemistry* **2003**, 14, (4), 774-781.
 19. Riley, T.; Heald, C. R.; Stolnik, S.; Garnett, M. C.; Illum, L.; Davis, S. S.; King, S. M.; Heenan, R. K.; Purkiss, S. C.; Barlow, R. J.; Gellert, P. R.; Washington, C., Core-Shell Structure of PLA-PEG Nanoparticles Used for Drug Delivery. *Langmuir* **2003**, 19, (20), 8428-8435.
 20. Tang, Y.; Liu, S. Y.; Armes, S. P.; Billingham, N. C., Solubilization and Controlled Release of a Hydrophobic Drug Using Novel Micelle-Forming ABC Triblock Copolymers. *Biomacromolecules* **2003**, 4, (6), 1636-1645.
 21. Nojiri, C.; Okano, T.; Jacobs, H. A.; Park, K. D.; Mohammad, S. F.; Olsen, D. B.; Kim, S. W., Blood compatibility of PEO grafted polyurethane and HEMA/styrene block copolymer surfaces. *Journal of Biomedical Materials Research* **1990**, 24, (9), 1151-1171.
 22. Zalipsky, S.; Harris, J. M., Introduction to Chemistry and Biological Applications of Poly(ethylene glycol). In *Poly(ethylene glycol)*, American Chemical Society: Washington DC, 1997; Vol. 680, pp 1-13.

-
23. Seregina, M. V.; Bronstein, L. M.; Platonova, O. A.; Chernyshov, D. M.; Valetsky, P. M.; Hartmann, J.; Wenz, E.; Antonietti, M., Preparation of Noble-Metal Colloids in Block Copolymer Micelles and Their Catalytic Properties in Hydrogenation. *Chemistry of Materials* **1997**, 9, (4), 923-931.
24. Bronstein, L. M.; Vamvakaki, M.; Kostylev, M.; Katsamanis, V.; Stein, B.; Anastasiadis, S. H., Transformations of Poly(methoxy hexa(ethylene glycol) methacrylate)-b-(2-(diethylamino)ethyl methacrylate) Block Copolymer Micelles upon Metalation. *Langmuir* **2005**, 21, (21), 9747-9755.
25. Klingelhoefer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Frster, S.; Antonietti, M., Preparation of Palladium Colloids in Block Copolymer Micelles and Their Use for the Catalysis of the Heck Reaction. *Journal of the American Chemical Society* **1997**, 119, (42), 10116-10120.
26. Mayer, A.; Mark, J., Transition metal nanoparticles protected by amphiphilic block copolymers as tailored catalyst systems. *Colloid & Polymer Science* **1997**, 275, (4), 333-340.
27. Jaramillo, T. F.; Baeck, S.-H.; Cuenya, B. R.; McFarland, E. W., Catalytic Activity of Supported Au Nanoparticles Deposited from Block Copolymer Micelles. *Journal of the American Chemical Society* **2003**, 125, (24), 7148-7149.
28. Platonova, O.; Bronstein, L.; Solodovnikov, S.; Yanovskaya, I.; Obolonkova, E.; Valetsky, P.; Wenz, E.; Antonietti, M., Cobalt nanoparticles in block copolymer micelles: Preparation and properties. *Colloid & Polymer Science* **1997**, 275, (5), 426-431.

-
29. Rutnakornpituk, M.; Thompson, M. S.; Harris, L. A.; Farmer, K. E.; Esker, A. R.; Riffle, J. S.; Connolly, J.; St. Pierre, T. G., Formation of cobalt nanoparticle dispersions in the presence of polysiloxane block copolymers. *Polymer* **2002**, 43, (8), 2337-2348.
30. Diana, F. d. r. S.; Lee, S.-H.; Petroff, P. M.; Kramer, E. J., Fabrication of hcp-Co Nanocrystals via Rapid Pyrolysis in Inverse PS-b-PVP Micelles and Thermal Annealing. *Nano Letters* **2003**, 3, (7), 891-895.
31. Förster, S.; Antonietti, M., Amphiphilic Block Copolymers in Structure-Controlled Nanomaterial Hybrids. *Advanced Materials* **1998**, 10, (3), 195-217.
32. Möller, M.; Spatz, J. P.; Roescher, A., Gold nanoparticles in micellar poly(styrene)-b-poly(ethylene oxide) films—size and interparticle distance control in monoparticulate films. *Advanced Materials* **1996**, 8, (4), 337-340.
33. Sidorov, S. N.; Bronstein, L. M.; Kabachii, Y. A.; Valetsky, P. M.; Soo, P. L.; Maysinger, D.; Eisenberg, A., Influence of Metalation on the Morphologies of Poly(ethylene oxide)-block-poly(4-vinylpyridine) Block Copolymer Micelles. *Langmuir* **2004**, 20, (9), 3543-3550.
34. Zubarev, E. R.; Xu, J.; Sayyad, A.; Gibson, J. D., Amphiphilic Gold Nanoparticles with V-Shaped Arms. *Journal of the American Chemical Society* **2006**, 128, (15), 4958-4959.
35. Sanchez-Gaytan, B. L.; Cui, W.; Kim, Y.; Mendez-Polanco, M. A.; Duncan, T. V.; Fryd, M.; Wayland, B. B.; Park, S.-J., Interfacial Assembly of Nanoparticles in Discrete Block-Copolymer Aggregates. *Angewandte Chemie International Edition* **2007**, 46, (48), 9235-9238.

-
36. Spatz, J. P.; Herzog, T.; Mößmer, S.; Ziemann, P.; Möller, M., Micellar Inorganic-Polymer Hybrid Systems—A Tool for Nanolithography. *Advanced Materials* **1999**, 11, (2), 149-153.
37. Loginova, T. P.; Kabachii, Y. A.; Sidorov, S. N.; Zhironov, D. N.; Valetsky, P. M.; Ezernitskaya, M. G.; Dybrovina, L. V.; Bragina, T. P.; Lependina, O. L.; Stein, B.; Bronstein, L. M., Molybdenum Sulfide Nanoparticles in Block Copolymer Micelles: Synthesis and Tribological Properties. *Chemistry of Materials* **2004**, 16, (12), 2369-2378.
38. Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W., Biodegradable block copolymers as injectable drug-delivery systems. *Nature* **1997**, 388, (6645), 860-862.
39. Otsuka, H.; Nagasaki, Y.; Kataoka, K., PEGylated nanoparticles for biological and pharmaceutical applications. *Advanced Drug Delivery Reviews* **2003**, 55, (3), 403-419.
40. Moffitt, M.; McMahon, L.; Pessel, V.; Eisenberg, A., Size Control of Nanoparticles in Semiconductor-Polymer Composites. 2. Control via Sizes of Spherical Ionic Microdomains in Styrene-Based Diblock Ionomers. *Chemistry of Materials* **1995**, 7, (6), 1185-1192.
41. Saito, R.; Okamura, S.-i.; Ishizu, K., Introduction of colloidal silver into poly(2-vinyl pyridine) microdomains of microphase separated poly(styrene-*b*-2-vinyl pyridine) film: 3. Poly(2-vinyl pyridine) spherical microdomain. *Polymer* **1993**, 34, (6), 1189-1195.
42. Underhill, R. S.; Liu, G., Triblock Nanospheres and Their Use as Templates for Inorganic Nanoparticle Preparation. *Chemistry of Materials* **2000**, 12, (8), 2082-2091.

-
43. Lu, Z.; Liu, G.; Phillips, H.; Hill, J. M.; Chang, J.; Kydd, R. A., Palladium Nanoparticle Catalyst Prepared in Poly(Acrylic Acid)-lined Channels of Diblock Copolymer Microspheres. *Nano Letters* **2001**, 1, (12), 683-687.
44. Yan, X.; Liu, G.; Liu, F.; Tang, B. Z.; Peng, H.; Pakhomov, A. B.; Wong, C. Y., Superparamagnetic Triblock Copolymer/Fe₂O₃ Hybrid Nanofibers. *Angewandte Chemie International Edition* **2001**, 40, (19), 3593-3596.
45. Jinnai, H.; Kaneko, T.; Nishioka, H.; Hasegawa, H.; Nishi, T., Spatial arrangement of metal nanoparticles supported by porous polymer substrates studied by transmission electron microtomography. *The Chemical Record* **2006**, 6, (5), 267-274.
46. Bronstein, L. M.; Sidorov, S. N.; Valetsky, P. M.; Hartmann, J.; Cölfen, H.; Antonietti, M., Induced Micellization by Interaction of Poly(2-vinylpyridine)-block-poly(ethylene oxide) with Metal Compounds. Micelle Characteristics and Metal Nanoparticle Formation. *Langmuir* **1999**, 15, (19), 6256-6262.
47. Moffitt, M.; Vali, H.; Eisenberg, A., Spherical Assemblies of Semiconductor Nanoparticles in Water-Soluble Block Copolymer Aggregates. *Chemistry of Materials* **1998**, 10, (4), 1021-1028.
48. Rodríguez-Hernández, J.; Chécot, F.; Gnanou, Y.; Lecommandoux, S., Toward 'smart' nano-objects by self-assembly of block copolymers in solution. *Progress in Polymer Science* **2005**, 30, (7), 691-724.
49. Prato, M., [60]Fullerene chemistry for materials science applications. *Journal of Materials Chemistry* **1997**, 7, (7), 1097-1109.
50. Wudl, F., Fullerene materials. *Journal of Materials Chemistry* **2002**, 12, (7), 1959-1963.

-
51. Wudl, F., The chemical properties of buckminsterfullerene (C₆₀) and the birth and infancy of fulleroids. *Accounts of Chemical Research* **1992**, 25, (3), 157-161.
52. Bezmel'nitsyn, V. N.; et al., Fullerenes in solutions. *Physics-Uspekhi* **1998**, 41, (11), 1091.
53. Geckeler, K. E.; Samal, S., Syntheses and properties of macromolecular fullerenes, a review. *Polymer International* **1999**, 48, (9), 743-757.
54. Wang, C.; Guo, Z.-X.; Fu, S.; Wu, W.; Zhu, D., Polymers containing fullerene or carbon nanotube structures. *Progress in Polymer Science* **2004**, 29, (11), 1079-1141.
55. Nierengarten, J. F.; Gutiérrez-Nava, M.; Zhang, S.; Masson, P.; Oswald, L.; Bourgogne, C.; Rio, Y.; Accorsi, G.; Armaroli, N.; Setayesh, S., Fullerene-containing macromolecules for materials science applications. *Carbon* **2004**, 42, (5-6), 1077-1083.
56. Ball, Z. T.; Sivula, K.; Frechet, J. M. J., Well-Defined Fullerene-Containing Homopolymers and Diblock Copolymers with High Fullerene Content and Their Use for Solution-Phase and Bulk Organization. *Macromolecules* **2005**, 39, (1), 70-72.
57. Sivula, K.; Ball, Z.; Watanabe, N.; Fréchet, J., Amphiphilic Diblock Copolymer Compatibilizers and Their Effect on the Morphology and Performance of Polythiophene:Fullerene Solar Cells. *Advanced Materials* **2006**, 18, (2), 206-210.
58. Huang, X. D.; Goh, S. H.; Lee, S. Y.; Huan, C. H. A., Complexation between hydrogensulfated fullerenol and poly(4-vinylpyridine). *Macromolecular Chemistry and Physics* **2000**, 201, (2), 281-287.
59. Fujita, N.; Yamashita, T.; Asai, M.; Shinkai, S., Formation of [60]Fullerene Nanoclusters with Controlled Size and Morphology through the Aid of Supramolecular

-
- Rod-Coil Diblock Copolymers. *Angewandte Chemie International Edition* **2005**, 44, (8), 1257-1261.
60. Yu, H.; Gan, L. H.; Hu, X.; Venkatraman, S. S.; Tam, K. C.; Gan, Y. Y., A Novel Amphiphilic Double-[60]Fullerene-Capped Triblock Copolymer. *Macromolecules* **2005**, 38, (23), 9889-9893.
61. Ravi, P.; Dai, S.; Changwang; Tam, K., Fullerene Containing Polymers: A Review on Their Synthesis and Supramolecular Behavior in Solution. *Journal of Nanoscience and Nanotechnology* **2007**, 7, (4-5), 1176-1196.
62. Ravi, P.; Dai, S.; Meng Hong, K.; Tam, K. C.; Gan, L. H., Self-assembly of C60 containing poly(methyl methacrylate) in ethyl acetate/decalin mixtures solvent. *Polymer* **2005**, 46, (13), 4714-4721.
63. Song, T.; Goh, S. H.; Lee, S. Y., Interpolymer Complexes through Hydrophobic Interactions: C60-End-Capped Linear or Four-Arm Poly(ethylene oxide)/Poly(acrylic acid) Complexes. *Macromolecules* **2002**, 35, (10), 4133-4137.
64. Song, T.; Dai, S.; Tam, K. C.; Lee, S. Y.; Goh, S. H., Aggregation behavior of two-arm fullerene-containing poly(ethylene oxide). *Polymer* **2003**, 44, (8), 2529-2536.
65. Yang, J.; Li, L.; Wang, C., Synthesis of a Water Soluble, Monosubstituted C60 Polymeric Derivative and Its Photoconductive Properties. *Macromolecules* **2003**, 36, (16), 6060-6065.
66. Kawauchi, T.; Kumaki, J.; Yashima, E., Nanosphere and Nanonetwork Formations of [60]Fullerene-End-Capped Stereoregular Poly(methyl methacrylate)s through Stereocomplex Formation Combined with Self-Assembly of the Fullerenes. *Journal of the American Chemical Society* **2006**, 128, (32), 10560-10567.

-
67. Dai, S.; Ravi, P.; Tan, C. H.; Tam, K. C., Self-Assembly Behavior of a Stimuli-Responsive Water-Soluble [60]Fullerene-Containing Polymer. *Langmuir* **2004**, 20, (20), 8569-8575.
68. Laiho, A.; Ras, R. H. A.; Valkama, S.; Ruokolainen, J.; Österbacka, R.; Ikkala, O., Control of Self-Assembly by Charge-Transfer Complexation between C60 Fullerene and Electron Donating Units of Block Copolymers. *Macromolecules* **2006**, 39, (22), 7648-7653.
69. Tsarevsky, N. V.; Matyjaszewski, K., "Green:atom transfer radical polymerization: From process design to preparation of well-defined environmentally friendly polymeric materials. *Chemical Reviews* **2007**, 107, (6), 2270-2299.
70. Teodorescu, M.; Matyjaszewski, K., Atom Transfer Radical Polymerization of (Meth)acrylamides. *Macromolecules* **1999**, 32, (15), 4826-4831.
71. Rademacher, J. T.; Baum, M.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J., Atom Transfer Radical Polymerization of N,N-Dimethylacrylamide. *Macromolecules* **1999**, 33, (2), 284-288.
72. Matyjaszewski, K.; Xia, J., Atom transfer radical polymerization. *Chemical Reviews* **2001**, 101, (9), 2921-2990.
73. Chen, L. M.; Hong, Z.; Li, G.; Yang, Y., Recent Progress in Polymer Solar Cells: Manipulation of Polymer:Fullerene Morphology and the Formation of Efficient Inverted Polymer Solar Cells. *Advanced Materials* **2009**, 21, (14-15), 1434-1449.
74. Po, R.; Maggini, M.; Camaioni, N., Polymer Solar Cells: Recent Approaches and Achievements. *The Journal of Physical Chemistry C* **2010**, 114, (2), 695-706.

-
75. Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I.; Heeger, A. J.; Stucky, G.; Wudl, F., Semiconducting polymer-buckminsterfullerene heterojunctions: Diodes, photodiodes, and photovoltaic cells. *Applied Physics Letters* **1993**, 62, (6), 585-587.
76. Orfanopoulos, M.; Kambourakis, S., Chemical evidence of singlet oxygen production from C60 and C70 in aqueous and other polar media. *Tetrahedron Letters* **1995**, 36, (3), 435-438.
77. Sary, N.; Richard, F.; Brochon, C.; Leclerc, N.; Lvque, P.; Audinot, J. N.; Berson, S.; Heiser, T.; Hadziioannou, G.; Mezzenga, R., A New Supramolecular Route for Using Rod-Coil Block Copolymers in Photovoltaic Applications. *Advanced Materials* **2010**, 22, (6), 763-768.
78. Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S., Photophysical Characterization and Singlet Oxygen Yield of a Dihydrofullerene. *Journal of the American Chemical Society* **1994**, 116, (21), 9763-9764.
79. Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F., Radical Reactions of C60. *Science* **1991**, 254, (5035), 1183-1185.
80. Markovic, Z.; Trajkovic, V., Biomedical potential of the reactive oxygen species generation and quenching by fullerenes (C60). *Biomaterials* **2008**, 29, (26), 3561-3573.
81. Bourtine, A. S.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Hlne, C., Fulleren-Oligonucleotid-Konjugate: photoinduzierte sequenzspezifische DNA-Spaltung. *Angewandte Chemie* **1994**, 106, (23-24), 2526-2529.
82. Zhu, C. C.; Xu, Y.; Liu, Y. Q.; Zhu, D. B., Preparation and Characterization of Novel Amphiphilic C60 Derivatives. *The Journal of Organic Chemistry* **1997**, 62, (7), 1996-2000.

-
83. Ford, W. T.; Nishioka, T.; McCleskey, S. C.; Mourey, T. H.; Kahol, P., Structure and Radical Mechanism of Formation of Copolymers of C60 with Styrene and with Methyl Methacrylate. *Macromolecules* **2000**, 33, (7), 2413-2423.
84. Mehrotra, S.; Nigam, A.; Malhotra, R., Effect of [60]fullerene on the radical polymerization of alkenes. *Chemical Communications* **1997**, (5), 463-464.
85. Hamano, T.; Okuda, K.; Mashino, T.; Hirobe, M.; Arakane, K.; Ryu, A.; Mashiko, S.; Nagano, T., Singlet oxygen production from fullerene derivatives: effect of sequential functionalization of the fullerene core. *Chemical Communications* **1997**, (1), 21-22.
86. Guldi, D. M.; Asmus, K.-D., Photophysical Properties of Mono- and Multiply-Functionalized Fullerene Derivatives. *The Journal of Physical Chemistry A* **1997**, 101, (8), 1472-1481.
87. Prat, F.; Stackow, R.; Bernstein, R.; Qian, W.; Rubin, Y.; Foote, C. S., Triplet-State Properties and Singlet Oxygen Generation in a Homologous Series of Functionalized Fullerene Derivatives. *The Journal of Physical Chemistry A* **1999**, 103, (36), 7230-7235.
88. Chen, X. L.; Jenekhe, S. A., Solubilization and Encapsulation of Fullerenes by Amphiphilic Block Copolymers. *Langmuir* **1999**, 15, (23), 8007-8017.
89. Wang, X.-S.; Metanawin, T.; Zheng, X.-Y.; Wang, P.-Y.; Ali, M.; Vernon, D., Structure-Defined C60/Polymer Colloids Supramolecular Nanocomposites in Water. *Langmuir* **2008**, 24, (17), 9230-9232.
90. Yu, H.; Gan, L. H.; Hu, X.; Gan, Y. Y., A pH-sensitive double [60]fullerene-end-capped polymers via ATRP: Synthesis and aggregation behavior. *Polymer* **2007**, 48, (8), 2312-2321.

91. Buttke, T. M.; McCubrey, J. A.; Owen, T. C., Use of an aqueous soluble tetrazolium/formazan assay to measure viability and proliferation of lymphokine-dependent cell lines. *Journal of Immunological Methods* **1993**, 157, (1-2), 233-240.
92. Mosmann, T., Rapid colorimetric assay for cellular growth and survival: Application to proliferation and cytotoxicity assays. *Journal of Immunological Methods* **1983**, 65, (1-2), 55-63.
93. Malich, G.; Markovic, B.; Winder, C., The sensitivity and specificity of the MTS tetrazolium assay for detecting the in vitro cytotoxicity of 20 chemicals using human cell lines. *Toxicology* **1997**, 124, (3), 179-192.
94. Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S.; Banerjee, M.; Mukherjee, A. K., Study of Molecular Complex Formation between [60]Fullerene and Two Series of Donors by the NMR Method. *The Journal of Physical Chemistry A* **2001**, 105, (43), 9865-9868.
95. Bhattacharya, S.; Nayak, S. K.; Chattopadhyay, S. K.; Banerjee, M.; Mukherjee, A. K., Absorption spectroscopic study of EDA complexes of [70] fullerene with a series of methyl benzenes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2001**, 57, (2), 309-313.
96. Ezra, G.; Zilkha, A., Grafting of preformed polyethylene oxide on starch. *Journal of Applied Polymer Science* **1969**, 13, (7), 1493-1496.
97. Yun, S.-H.; Yoo, S. I.; Jung, J. C.; Zin, W.-C.; Sohn, B.-H., Highly Ordered Arrays of Nanoparticles in Large Areas from Diblock Copolymer Micelles in Hexagonal Self-Assembly. *Chemistry of Materials* **2006**, 18, (24), 5646-5648.

-
98. Shen, W.; Wang, H.; Peng, H.; Nie, L.; Chen, D.; Jiang, M., Facile preparation of stabilized polymeric nanotubes using sacrificial yttrium hydroxide nanotubes as template and block copolymer micelles as precursor. *Chemical Communications* **2007**, (23), 2360-2362.
99. Li, T.; Wu, L.; Suthiwangcharoen, N.; Bruckman, M. A.; Cash, D.; Hudson, J. S.; Ghoshroy, S.; Wang, Q., Controlled assembly of rodlike viruses with polymers. *Chemical Communications* **2009**, (20), 2869-2871.
100. Gharbi, N.; Pressac, M.; Hadchouel, M.; Szwarc, H.; Wilson, S. R.; Moussa, F., [60]Fullerene is a Powerful Antioxidant in Vivo with No Acute or Subacute Toxicity. *Nano Letters* **2005**, 5, (12), 2578-2585.
101. Ryan, J. J.; Bateman, H. R.; Stover, A.; Gomez, G.; Norton, S. K.; Zhao, W.; Schwartz, L. B.; Lenk, R.; Kepley, C. L., Fullerene Nanomaterials Inhibit the Allergic Response. *The Journal of Immunology* **2007**, 179, (1), 665-672.
102. Dresselhaus, M., S; Dresselhaus, G.; Eklund, P., C, Science of Fullerenes and Carbon Nanotubes. *Academic Press, New York, NY* **1996**
103. Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R., Superconductivity at 18 K in potassium-doped C₆₀. *Nature* **1991**, 350, (6319), 600-601.
104. Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F., Photoinduced Electron Transfer from a Conducting Polymer to Buckminsterfullerene. *Science* **1992**, 258, (5087), 1474-1476.
105. Wang, Y., Photoconductivity of fullerene-doped polymers. *Nature* **1992**, 356, (6370), 585-587.

-
106. Hirsch, A., *The Chemistry of the Fullerenes In: , Georg Thieme Verlag, Stuttgart* 1994.
107. Andreoni, W., *The Chemical Physics of Fullerenes 10 (and 5) Years Later.* Kluwer Academic Publishers: Dordrecht, The Netherlands: 1996
108. Kajii, H.; Araki, H.; Zakhidov, A. A.; Yakushi, K.; Yoshino, K., Low-field microwave absorption and ESR in "conducting polymer-fullerene-alkali metal" superconductors: Comparative study of various host matrices. *Synthetic Metals* **1997**, 86, (1-3), 2351-2352.
109. Wang, Y.; Suna, A., Fullerenes in Photoconductive Polymers. Charge Generation and Charge Transport. *The Journal of Physical Chemistry B* **1997**, 101, (29), 5627-5638.
110. Zakhidov, A. A.; Araki, H.; Tada, K.; Yakushi, K.; Yoshino, K., Granular superconductivity in a conducting polymer-fullerene-alkali metal composite. *Physics Letters A* **1995**, 205, (4), 317-326.
111. Ros, a. D.; Spalluto, G.; Prato, M., Biological Applications of Fullerene Derivatives: A Brief Overview. *Croatica Chemica Acta* **2001**, 74, (4), 743-755.
112. Braun, C. H.; Richter, T. V.; Schacher, F.; Müller, A. H. E.; Crossland, E. J. W.; Ludwigs, S., Block Copolymer Micellar Nanoreactors for the Directed Synthesis of ZnO Nanoparticles. In *Macromolecular Rapid Communications*, WILEY-VCH Verlag: Vol. 31, pp 729-734.
113. Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Rao, P. R. V.; Mathews, C. K., Solubility of C₆₀ in organic solvents. *The Journal of Organic Chemistry* **1992**, 57, (22), 6077-6079.

-
114. Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C., Solubility of fullerene (C₆₀) in a variety of solvents. *The Journal of Physical Chemistry* **1993**, 97, (13), 3379-3383.
115. Deguchi, S.; Alargova, R. G.; Tsujii, K., Stable Dispersions of Fullerenes, C₆₀ and C₇₀, in Water. Preparation and Characterization. *Langmuir* **2001**, 17, (19), 6013-6017.
116. Abetz, V., *Assemblies in Complex Block Copolymer Systems*, Marcel Dekker: New York . pp. 215-262. 2000.
117. Ruokolainen, J.; aumli; kinen, R.; Torkkeli, M.; kel; T.; Serimaa, R.; Brinke, G. t.; Ikkala, O., Switching Supramolecular Polymeric Materials with Multiple Length Scales. *Science* **1998**, 280, (5363), 557-560.
118. Hamley, I. W., Nanotechnology with Soft Materials. *Angewandte Chemie International Edition* **2003**, 42, (15), 1692-1712.
119. Ikkala, O.; ten Brinke, G., Hierarchical self-assembly in polymeric complexes: Towards functional materials. *Chemical Communications* **2004**, (19), 2131-2137.
120. Stalmach, U.; de Boer, B.; Videlot, C.; van Hutten, P. F.; Hadziioannou, G., Semiconducting Diblock Copolymers Synthesized by Means of Controlled Radical Polymerization Techniques. *Journal of the American Chemical Society* **2000**, 122, (23), 5464-5472.
121. Okamura, H.; Ide, N.; Minoda, M.; Komatsu, K.; Fukuda, T., Solubility and Micellization Behavior of C₆₀ Fullerenes with Two Well-Defined Polymer Arms. *Macromolecules* **1998**, 31, (6), 1859-1865.

-
122. Asai, M.; Fujita, N.; Shinkai, S., Silica Gel Fabrication of [60]Fullerene Aggregates Utilizing Poly(N-vinylpyrrolidone) as a "Glue". *Chemistry Letters* **2003**, 32, (2), 186-187.
123. Ruokolainen, J.; ten Brinke, G.; Ikkala, O.; Torkkeli, M.; Serimaa, R., Mesomorphic Structures in Flexible Polymer–Surfactant Systems Due to Hydrogen Bonding: Poly(4-vinylpyridine)–Pentadecylphenol. *Macromolecules* **1996**, 29, (10), 3409-3415.
124. Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Vahvaselka, S.; Saariaho, M.; ten Brinke, G.; Ikkala, O., Critical Interaction Strength for Surfactant-Induced Mesomorphic Structures in Polymer–Surfactant Systems. *Macromolecules* **1996**, 29, (20), 6621-6628.
125. Sin, S. L.; Gan, L. H.; Hu, X.; Tam, K. C.; Gan, Y. Y., Photochemical and Thermal Isomerizations of Azobenzene-Containing Amphiphilic Diblock Copolymers in Aqueous Micellar Aggregates and in Film. *Macromolecules* **2005**, 38, (9), 3943-3948.
126. Duan, H.; Chen, D.; Jiang, M.; Gan, W.; Li, S.; Wang, M.; Gong, J., Self-Assembly of Unlike Homopolymers into Hollow Spheres in Nonselective Solvent. *Journal of the American Chemical Society* **2001**, 123, (48), 12097-12098.
127. Mignard, E.; Hiorns, R. C.; François, B., Synthesis and Characterization of Star Copolymers Consisting of Fullerene and Conjugated Polyphenylene: 6-star-C60[styrene–poly(1,4-phenylene)-block-polystyrene] and 6-star-C60[polystyrene-block-poly(1,4-phenylene)]. *Macromolecules* **2002**, 35, (16), 6132-6141.
128. Chaurasia, A.; Gan, L. H.; Hu, X., Dramatic solvent effect on interaction kinetics and self-organization of phenyl-C61-butyric-acid-methyl-ester (PCBM) in a tri-block copolymer. *Macromolecular Chemistry and Physics, accepted and in press.* **2011**

-
129. Laiho, A.; Ras, R. H. A.; Valkama, S.; Ruokolainen, J.; Åsterbacka, R.; Ikkala, O., Control of Self-Assembly by Charge-Transfer Complexation between C60 Fullerene and Electron Donating Units of Block Copolymers. *Macromolecules* **2006**, 39, (22), 7648-7653.
130. Beek, W.; Slooff, L.; Wienk, M.; Kroon, J.; Janssen, R., Hybrid Solar Cells Using a Zinc Oxide Precursor and a Conjugated Polymer. *Advanced Functional Materials* **2005**, 15, (10), 1703-1707.
131. Willander, M.; et al., Zinc oxide nanorod based photonic devices: recent progress in growth, light emitting diodes and lasers. *Nanotechnology* **2009**, 20, (33), 332001.
132. Oosterhout, S. D.; Wienk, M. M.; van Bavel, S. S.; Thiedmann, R.; Jan Anton Koster, L.; Gilot, J.; Loos, J.; Schmidt, V.; Janssen, R. A. J., The effect of three-dimensional morphology on the efficiency of hybrid polymer solar cells. *Nat Mater* **2009**, 8, (10), 818-824.
133. Ong, B. S.; Li, C.; Li, Y.; Wu, Y.; Loutfy, R., Stable, Solution-Processed, High-Mobility ZnO Thin-Film Transistors. *Journal of the American Chemical Society* **2007**, 129, (10), 2750-2751.
134. Guo, D.; Wu, C.; Jiang, H.; Li, Q.; Wang, X.; Chen, B., Synergistic cytotoxic effect of different sized ZnO nanoparticles and daunorubicin against leukemia cancer cells under UV irradiation. *Journal of Photochemistry and Photobiology B: Biology* **2008**, 93, (3), 119-126.
135. Ravirajan, P.; Peiro, A. M.; Nazeeruddin, M. K.; Graetzel, M.; Bradley, D. D. C.; Durrant, J. R.; Nelson, J., Hybrid Polymer/Zinc Oxide Photovoltaic Devices with

Vertically Oriented ZnO Nanorods and an Amphiphilic Molecular Interface Layer. *The Journal of Physical Chemistry B* **2006**, 110, (15), 7635-7639.

136. Ji, L.; Shih, W.; Fang, T.; Wu, C.; Peng, S.; Meen, T., Preparation and characteristics of hybrid ZnO-polymer solar cells. *Journal of Materials Science* **2010**, 45, (12), 3266-3269.

137. Ohyama, M.; Kouzuka, H.; Yoko, T., Sol-gel preparation of ZnO films with extremely preferred orientation along (002) plane from zinc acetate solution. *Thin Solid Films* **1997**, 306, (1), 78-85.

138. Lim, J. H.; Kang, C. K.; Kim, K. K.; Park, I. K.; Hwang, D. K.; Park, S. J., UV Electroluminescence Emission from ZnO Light-Emitting Diodes Grown by High-Temperature Radiofrequency Sputtering. *Advanced Materials* **2006**, 18, (20), 2720-2724.

139. Hofstetter, D.; Bonetti, Y.; Giorgetta, F. R.; El-Shaer, A.-H.; Bakin, A.; Waag, A.; Schmidt-Grund, R.; Schubert, M.; Grundmann, M., Demonstration of an ultraviolet ZnO-based optically pumped third order distributed feedback laser. *Applied Physics Letters* **2007**, 91, (11), 111108-3.

140. Stouwdam, J. W.; Janssen, R. A. J., Red, green, and blue quantum dot LEDs with solution processable ZnO nanocrystal electron injection layers. *Journal of Materials Chemistry* **2008**, 18, (16), 1889-1894.

141. Wu, Y. L.; et al., A dual-colored bio-marker made of doped ZnO nanocrystals. *Nanotechnology* **2008**, 19, (34), 345-605.

142. Senthilkumar, K.; et al., Preparation of ZnO nanoparticles for bio-imaging applications. *physica status solidi (b)* **2009**, NA.

-
143. Sofos, M.; Goldberger, J.; Stone, D. A.; Allen, J. E.; Ma, Q.; Herman, D. J.; Tsai, W.-W.; Lauhon, L. J.; Stupp, S. I., A synergistic assembly of nanoscale lamellar photoconductor hybrids. *Nat Mater* **2009**, 8, (1), 68-75.
144. Lee, J. K.; Tewell, C. R.; Schulze, R. K.; Nastasi, M.; Hamby, D. W.; Lucca, D. A.; Jung, H. S.; Hong, K. S., Synthesis of ZnO nanocrystals by subsequent implantation of Zn and O species. *Applied Physics Letters* **2005**, 86, (18), 183111-3.
145. Kim, S.-W.; Ueda, M.; Funato, M.; Fujita, S.; Fujita, S., Artificial control of ZnO nanodots by ion-beam nanopatterning. *Journal of Applied Physics* **2005**, 97, (10), 104316-9.
146. Jing, L.; Suntao, W.; Junyong, K. In *ZnO films deposited by RF magnetron sputtering*, Semiconducting and Insulating Materials, 2004. SIMC-XIII-2004. 13th International Conference on, 2005; 2005; pp 77-80.
147. Kim, K.-K.; Koguchi, N.; Ok, Y.-W.; Seong, T.-Y.; Park, S.-J., Fabrication of ZnO quantum dots embedded in an amorphous oxide layer. *Applied Physics Letters* **2004**, 84, (19), 3810-3812.
148. Lu, J. G.; Ye, Z. Z.; Huang, J. Y.; Zhu, L. P.; Zhao, B. H.; Wang, Z. L.; Fujita, S., ZnO quantum dots synthesized by a vapor phase transport process. *Applied Physics Letters* **2006**, 88, (6), 063110-063110-3.
149. Lin, K.-F.; Cheng, H.-M.; Hsu, H.-C.; Lin, L.-J.; Hsieh, W.-F., Band gap variation of size-controlled ZnO quantum dots synthesized by sol-gel method. *Chemical Physics Letters* **2005**, 409, (4-6), 208-211.

-
150. Zhang, L.; Yin, L.; Wang, C.; Lun, N.; Qi, Y., Sol-Gel Growth of Hexagonal Faceted ZnO Prism Quantum Dots with Polar Surfaces for Enhanced Photocatalytic Activity. *ACS Applied Materials & Interfaces* **2**, (6), 1769-1773.
151. Patra, M. K.; Manoth, M.; Singh, V. K.; Siddaramana Gowd, G.; Choudhry, V. S.; Vadera, S. R.; Kumar, N., Synthesis of stable dispersion of ZnO quantum dots in aqueous medium showing visible emission from bluish green to yellow. *Journal of Luminescence* **2009**, 129, (3), 320-324.
152. Spanhel, L.; Anderson, M. A., Semiconductor clusters in the sol-gel process: quantized aggregation, gelation, and crystal growth in concentrated zinc oxide colloids. *Journal of the American Chemical Society* **1991**, 113, (8), 2826-2833.
153. Ostwald, W., *Z. Phys. Chem* **1901**, 37, 385.
154. Meulenkamp, E. A., Synthesis and Growth of ZnO Nanoparticles. *The Journal of Physical Chemistry B* **1998**, 102, (29), 5566-5572.
155. Feng, Y.; Zhang, M.; Guo, M.; Wang, X., Studies on the PEG-Assisted Hydrothermal Synthesis and Growth Mechanism of ZnO Microrod and Mesoporous Microsphere Arrays on the Substrate. *Crystal Growth & Design* **10**, (4), 1500-1507.
156. Yang, M.; Pang, G.; Li, J.; Jiang, L.; Liang, D.; Feng, S., Fabrication of Two-Dimensional ZnO Nanostructures from Nanoparticles. *The Journal of Physical Chemistry C* **2007**, 111, (46), 17213-17220.
157. HAN, D.; ZHANG, S.-C., Synthesis of Hexagonal Cone-Shaped ZnO Nanoparticles Using Solvothermal Reaction and Its Photoluminescence Property. *Acta Phys. -Chim. Sin* **2008**, 24(03), 539-542

-
158. Wang, M.; Na, E. K.; Kim, J. S.; Kim, E. J.; Hahn, S. H.; Park, C.; Koo, K.-K., Photoluminescence of ZnO nanoparticles prepared by a low-temperature colloidal chemistry method. *Materials Letters* **2007**, 61, (19-20), 4094-4096.
159. Wu, C.; Zeng, T., Size-Tunable Synthesis of Metallic Nanoparticles in a Continuous and Steady-Flow Reactor. *Chemistry of Materials* **2006**, 19, (2), 123-125.
160. Hartlieb, K. J.; Raston, C. L.; Saunders, M., Controlled Scalable Synthesis of ZnO Nanoparticles. *Chemistry of Materials* **2007**, 19, (23), 5453-5459.
161. Li, M.; Hari, B.; Lv, X.; Ma, X.; Sun, F.; Tang, L.; Wang, Z., Direct synthesis of monodispersed ZnO nanoparticles in an aqueous solution. *Materials Letters* **2007**, 61, (3), 690-693.
162. Panchakarla, L.; Govindaraj, A.; Rao, C., Formation of ZnO Nanoparticles by the Reaction of Zinc Metal with Aliphatic Alcohols. *Journal of Cluster Science* **2007**, 18, (3), 660-670.
163. Wang, C.; Li, Q.; Mao, B.; Wang, E.; Tian, C., A different chemical route to synthesize ZnO nanoparticles. *Materials Letters* **2008**, 62, (8-9), 1339-1341.
164. Dong Ick, S.; Chan H, Y.; Won T, K.; Tae W, K., White light-emitting diodes fabricated utilizing hybrid polymer-colloidal ZnO quantum dots. *Nanotechnology* **2009**, 20, (36), 365206.
165. Ji, L.; Shih, W.; Fang, T.; Wu, C.; Peng, S.; Meen, T., Preparation and characteristics of hybrid ZnO-polymer solar cells. *Journal of Materials Science* **45**, (12), 3266-3269.

-
166. Khrenov, V.; Klapper, M.; Koch, M.; Müllen, K., Surface Functionalized ZnO Particles Designed for the Use in Transparent Nanocomposites. *Macromolecular Chemistry and Physics* **2005**, 206, (1), 95-101.
167. Sun, D.; Sue, H.-J.; Miyatake, N., Optical Properties of ZnO Quantum Dots in Epoxy with Controlled Dispersion. *The Journal of Physical Chemistry C* **2008**, 112, (41), 16002-16010.
168. Carrey, J.; et al., Photoconductivity of self-assembled ZnO nanoparticles synthesized by organometallic chemistry. *Semiconductor Science and Technology* **2008**, 23, (2), 025003.
169. Monge, M.; Kahn, M. L.; Maisonnat, A.; Chaudret, B., Room-Temperature Organometallic Synthesis of Soluble and Crystalline ZnO Nanoparticles of Controlled Size and Shape. *Angewandte Chemie International Edition* **2003**, 42, (43), 5321-5324.
170. Kahn, M.; Monge, M.; Snoeck, E.; Maisonnat, A.; Chaudret, B., Spontaneous Formation of Ordered 2D and 3D Superlattices of ZnO Nanocrystals. *Small* **2005**, 1, (2), 221-224.
171. Braun, C. H.; Richter, T. V.; Schacher, F.; Müller, A. H. E.; Crossland, E. J. W.; Ludwigs, S., Block Copolymer Micellar Nanoreactors for the Directed Synthesis of ZnO Nanoparticles. *Macromolecular Rapid Communications* **2010**, 31, (8), 729-734.
172. Mela, P.; Gorzolnik, B.; Bückins, M.; Mourran, A.; Mayer, J.; Möller, M., Low-Ion-Dose FIB Modification of Monomicellar Layers for the Creation of Highly Ordered Metal Nanodot Arrays. *Small* **2007**, 3, (8), 1368-1373.

-
173. Spatz, J. P.; Mössmer, S.; Hartmann, C.; Möller, M.; Herzog, T.; Krieger, M.; Boyen, H.-G.; Ziemann, P.; Kabius, B., Ordered Deposition of Inorganic Clusters from Micellar Block Copolymer Films. *Langmuir* **1999**, 16, (2), 407-415.
174. Antonietti, M.; Thünemann, A.; Wenz, E., Synthesis and characterization of non-spherical gold colloids in block-copolymer micelles. *Colloid & Polymer Science* **1996**, 274, (8), 795-800.
175. Li, X.; Lau, K. H. A.; Kim, D. H.; Knoll, W., High-Density Arrays of Titania Nanoparticles Using Monolayer Micellar Films of Diblock Copolymers as Templates. *Langmuir* **2005**, 21, (11), 5212-5217.
176. Kim, D. H.; Kim, S. H.; Lavery, K.; Russell, T. P., Inorganic Nanodots from Thin Films of Block Copolymers. *Nano Letters* **2004**, 4, (10), 1841-1844.
177. Bennett, R. D.; Miller, A. C.; Kohen, N. T.; Hammond, P. T.; Irvine, D. J.; Cohen, R. E., Strategies for Controlling the Planar Arrangement of Block Copolymer Micelles and Inorganic Nanoclusters. *Macromolecules* **2005**, 38, (26), 10728-10735.
178. Yoo, S. I.; Sohn, B.-H.; Zin, W.-C.; An, S.-J.; Yi, G.-C., Self-assembled arrays of zinc oxide nanoparticles from monolayer films of diblock copolymer micelles. *Chemical Communications* **2004**, (24), 2850-2851.
179. Pál, E.; Oszkó, A.; Mela, P.; Möller, M.; Dékány, I., Preparation of hexagonally aligned inorganic nanoparticles from diblock copolymer micellar systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, 331, (3), 213-219.
180. Ishizu, K.; Shiratori, S., Architecture of polymeric superstructures: Locking of cubic lattices by graft polymerization from photofunctional core-shell polymer microspheres. *Journal of Materials Science Letters* **2000**, 19, (23), 2105-2107.

-
181. Machida, S.; Nakata, H.; Yamada, K.; Itaya, A., Morphological change of a diblock copolymer film induced by selective doping of a photoactive chromophore. *Journal of Polymer Science Part B: Polymer Physics* **2007**, 45, (3), 368-375.
182. Beek, W. J. E.; Wienk, M. M.; Kemerink, M.; Yang, X.; Janssen, R. A. J., Hybrid Zinc Oxide Conjugated Polymer Bulk Heterojunction Solar Cells. *The Journal of Physical Chemistry B* **2005**, 109, (19), 9505-9516.
183. Lam, Y. M.; Song, L.; Moy, Y. C.; Xi, L.; Boothroyd, C., Controlled chemical stabilization of self-assembled PS-P4VP nanostructures. *Journal of Colloid and Interface Science* **2008**, 317, (1), 255-263.
184. Ningrum, E. O.; Lin, W.-T.; Lo, C.-T., The nanostructure and dewetting of block copolymer thin films annealed in different neutral solvents. *Polymer Engineering & Science*, n/a-n/a.
185. Peng, J.; Kim, D. H.; Knoll, W.; Xuan, Y.; Li, B.; Han, Y., Morphologies in solvent-annealed thin films of symmetric diblock copolymer. *The Journal of Chemical Physics* **2006**, 125, (6), 064702-8.
186. Ishizu, K.; Hosokawa, T.; Tsubaki, K.-i., Cross-linking reaction of segregated microdomains formed by diblock copolymer films. *European Polymer Journal* **2000**, 36, (7), 1333-1338.
187. Ishizu, K.; Fukutomi, T., Core-shell type polymer microspheres prepared from block copolymers. *Journal of Polymer Science Part C: Polymer Letters* **1988**, 26, (7), 281-286.
188. Ishizu, K., Surface changes on block copolymers by crosslinking of spherical microdomains. *Polymer* **1989**, 30, (5), 793-798.

-
189. Panda, S. K.; Dev, A.; Chaudhuri, S., Fabrication and Luminescent Properties of c-Axis Oriented ZnO–ZnS Core–Shell and ZnS Nanorod Arrays by Sulfidation of Aligned ZnO Nanorod Arrays. *The Journal of Physical Chemistry C* **2007**, 111, (13), 5039-5043.
190. Myung, Y.; Jang, D. M.; Sung, T. K.; Sohn, Y. J.; Jung, G. B.; Cho, Y. J.; Kim, H. S.; Park, J., Composition-Tuned ZnO–CdSSe Core–Shell Nanowire Arrayss. *ACS Nano* **4**, (7), 3789-3800.
191. Chen, Z.; He, C.; Li, F.; Tong, L.; Liao, X.; Wang, Y., Responsive Micellar Films of Amphiphilic Block Copolymer Micelles: Control on Micelle Opening and Closing. *Langmuir* **26**, (11), 8869-8874.
192. Zhang, L.; Eisenberg, A., Multiple Morphologies and Characteristics of Crew-Cut Micelle-like Aggregates of Polystyrene-b-poly(acrylic acid) Diblock Copolymers in Aqueous Solutions. *Journal of the American Chemical Society* **1996**, 118, (13), 3168-3181.
193. Alexandridis, P.; Olsson, U.; Lindman, B. r., A Record Nine Different Phases (Four Cubic, Two Hexagonal, and One Lamellar Lyotropic Liquid Crystalline and Two Micellar Solutions) in a Ternary Isothermal System of an Amphiphilic Block Copolymer and Selective Solvents (Water and Oil). *Langmuir* **1998**, 14, (10), 2627-2638.
194. Xiong, H. M.; Wang, Z. D.; Liu, D. P.; Chen, J. S.; Wang, Y. G.; Xia, Y. Y., Bonding Polyether onto ZnO Nanoparticles: An Effective Method for Preparing Polymer Nanocomposites with Tunable Luminescence and Stable Conductivity. *Advanced Functional Materials* **2005**, 15, (11), 1751-1756.

195. Li, S.; Toprak, M.; Jo, Y.; Dobson, J.; Kim, D.; Muhammed, M., Bulk Synthesis of Transparent and Homogeneous Polymeric Hybrid Materials with ZnO Quantum Dots and PMMA. *Advanced Materials* **2007**, 19, (24), 4347-4352.
196. Vanheusden, K.; Warren, W. L.; Seager, C. H.; Tallant, D. R.; Voigt, J. A.; Gnade, B. E., Mechanisms behind green photoluminescence in ZnO phosphor powders. *Journal of Applied Physics* **1996**, 79, (10), 7983-7990.
197. van Dijken, A.; Meulenlamp, E. A.; Vanmaekelbergh, D.; Meijerink, A., Identification of the transition responsible for the visible emission in ZnO using quantum size effects. *Journal of Luminescence* **2000**, 90, (3-4), 123-128.
198. Lin, C.-C.; Li, Y.-Y., Synthesis of ZnO nanowires by thermal decomposition of zinc acetate dihydrate. *Materials Chemistry and Physics* **2009**, 113, (1), 334-337.

List of publications

Posters and Presentations

1. "Interaction kinetics and supramolecular structure of charge transfer complex of a fullerene derivative and a tri-block copolymer" by A. Chaurasia, L. Gan and X. Hu .**215th ECS Meeting 2009 (USA)** (Oral presentation).
2. Supramolecular structure and interaction kinetics of fullerene derivative and blockcopolymer charge transfer complex by A. Chaurasia, L. Gan and X. Hu . **Macro 2010, 43rd IUPAC World Polymer Congress, Glasgow, 2010 (UK)**. (Oral presentation).

Journal Articles

1. A. Chaurasia, L. Gan and X. Hu; "Dramatic solvent effect on interaction kinetics and self-organization of phenyl-C61-butyric-acid-methyl-ester (PCBM) in a tri-block copolymer" **MACROMOLECULAR CHEMISTRY AND PHYSICS**, 212(8): 813-820, 2011.
2. A. Chaurasia, L. Gan and X. Hu; "A facile method based on block-copolymer assisted preparation of functional hybrid materials containing ZnO quantum dots" [Manuscript in preparation].
3. A. Chaurasia, L. Gan and X. Hu; "Biocompatible self-assembled amphiphilic polymer/[60] fullerene supramolecular composite in aqueous through non-aqueous via complex formation"[Manuscript in preparation].

4. A. Chaurasia, L. Gan and X. Hu; “Tuning rate of complexation and supramolecular co-assembly of underivatized fullerene with polymer” [Manuscript in preparation].

Appendix

A1. Gel Permeation Chromatography (GPC).

An Agilent 1100 series GPC system equipped with a liquid chromatography pump, DMF column, and refractive index detector was used to determinate the molecular weights and molecular weight distributions of P4VP-*b*-PEO-*b*-P4VP tri-block copolymer. The column was calibrated with the narrow molecular weight polystyrene standards. The eluent was HPLC grade DMF at a flow rate of 1.0 ml/min. GPC curve for P4VP-*b*-PEO-*b*-P4VP tri-block copolymer is shown in Figure A1. A comparison of M_n obtained from NMR and GPC analysis has been tabulated in Table A1.

Figure. A1. GPC curve for P4VP-*b*-PEO-*b*-P4VP tri-block copolymer.

Table A1

Sample	M_n , $^1\text{H NMR}$ ^(a) ($\times 10^3$)	M_n , GPC ^(b) ($\times 10^3$)	M_w/M_n (GPC)
P4VP ₈ - <i>b</i> -PEO ₁₀₅ - <i>b</i> -P4VP ₈	6.3	8.4	1.21

(a) M_n of P4VP-*b*-PEO-*b*-P4VP estimated by $^1\text{HNMR}$.

(b) M_n of P4VP-*b*-PEO-*b*-P4VP determined by GPC.

A2. Study the effect of crosslinking agent on surface morphology by atomic force microscopy (AFM) study

Atomic force microscopy (AFM) was performed with a Nanoscope III from Digital Instruments operating in the tapping model of scan rate 1.795 Hz using silicon probes. Samples for the AFM experiments were prepared by spin casting of PS-*b*-P4VP/Zn(Ac)₂ solution on silicon. Figure A2. (a) is PS-*b*-P4VP/Zn(Ac)₂ with DBB and Figure A2.(b) is PS-*b*-P4VP/Zn(Ac)₂ without DBB. Both figures are looking almost same with nicely arranged micelle with long range order. The height of film is ~30 nm.

Figure A2. Atomic force microscopy (AFM) phase diagram images of (a) PS-*b*-P4VP/Zn(Ac)₂ with DBB crosslinker; (b) PS-*b*-P4VP/Zn(Ac)₂ without DBB. (Scale bar in 1.00 micron).

The morphology of the samples was changed after heating for 200 °C for 30 min on silicon substrate which are shown in. A2. (c) & (d)

Figure A2. Atomic force microscopy (AFM) phase diagram images of (c) PS-*b*-P4VP/ZnO QDs with DBB crosslinker; (d) PS-*b*-P4VP/ZnO QDs without DBB.

The effect of heat on morphology was much more severe for sample without crosslinking agent (DBB) whereas with crosslinking, the morphology of sample was retained. Film thicknesses become less than 10 nm after heating.

A scheme for crosslinking of the P4VP of PS-*b*-P4VP by 1,4-dibromobutane is given in Figure A2A

Figure A2A Scheme for crosslinking of the P4VP of PS-*b*-P4VP by 1,4-dibromobutane.

A3. Energy-dispersive X-ray (EDX)

Figure A3 shows ZnO energy-dispersive X-ray (EDX) spectra which confirm the presence of ZnO. The weak copper signal was originated from the TEM copper grids whereas Si signal is from the sample holder.

Figure A3. Energy-dispersive X-ray (EDX) spectra of PS-*b*-P4VP/ZnO QDs thin film.

A4. Thermogravimetric Analysis (TGA) study:

The amount of ZnO in ZnO/Polymer nanocomposite was measured using an instruments Q500 thermogravimetric Analyzer (TGA).

The sample for the TGA was prepared by evaporating the toluene from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ /Polymer solution at 90 °C for 2h. The ratio of polymer : $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in toluene was 20:19 (w/w) before heat evaporation. Water (H_2O , m/z : 18) was released from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ during evaporation of toluene at 90 °C.

It was reported that water (H_2O , m/z : 18) content in $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is released as the temperature reach $50\text{ }^\circ\text{C}$.¹⁹⁸ Therefore, the final composition in TGA sample was $\text{Zn}(\text{CH}_3\text{COO})_2/\text{Polymer}$ instead of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}/\text{Polymer}$. A temperature range from ambient to $800\text{ }^\circ\text{C}$ at the rate of $10\text{ }^\circ\text{C min}^{-1}$ under air atmosphere, with a gas flow of 60 ml min^{-1} was used during TGA. TGA curve which is shown in Figure A4, confirmed that the 20.47% residual content was left at $500\text{ }^\circ\text{C}$ and remains same even at $800\text{ }^\circ\text{C}$. The amount of ZnO in final polymer nanocomposite with respect to of ZnO/Polymer nanocomposite is about $\sim 25\%$. This result is well matched with the theoretical calculated result.

Used for TGA analysis

Figure A4. TGA curve for $\text{Zn}(\text{CH}_3\text{COO})_2/\text{Polymer}$ at temperature range from ambient to $800\text{ }^\circ\text{C}$ at the rate of $10\text{ }^\circ\text{C min}^{-1}$ under air atmosphere, with a gas flow of 60 ml min^{-1} .

A4.1. Theoretical calculation for loading of ZnO QDs in polymer

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP), $M_{PS} = 11,800$ g/mol, $M_{P4VP} = 15,000$ g/mol, $M_w/M_n = 1.04$)

PS-*b*-P4VP block polymer was dissolved in toluene at room temperature (2 mg/ml)

Zn(OAc)₂/methanol solution was added to solution of PS-*b*-P4VP to keep the mole ratio of 4VP: Zn(OAc)₂ as 1:0.8 in final solution.

For 20 ml polymer solution = 40 mg of PS-*b*-P4VP

One mole zinc acetate dihydrate, Zn(O₂CCH₃)₂(H₂O)₂, decompose leads one mole of ZnO

Molecular wt of ZnO = 81.41

$$\begin{aligned} \text{Amount of ZnO is formed} &= \frac{\left(\frac{15000}{11800 + 15000} \right) \times 40}{105.14} \times 0.8 \times 81.41 \\ &= 13.87 \end{aligned}$$

$$\begin{aligned} \text{Wt\% of ZnO in ZnO/polymer composite} &= \frac{13.87}{13.87 + 40} \times 100 \\ &\approx 25.9 \end{aligned}$$

A5. Possible implementation of finding from this work into other polymer system

The above process can be applied to PS-*b*-PMMA block polymer or even other polymers.

In Figure A5, ZnO QDs are dispersed in PS-*b*-PMMA block copolymer. Composite of PS-*b*-PMMA/ZnO QDs was formed after heat treatment at 200 °C for 30 min of PS-*b*-PMMA/Zn(Ac)₂. So, we can claim that method we have shown here is very facile and can be used for design other nanomaterials.

Figure A5. TEM images of (a) self-assembled PS-*b*-PMMA/ZnO QDs formed after heat treatment of PS-*b*-PMMA/Zn(Ac)₂ film cast from toluene at 200 °C for 30 min; (b) HR-TEM of ZnO QDs embedded in PS-*b*-PMMA matrix with visible fringes.

Figure A6. HR-TEM of ZnO QDs embedded in PS-*b*-P4VP matrix with visible fringes.

Figure A7 HR-TEM of ZnO QDs embedded in PS-*b*-P4VP matrix with visible fringes