

Nanostructured Block Copolymer Blends and Complexes via Hydrogen Bonding Interactions

by

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Submitted in fulfilment of the requirements for the degree of
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“This thesis is dedicated to my family”

Nisa

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- 2) **Nisa V. Salim** and Qipeng Guo. *Journal of Physical Chemistry B* 2011, 115, 9528–9536 “Vesicular Morphologies in AB/AC Block Copolymer Complexes through Hydrogen Bonding Interactions”.
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- 1) **Nisa V. Salim**, Tracey L. Hanley, Qipeng Guo. “Investigation of Block Copolymer/Homopolymer Blends and Complexes using Small Angle X-ray Scattering (SAXS) Technique”, *SAS2012 International Small-Angle Scattering Conference*, Sydney, Australia 18 - 23 November 2012.
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- 3) Nishar Hameed, **Nisa V. Salim**, Qipeng Guo. “Plastics from renewable resources using ionic liquids”, *5th Australasian Symposium on Ionic Liquids (ASIL-5)*, Melbourne, Australia, 3&4 May 2012
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- 6) Nishar Hameed, Mrunali Sona, **Nisa V. Salim**, Tracey L. Hanley, Qipeng Guo. Improving the Dispersion and Mechanical Properties of Epoxy/Carbon Nanotube Composites, *ISACS6 - Challenges in Organic Materials & Supramolecular Chemistry*, Peking University, Beijing, China, 2-5 September 2011.

- 7) Qipeng Guo, Nishar Hameed, **Nisa V. Salim** “Self-Assembly in Hydrogen Bonded Block Copolymer Systems”. *POLYCHAR19 – World Forum on Advanced Materials*, Kathmandu, Nepal, March 20-24, 2011.

- 8) Qipeng Guo, Nishar Hameed, **Nisa V. Salim**. “Hydrogen Bonded Block Copolymer Systems: From Microphase Separation in Solid State to Self-Assembly in Aqueous Solutions”. *The 32 Australasian Polymer Symposium*, Coffs Harbour, Sydney, Australia, 13-16 February, 2011.

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- 10) **Nisa V. Salim**, Tracey L. Hanley, Qipeng Guo. “Self-Assembled Nanostructured Complexes and Blends via Hydrogen bonding Interactions”. *The Australian X-ray Analytical Association Conference, AXAA-2011*, Sydney, Australia, 6-11 February, 2011.

- 11) **Nisa V. Salim**, Tracey L. Hanley, Qipeng Guo. “Microphase separation in double crystalline poly (ethylene oxide)-block-poly (caprolactone)/poly (4-vinyl phenol) blends”. Book of Abstracts - *Fifth International Symposium on the Separation and Characterization of Natural and Synthetic Macromolecules (SCM-5)* Amsterdam, The Netherlands, January 26th - 28th, 2011. ISBN 9781616279431.

- 12) Nishar Hameed, **Nisa V. Salim**, Qipeng Guo., “Microphase separation through competitive hydrogen bonding in A-b-B/C diblock copolymer/homopolymer systems,” *Zing Polymer Chemistry Conference 2010*, Puerto Morelos, Mexico, 19-22 November 2010.

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LIST OF ABBREVIATIONS AND TERMS

Co	Cobalt
DMF	Dimethylformamide
PAA	Poly acrylic acid
PB	Poly butadiene
PBO	Poly butylene oxide
PBMA	Poly butyl methacrylate
PCEMA- <i>b</i> -PAA	Poly(2-cinnamoyl ethyl methacrylate)- <i>b</i> -poly(acrylic acid)
PCL- <i>b</i> -PMAA	Poly(ϵ -caprolactone)- <i>block</i> -poly(methacrylic acid)
PDP	Pentadecyl phenol
P2EHA- <i>b</i> -PMMA- <i>b</i> -PAA	Poly(2-ethylhexyl acrylate) - <i>block</i> -poly(methyl methacrylate) <i>block</i> - poly(acrylic acid)
PEO- <i>b</i> -PAA	Poly(ethylene oxide)- <i>block</i> -poly(acrylic acid)
PEO- <i>b</i> -PB	Poly(ethylene oxide)- <i>block</i> - polybutadiene
PEO- <i>b</i> -PBO	Poly(ethylene oxide)- <i>block</i> -poly(butylene oxide)
PEO- <i>b</i> -PCL	Poly(ethylene oxide)- <i>block</i> -poly(ϵ -caprolactone)
PEP- <i>b</i> -PEE	Poly(ethylene propylene)- <i>block</i> -poly(ethylethylene)
PEO- <i>b</i> -PPO	Poly(ethylene oxide)- <i>block</i> -poly(propylene oxide)
PEO- <i>b</i> -P2VP- <i>b</i> -PEO	Poly(ethylene oxide)- <i>block</i> -poly(2-vinyl pyridine)- <i>block</i> - poly(ethylene oxide)
PEO- <i>b</i> -PPO- <i>b</i> -PEO	Poly(ethylene oxide)- <i>block</i> -poly(propylene oxide)- <i>block</i> - poly(ethylene oxide)
PHB	Poly 3-hydroxybutyrate
PHV	Poly 3-hydroxyvalerate
Phenoxy	Poly hydroxyether of bisphenol A
PI- <i>b</i> -P2VP	Polyisoprene- <i>block</i> -poly(2-vinyl pyridine)

PMAA	Poly(methacrylic acid)
PMMA	Poly(methyl methacrylate)
PMMA- <i>b</i> -PEO	Poly(methyl methacrylate)- <i>block</i> -poly(ethylene oxide)
PMVE	Poly methyl vinyl ether
PNIPAM	Poly N-isopropylacrylamide
P2VP- <i>b</i> -PMMA	Poly(2-vinyl pyridine)- <i>block</i> -poly(methyl methacrylate)
PPO	Poly propylene oxide
PS- <i>b</i> -PMMA- <i>b</i> -PtBA	Polystyrene- <i>block</i> -poly(methyl methacrylate) <i>block</i> - poly(tert-butyl acrylate)
PS	Polystyrene
PS- <i>b</i> -PAA	Polystyrene- <i>block</i> -poly(acrylic acid)
PS- <i>b</i> -PB	Polystyrene- <i>block</i> -polybutadiene
PS- <i>b</i> -PB- <i>b</i> -PS	Polystyrene- <i>block</i> -polybutadiene- <i>block</i> - polystyrene
PS- <i>b</i> -PEO	Polystyrene- <i>block</i> -poly(ethylene oxide)
PS- <i>b</i> -PFS	Polystyrene - <i>block</i> - poly(ferrocenyldimethylsilane)
PS- <i>b</i> -PI	Polystyrene- <i>block</i> - polyisoprene
PS- <i>b</i> -PMMA	Polystyrene- <i>block</i> -poly(methyl methacrylate)
PS- <i>b</i> -P2VP	Polystyrene- <i>block</i> -poly(2-vinyl pyridine)
PS- <i>b</i> -P2VP- <i>b</i> -PEO	Polystyrene- <i>block</i> -poly(2-vinyl pyridine)- <i>block</i> - poly(ethylene oxide)
PS- <i>b</i> -P4VP	Polystyrene- <i>block</i> -poly(4-vinyl pyridine)
PS- <i>b</i> -PVPh	Polystyrene- <i>block</i> -poly(4-vinyl phenol)
PtBA	Poly tert-butyl acrylate
PtBA- <i>b</i> -PNIPAM	Poly(tert-butyl acrylate)- <i>block</i> -poly(N- isopropylacrylamide)

PtBA- <i>b</i> -P4VP	Poly(tert-butyl acrylate)- <i>block</i> - poly(4-vinyl pyridine)
PtBMA	Poly(tert-butyl methacrylate)
PVAc	Poly vinyl acetate
PVAL	Poly vinyl alcohol
PVME	Poly vinyl methyl ether
P2VP- <i>b</i> -PEO	Poly(2-vinyl pyridine)- <i>block</i> - poly(ethylene oxide)
P4VP	Poly 4-vinyl pyridine
P4VP- <i>b</i> -PNIPAM	Poly 4-vinyl phenol- <i>block</i> -poly(N-isopropylacrylamide)
PVPh	Poly 4-vinyl phenol
PVPh- <i>b</i> -PMMA	Poly 4-vinyl phenol- <i>block</i> -poly(methyl methacrylate)
SBM	Polystyrene- <i>block</i> - polybutadiene- <i>block</i> -poly(methyl methacrylate)
SVPEO	Polystyrene- <i>block</i> -poly(4-vinyl pyridine)- <i>block</i> -poly(ethylene oxide)
THF	Tetrahydrofuran
PU- <i>b</i> -PE	Polyurethane- <i>block</i> -polyether

AFM	Atomic force microscopy
BCP	Block copolymer
BCC	Body centred cubic lattices
CMC	Critical micelle concentration
cryo-TEM	Cryogenic transmission electron microscopy
D_h	Average hydrodynamic diameter
DSC	Differential scanning calorimetry
DLS	Dynamic light scattering
FCC	Face centred cubic lattices
FTIR	Fourier transform infrared
HCP	Hexagonally close packed
IAs	Irregular aggregates
ICCVs	Interconnected compound vesicles
LCVs	Large compound vesicles
MLVs	Multilamellar vesicles
POM	Polarized optical microscopy
PDI	Polydispersity index
SAXS	Small-angle X-ray scattering
T_c	Crystallization Temperature
TEM	Transmission electron microscopy
T_f	Freezing temperature
T_g	Glass transition temperature
T_m	Melting temperature
TPEs	Thermoplastic elastomers
TWVs	Thick-walled vesicles
WAXS	Wide-angle X-ray scattering

χ	Flory-Huggins interaction parameter
ΔH_f	Heats of fusion
ΔH_c	Heats of crystallization

ABSTRACT

Many researchers have studied the self-assembly and microphase separation of block copolymer blends involving hydrogen bonding interactions. However, self-assembly via competitive hydrogen bonding has never been investigated due to the delusion that such systems become completely homogeneous and unable to self-assemble under any chemical or physical circumstances because of more than one type of intermolecular hydrogen bonding. In my project, we have proven that careful selection of the polymers, specifically block copolymers, molecular weight of the homopolymer and experimental conditions can lead to self-assembled structures in blends and complexes exhibiting competitive hydrogen bonding.

In this thesis, we have focussed on the phase behaviour, self-assembly and nanostructures from block copolymer/homopolymer mixtures involving both competitive and selective hydrogen bonding interactions. We report different combinations of self-assembled block copolymer/homopolymer blends and complexes of AB/C, AB/CD, and ABC/D types. The self-assembly via competitive hydrogen bonding is based on the competition between different blocks of the block copolymer to form more than one kind of intermolecular interaction with the complimentary polymer in the system. The microphase separated structures were formed due to the disparity in hydrogen bonding interaction between each pair of the block copolymer and homopolymer. Poly(2-vinyl pyridine)-*block*-poly(methyl methacrylate)/poly(hydroxyether of bisphenol A) (P2VP-*b*-PMMA/phenoxy), poly(ϵ -caprolactone)-*block*-poly(ethylene oxide)/poly(4-vinyl phenol) (PCL-*b*-PEO/PVPh) and polystyrene-*block*-poly(4-vinyl pyridine)-*block*-poly(ethylene oxide) and PVPh (SVPEO/PVPh) systems were thoroughly studied in this category. In selective hydrogen bonding interactions, the homopolymer C can interact with only one block of the block copolymer and the non-interacting block gets phase separated. The complexes like polystyrene-*block*-poly(acrylic acid)/poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PAA/PS-*b*-PEO) and PS-*b*-PEO/PAA were studied in this category. We have discussed the conditions for the formation of complex morphologies via selective hydrogen bonding

interactions between one block of the block copolymer and the homopolymer. Finally, we have detailed the importance of non-covalent hydrogen bonding interactions for the formation of morphological transitions and self-assembly in different block copolymer/homopolymer systems

ABSTRACT

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In this thesis, we have focussed on the phase behaviour, self-assembly and nanostructures from block copolymer/homopolymer mixtures involving both competitive and selective hydrogen bonding interactions. We report different combinations of self-assembled block copolymer/homopolymer blends and complexes of AB/C, AB/CD, and ABC/D types. The self-assembly via competitive hydrogen bonding is based on the competition between different blocks of the block copolymer to form more than one kind of intermolecular interaction with the complimentary polymer in the system. The microphase separated structures were formed due to the disparity in hydrogen bonding interaction between each pair of the block copolymer and homopolymer. Poly(2-vinyl pyridine)-*block*-poly(methyl methacrylate)/poly(hydroxyether of bisphenol A) (P2VP-*b*-PMMA/phenoxy), poly(ϵ -caprolactone)-*block*-poly(ethylene oxide)/poly(4-vinyl phenol) (PCL-*b*-PEO/PVPh) and polystyrene-*block*-poly(4-vinyl pyridine)-*block*-poly(ethylene oxide) and PVPh (SVPEO/PVPh) systems were thoroughly studied in this category. In selective hydrogen bonding interactions, the homopolymer C can interact with only one block of the block copolymer and the non-interacting block gets phase separated. The complexes like polystyrene-*block*-poly(acrylic acid)/poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PAA/PS-*b*-PEO) and PS-*b*-PEO/PAA were studied in this category. We have discussed the conditions for the formation of complex morphologies via selective hydrogen bonding

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General Introduction

1.1 The project aims

Self-assembly of block copolymer (BCP)/homopolymer systems is a versatile method to fabricate useful functional materials which merges properties like reversibility, control of composition and concurrent phase behaviour. Such systems may provide new opportunities for the tailoring of novel, tunable materials with new properties such as improved processing, self-healing behaviour or stimuli responsiveness. Furthermore, a wide range of ordered and disordered nanostructures can be created in BCP mixtures based on the attraction and repulsion among the chemically connected chains. The nanostructure formation can be controlled by changing the parameters like molecular weights, chemical structure and composition of the BCP.

Self-assembled nanostructures from BCPs with homopolymer involving secondary interactions like hydrogen bonding, or electrostatic interactions opened a new strategy to construct ordered nanoscale domains for various applications.¹⁻¹⁰ Among these, hydrogen bonding interactions in the BCP blends and complexes can show macroscopic changes on their physical properties like melting temperature, glass transition temperature, surface properties, crystal structure and dielectric properties.⁷⁻¹² In addition, BCP blends and complexes involving hydrogen bonding interactions provide a new mechanism of self-assembly, that leads to the fabrication of functional advanced materials. Here, we report different combinations of self-assembled BCP blends and complexes of AB/C, AB/CD, and ABC/D types.

The research described in this thesis aims to develop novel microphase separated BCP nanostructures achieved through the competitive and selective hydrogen bonding interactions in the bulk and in solution. In competitive hydrogen bonded blends and complexes, the homopolymer forms hydrogen bonding with more than one block of the BCP but with unequal interactions. On the other hand, in selective hydrogen bonding interactions, the

homopolymer can interact with only one block of the BCP and the non-interacting block gets phase separated. In this work, we have investigated how these selective and competitive hydrogen-bonding interactions in BCP/homopolymer systems can generate various composition-dependent nanostructures both in solid state as well as in solution.

1.2 Thesis organization

Chapter 2 is a literature overview on BCPs, their phase behaviour and morphologies along with an emphasis on structure and properties of block copolymers. This review discusses the influences of non-covalent bonding interactions mainly hydrogen bonding on the morphologies of BCP mixtures in the bulk and in solution and their potential applications.

In Chapter 3, the competitive hydrogen bonding interactions of P2VP-*b*-PMMA and phenoxy is discussed. A model is proposed to describe the self-assembled nanostructures of the P2VP-*b*-PMMA/phenoxy blends and detailed how the competitive hydrogen bonding is responsible for the morphological changes.

Chapter 4 describes the microphase separation of a double crystalline PEO-*b*-PCL di-BCP blended with PVPh induced by competitive hydrogen bonding interactions. The formation of various ordered and disordered nanostructures relative to the strength of hydrogen bonding interaction between each block of the BCP and the homopolymer were explained with the help of a structural model.

In Chapter 5, we have investigated the self-assembled nanostructures of a semicrystalline SVPEO tri-BCP with PVPh complexes. In these complexes, microphase separation takes place due to the disparity in intermolecular interactions; specifically PVPh and P4VP blocks interact strongly compared to PVPh and PEO.

In Chapter 6, a new strategy for the development of multiple vesicular morphologies in BCP complexes via hydrogen bonding interactions is detailed. A model AB/AC di-BCP system consisting of PS-*b*-PAA and PS-*b*-PEO was studied. In this study, a new morphology called ICCVs was observed.

In Chapter 7, we report for the first time, a simple and effective approach to trigger a spheres-to-vesicles morphological transition from amphiphilic BCP/polyelectrolyte complexes in aqueous solution. Vesicles and large compound vesicles were prepared via complexation of PS-*b*-PEO with PAA in water and directly visualized using cryo-TEM.

Chapter 8 presents the general summary and potential future works related to this thesis.

1.3 References

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Chapter Two

Literature review

2.1. Introduction

Block polymers today find application in nearly every area of life as they are used in many forms of materials in science, technology and industry. The nanoscale self-organization of block polymers is extensively investigated to create periodic structures using a variety of techniques.¹⁻⁴ This can be achieved simply by combining polymer chains together to form unique assemblies with specific functional and response characteristics. Correspondingly, theoretical and computational methods have also been developed to predict the self-assembling behaviour. These are the pre-eminent self-assembling materials with novel morphologies that can be controlled by varying the BCP structure, solution ionic strength, polymer concentration and molecular weight.⁵⁻¹⁴ The most common periodic morphologies of BCP comprise of spheres, hexagonal cylinders, gyroid and lamellae with dimensions from 10-100 nm. By combining these ordered geometries within lithography templates, BCPs can be used as scaffolds to create self-assembled patterns in energy storage devices. Furthermore, a variety of morphologies can be accessed with di and tri-BCPs.¹⁵ In block-selective solvents, amphiphilic BCPs can self-assemble into micelles (spheres, rods, lamellae) and vesicles. The structure of these aggregates comprises of an immiscible core surrounded by a miscible shell.¹⁶⁻²⁰ A binary mixture of self-assembled blends and complexes involving BCP and a homopolymer can also exhibit well-defined morphologies; these nanostructures are currently being used for many applications such as nanocarriers in drug delivery, gene therapy, diagnostic agents, flocculants, and in pharmaceutical applications.²¹⁻²⁵ In this review, a brief overview regarding the developments and advances in self-assembly of BCP and BCP/homopolymer mixtures are highlighted.

2.2 Block copolymers

BCPs are soft materials consist of two or more segments, or blocks, of simple, chemically distinct, and frequently immiscible polymers joined by the covalent bonding. For example an AABBA mode where A and B are different polymer components.²⁶ Depending on the number of distinct polymer segments, BCPs can be categorized into di-block, tri-block, and multi-block. Based on the arrangement of polymer chains, it can be further classified as linear and star BCPs. BCPs provide a versatile platform for fabricating large-area periodic nanostructures by controlling their self-assembly behaviour, with length scales varying from a few nanometers to several hundred nanometers. The repulsive and attractive interactions occur inside and between polymer segments and the covalent bond is the driving force for producing self-assembled nanostructures. BCPs having similar chemical structure but different molecular weights and block-ratios provide an effective way to control nanostructures.²⁷⁻³⁰ BCPs are important due to their unique structural properties. The applications of BCPs are made possible due to the combination of sequences, or blocks, of chemically distinct repeat units joined by covalent bonding. Hence, a separation can only take place on a nanoscopic level. Based on BCP composition and temperature, the phase separation of these polymers result in the spontaneous formation of wide array of well-ordered nanostructures. This property is largely applied in nanotechnology.

2.3 Block copolymers: Phase separation and morphologies

The simple and extensively investigated group is the linear AB di-BCP. In these BCPs, the groups of A and B molecules self-assemble to form nanostructures via the process of microphase separation which is driven by the enthalpy of demixing of the BCP components. This enthalpy is proportional to the product χN , where χ is the well-known Flory-Huggins interaction parameter and N is the degree of polymerization.³¹ BCPs with immiscible blocks has a general tendency to phase separate due to the repulsion between covalently connected blocks. There are three experimentally controllable factors for determining the chain organization and to form a final equilibrium structure; (1) N (2) χ and (3) comparative block length, f . Depending upon the

value of χN , it is possible to determine the degree of microphase separation of the di-BCP. The phase separation of BCP is driven by unfavourable enthalpic interactions and entropic elasticity. For minimizing the unfavourable interactions, the BCP blocks undergo phase separation. This consists of an interfacial free energy contribution and an elastic stretching contribution. Stretching free energy reduces the interfacial contribution and thereby reduces the interface area. When the two competing effects i.e. interfacial and stretching contribution are balanced, the equilibrium structure is formed. Figure 2.1 represents the schematics of the di-BCP equilibrium morphologies.³² Other than these equilibrium morphologies, various additional complex architectures can be formed, however those are thermodynamically unstable.³³

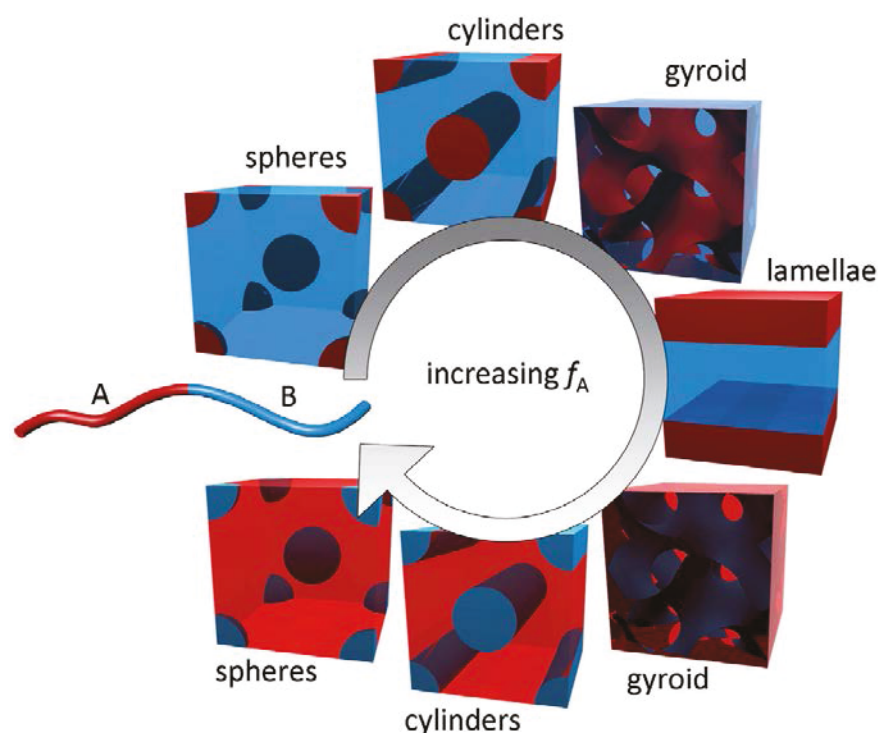


Figure 2.1 Schematics of equilibrium morphologies observed for a stable A-*b*-B di-BCP as an increasing volume fraction of A (diblocks are represented as simplified two-colour chains).³²

When $\chi N < 10$, the segregated domains in a BCP can pass through order–disorder temperature (ODT). Upon microphase separation, BCPs can form various equilibrium structures with respect to the composition. They include sphere, cylinder, gyroid and lamellae.³⁴ For nearly symmetric compositions,

the interfacial area of the BCP components has no curving temptation, therefore they form alternate layers known as lamellae. When the BCPs become asymmetric, the interface tends to curve that leads to hexagonally arranged cylindrical or spherical phase of minor block in the major block matrix. Body centred cubical structure is formed when $f_A \approx 0.2$. As the volume fraction of f_A increases further ($f_A \approx 0.38$), then the A block forms a bicontinuous gyroid or perforated layers, respectively.³³

2.4 Equilibrium block copolymers phases

2.4.1 Spherical phase

BCPs at volume fraction of the minority component is $\approx 20\%$ can align the spheres to form BCC and FCC or HCP spheres. The FCC and BCC spherical micelles with cubic packing is shown in Figure 2.2.³⁵ Almdal et al investigated the BCC pattern lattices of PEP-PEE BCP having volume fraction $f_{PEP}=0.83$.³⁶ BCPs exhibiting cubic phase was extensively studied by several groups including Mortensen et al.,^{37,38} Hamley et al.,^{16,26,35} Castelletto et al.³⁹ etc.

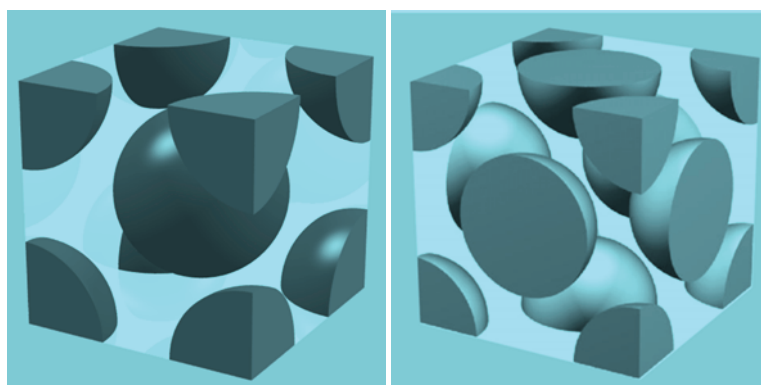


Figure 2.2 Schematic representation of molecules arranged in body centred cubic lattice, face centred cubic lattice or hexagonally close packed patterns.³⁵

2.4.2 Cylindrical phase

The BCPs form hexagonally arranged cylinders of one block within the matrix of the other block (volume fraction of the minority component is $\approx 30\%$). A sketch of cylinders is shown in Figure 2.3. Leibler's theory⁴⁰ proposes the first formation of spherical structures that subsequently form a hexagonal

cylindrical phase. The influences of surface fields for the orientation of cylinders were studied by various groups.⁴¹ Morkved et al.⁴² introduced electric field approach to align PS-*b*-PMMA cylindrical domains.

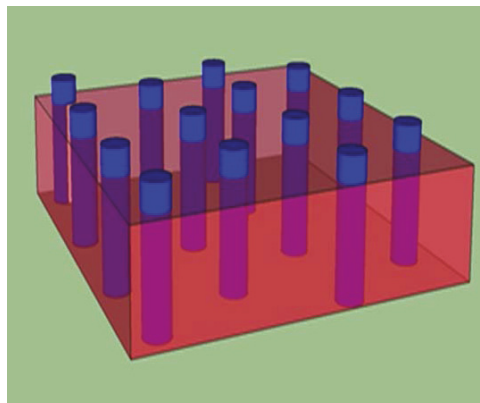


Figure 2.3 Schematic representation of hexagonal cylinders.

2.4.3 Gyroid phase

Gyroid morphology has been identified as a three-dimensionally connected interface at the boundary between cylinders and lamellae, close to the order–disorder transition as shown in Figure 2.4.^{35a} It was observed that [001] planes of the lamellar and the [10] planes of the hexagonal phase exhibit an epitaxial relationship with the [211] gyroid planes.⁴³ Schultz et al.⁴⁴ also studied epitaxial shift of hexagonal and gyroid morphologies in PS-*b*-P2VP BCP.

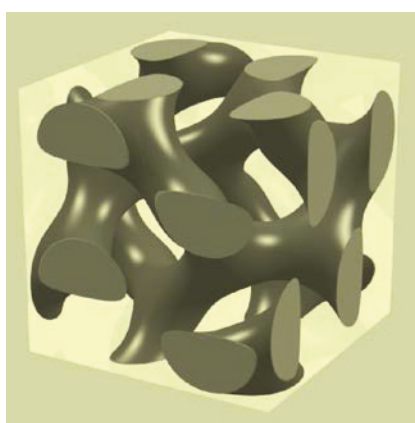


Figure 2.4 Schematic representation of a bicontinuous gyroid phase.^{35a}

2.4.4 Lamellar phase

Lamellae phase of BCP self-assembly is favoured at equal volume fractions of two blocks. The simplest ordered morphology is lamellar and the schematic view of lamellae is shown in Figure 2.5. The major theoretical investigations, applications and morphological orientations of lamellar BCPs were studied by several groups.⁴⁵⁻⁴⁷ The stability of the lamellar structure under deformation was theoretically studied by Amundson and Helfand,⁴⁸ and showed that the lamellar phase can be transformed into a disordered state if the deformation is large.

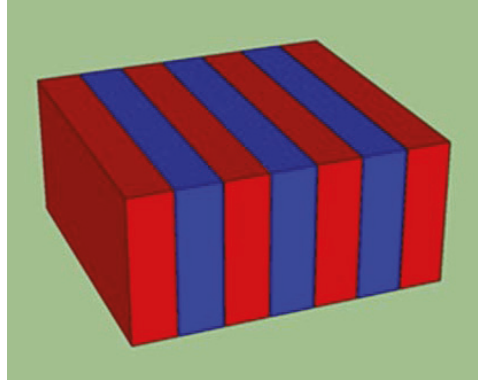


Figure 2.5 Schematic representation of lamellae.

2.5 Diblock copolymers

The basic structure of a di-BCP constitutes two distinct monomers linked together by covalent bonding. Schematic representation of a AB di-BCP is given in Figure 2.6



Figure 2.6 Scheme of a di-BCP

Other than the volume fraction, χ also describes the phase separation of di-BCPs using the following equation,

$$\chi_{AB} = \frac{z}{k_B T} \left[\epsilon_{AB} - \frac{\epsilon_{AA} - \epsilon_{BB}}{2} \right] \quad (1)$$

Where k_B = Boltzmann constant, z = number of nearest monomers, T denotes the temperature and ϵ_{AA} , ϵ_{BB} , ϵ_{AB} are the interaction energies of A-A, B-B and A-B interactions respectively. If $\chi_{AB} > 0$, then A and B blocks have repulsive interactions and when the $\chi_{AB} < 0$, the different components attract each other. The phase behaviour of a di-BCP depends on N (where, N is the sum of N_A and N_B), χ , and the volume fractions f_A and f_B , where $f_A = N_A/N$ and $f_A + f_B = 1$.⁴⁰ When χN exceeds a critical value, depending on the copolymer architecture and composition (which is parameterized by f), BCP can microphase separate to form periodically ordered nanostructures. Three different degree of segregation can be defined depending on the value of χN : (a) The weak segregation limit (WSL) when $\chi N \sim 10$; (b) the intermediate segregation region (ISR) for $\chi N \sim 10$ -100 and (c) the strong segregation limit (SSL) for $\chi N \gg 100$.

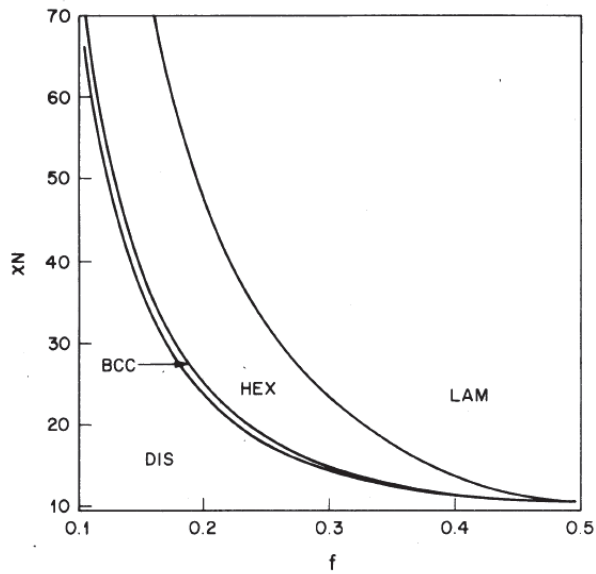


Figure 2.7 Liebler's phase diagram for a di-BCP in mean field theory.⁴⁰

The phase behaviour of different BCP systems is detailed theoretically by a range of methods.^{31,49} The phase diagram belonging to the regime of the WSL was first calculated by Leibler by making use of Landau's mean-field approximation.⁴⁰ His theory compares the free energy transformation from disordered to ordered phase. For an asymmetric di-BCP melts ($f \neq 0.5$), the theory predicts a first order transition to a BCC from the disordered state. According to the phase diagram in Figure 2.7, a symmetric BCP ($f = 0.5$)

undergo a transition directly to the lamellar phase.^{40,50} By further increasing χN , the theory suggests a transition from BCC to the thermodynamically stable hexagonal microphase and subsequently to the lamellar microphase. The composition fluctuation by a single wave function was approximated in WSL. On the other hand, SSL was described using the higher degree of segregation among the microdomains. Meier⁵¹ followed by Semenov⁵² developed elaborate theories for expressing the morphological free energies in SSL. The self-consistent field (SCF) theory developed by Helfand and Wasserman explained the earliest microphase separation of BCPs though it failed in the strong segregation regime.⁵³ Matsen and Bates combined the two limiting cases of WSL and SSL using SCF theory to describe morphological behaviour which is shown Figure 2.8.⁵⁴

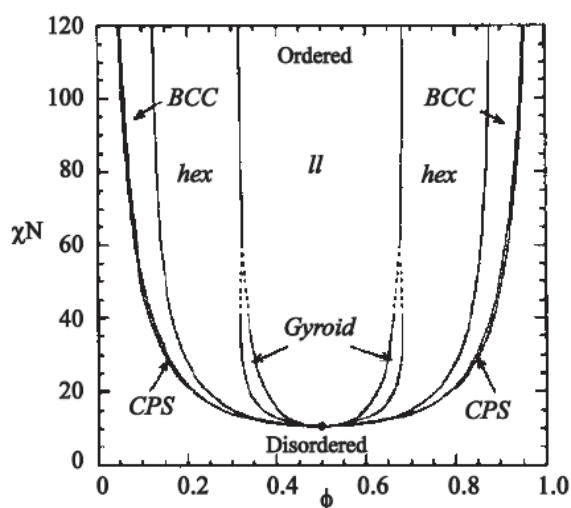


Figure 2.8 The morphology phase diagram of a symmetrical di-BCP computed with the help of SCF. The stable areas containing disordered, lamellae, gyroid, hexagonal and body-centred cubic states are shown.⁵⁴

2.6 Triblock copolymers

BCPs with three different distinct blocks linked by covalent bonds are called tri-BCPs. They can be obtained by combining only two chemically different species and called binary ABA tri-BCPs or by using three chemically different polymers making the ternary ABC tri-BCPs. These binary and ternary

tri-BCPs can be classified into linear or star depending upon the arrangements of polymer blocks. Figure 2.9 shows the sketch of linear and star tri-BCPs with equal chain length.

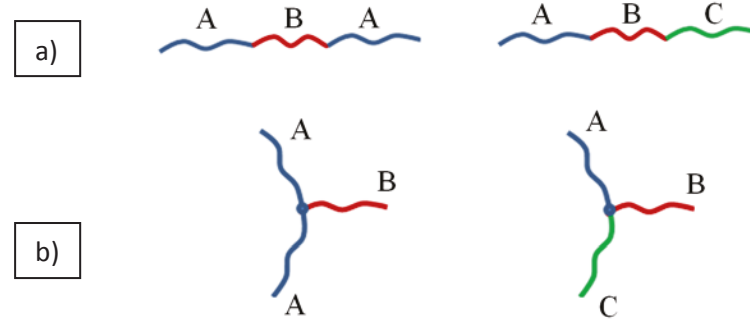


Figure 2.9 Sketch of [a] linear and [b] star tri-BCPs

In analogy to the AB di-BCPs or ABA tri-BCPs, a rich variety of nanostructures can be created via the microphase separation in ABC tri-BCPs because of the three different components. Generally, disordered states of ABC melts have better stability compared to AB with a similar length and composition. Tri-BCP systems have revealed a rich variety of well-ordered complex micro domain morphologies (Figure 2.10).^{15,55-57} In these BCPs, an equilibrium morphology can be defined using six parameters; (1) χ_{AB} , χ_{BC} and χ_{AC} . Here the relative immiscibility is expressed by the interfacial tension σ_{ij} , or by the interaction parameter ϕ_{ij} , between the directly connected A/B, B/C and the “nonlinked” blocks A/C.^{55a,58} (2) The formation of microphase separated assemblies is influenced by two independent composition parameters; f_A , f_B and N . According to the relative magnitude of χ_{AC} compared to χ_{AB} and χ_{BC} there may be three different types of systems.⁵⁹ When the value of χ_{AC} is smaller than that of χ_{AB} and χ_{BC} , it is denoted as F^2 system or *type II frustrations*. While $\chi_{AB} < \chi_{AC} < \chi_{BC}$ i.e., χ_{AC} is intermediate between the other two neighbouring blocks are said to have F^I system or *type I frustrations*. The third type of systems comprises of F^0 system or *no frustration*, where A/C interaction is higher than A/B or B/C interactions. As a result there is a rich variety of ABC tri-BCP structures. ABC tri-BCPs are more versatile than di-BCPs, due to the structural complexity and these materials show a greater

variety of morphologies.⁶⁰ Kotaka et al.⁶¹ gave the first more detailed picture of ABC tri-BCP morphologies, mainly based on styrene, butadiene, and vinyl pyridine. In the literature devoted to tri-BCPs, the most important theoretical and experimental studies have been carried out on SBM.^{62,63} There are a large number of studies regarding the morphological behaviour of SBM done by Stadler's group.⁶⁴ A wide range of ordered nanostructures was exhibited by SBM based on the fraction of the constituting blocks. In one case a lamellae phase of PS and PMMA was formed and a spherical PB was found as spherical domains in between the lamellae layers.^{65,66}

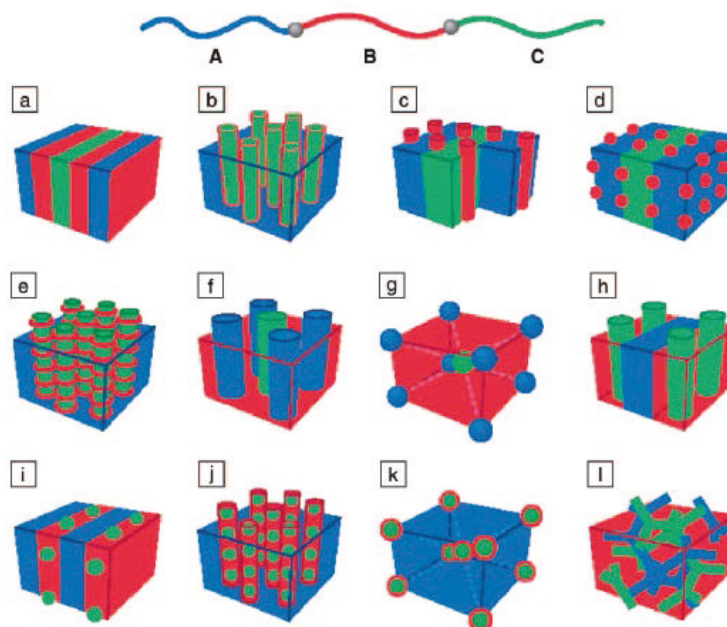


Figure 2.10 Schematic representations of morphologies for linear ABC tri-BCP.¹⁵

2.7 Self-assembled block copolymer morphologies in solution

BCP amphiphiles self-organize in solution to form a wide range of various structures in nanometer dimensions either in water or in organic solvents.⁶⁷ The reason for self-assembly is an unfavourable mixing enthalpy and a small mixing entropy, whereas the covalent bonding exists between the blocks avoid macrophase separation.⁶⁸ In fact, amphiphilic BCPs can show two behaviour in solvent media which are micellization and gelation. The behaviour of BCPs in aqueous phase, including micellization, is of great interest in the application

point of view. They can be used as toxic removing agents, nanocarriers for biomedical applications, protein conjugation, etc.⁶⁹ The micellization and their potential uses are comprehensively reported in the literature.^{22-25,69} When the BCP is mixed with block-selective solvents, the solvent-philic part stretch out to the solvent creates the ‘shell’ and solvent-phobic block centred within the shell form ‘core’ and this is how micellization usually occurs. One classic structure of BCP micelle is displayed in Figure 2.11.⁷⁰

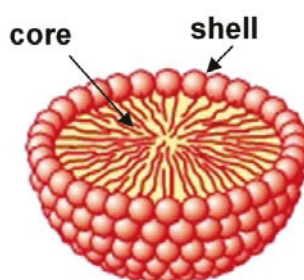


Figure 2.11 Schematic representation of a polymer micelle.⁷⁰

Micellization of BCP in selective solvents occurs above a certain concentration known as critical micelle concentration (CMC). With increasing BCP blocks, the amount of micelles also increases whereas the amount of non-associated blocks remains the same which is equivalent to CMC. Similarly the temperature at which, for a fixed polymer concentration, micellization occur is called critical micelle temperature. There are various methods to induce micellization in solution. In another method, BCP aggregation takes place in a neutral solvent, and followed by the addition of a selective solvent, and finally the complete removal of the common solvent by dialysis. Also, micellization favoured by changing size and shape of BCPs due to external parameters like temperature, pH or solvent composition can lead to polymer phase separation.⁷¹

2.7.1 Micelles

Based on the BCPs composition and various experimental methods, it is possible to form “crew-cut” or “star” micelles (Figure 2.12). Here, the amphiphilic BCPs having longer hydrophobic chain than the hydrophilic chain forms the crew-cut and if the hydrophobic block is shorter than the hydrophilic

chain, it forms star micelles. In both cases, BCP micelles offer potential advantages over low molecular weight lipid amphiphiles and surfactant systems. This is due to robust nanostructures obtained from BCPs and their flexibility which can be controlled by synthesis. Therefore, the application of BCPs especially for drug delivery has been a key area of research in recent years. Several systems comprising of BCPs, such as AB,⁷² ABA,⁷³ and ABC star-shaped⁷⁴ have been investigated extensively. Obviously, the change in the chemical factors (structure, composition and architecture)^{17,75} or solution parameters (concentration, temperature, solubility, pH, ionic strength etc.)⁷⁶ of amphiphilic BCPs, it has been possible to manipulate multi-compartment micellar structures, including core-shell-corona spheres,⁷⁷ cylinders,⁷⁸ and helices,⁷⁹ segmented wormlike micelles,⁸⁰ disks,⁸¹ plates,⁸² toroids,⁸³ and “raspberry-like” micelles.⁸⁴⁻⁸⁵ The morphology and structure of core-shell micelles determine the practical applications of BCP in solution.⁸⁵

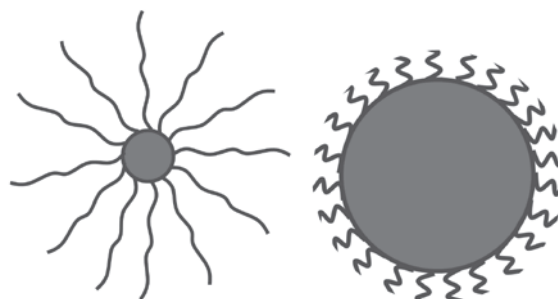


Figure 2.12 Schematic representations of star-like and crew-cut micelles.

Mostly, BCP micelles are spherical but under certain environmental conditions can change their shape and size distribution; forms various morphologies.⁷⁷⁻⁸⁴ A scheme of spherical micelle is shown in Figure 2.13. Mortensen and Pedersen reported the morphologies of PEO-*b*-PPO spherical micelles where the shell made up of PEO-blocks was found outside the PPO core-blocks.¹⁰⁸ Chou and Zhou detailed the solution properties of both PEO-*b*-PPO and PEO-*b*-PBO BCPs.¹⁰⁹ Eisenberg and co-workers extensively investigated the crew cut micellization of BCPs containing large hydrophobic blocks.¹¹⁰

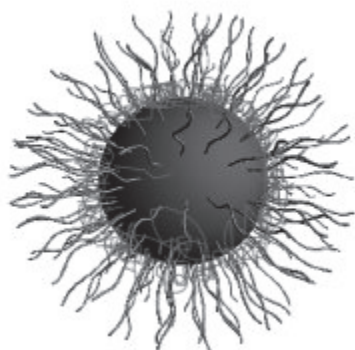


Figure 2.13 Scheme of a BCP spherical micelle.^{35a}

Other than the *crew cut* and *star*, other types of three layered micellar structures for example, *onion type* or *core shell corona* (CSC) were also made for different applications. Most of these micelles are made from ABC tri-BCPs.⁸⁶⁻⁹⁰ As an example, PS-*b*-P2VP-*b*-PEO,^{91,92} PS-*b*-PMMA-*b*-PtBA,⁹³ and P2EHA-*b*-PMMA-*b*-PAA⁹⁴ can self-assemble into CSC micelles with different phase structures. As the tri-BCPs are difficult to syntheses, CSC micelles are less investigated. Besides ABC tri-BCPs, Kabanov et al. proposed the synthesis of multilayer morphologies by the complexation of AB/BC BCPs.^{95,96} In addition, micellization through electrostatic or hydrogen bonding interactions is more facile method than block-selective micellization of BCPs.⁹⁷⁻¹⁰¹ Especially, hydrogen bonding and complexation can facilitate co-aggregation in blend solutions.⁹⁹⁻¹⁰¹ Other than the hydrogen bonded BCP aggregates, morphologies formed by the self-assembly of oppositely charged components are also useful for many potential applications.¹⁰²⁻¹⁰⁴ BCPs containing one neutral block and a polyelectrolyte block are generally called block ionomers. Micelles formed from block ionomers are given different names by different research groups. For example, Kabanov et al.¹⁰⁵ termed it as “block ionomer complexes” (BICs) or interpolyelectrolyte complex (IPEC), Kataoka et al.^{106,107} used the term “polyion complex micelles” (PIC). The final morphology of the self-assembled complexes could be influenced by the interfacial energy of the soluble/insoluble phase, core chain stretching, and entropy loss due to the insoluble blocks packed into aggregate micro domains.

2.7.2 Vesicles

BCP vesicle is a functional hollow lamellar bilayer structures and various agents can be encapsulated within the hollow core.¹¹¹ It has been established recently that these aggregates can be employed as novel carrier systems in advanced drug delivery. The high drug-loading capacity and the unique delivering characteristics make these BCP aggregates as efficient candidates in this application.¹¹² According to a theoretical study of Safran et al.,¹¹³ vesicles are more stable with respect to the lamellar phase. Vesicles can be used for encapsulating various agents within their hollow structure and therefore their potential applications are growing in different biomedical areas including targeted deliveries.^{114,115}

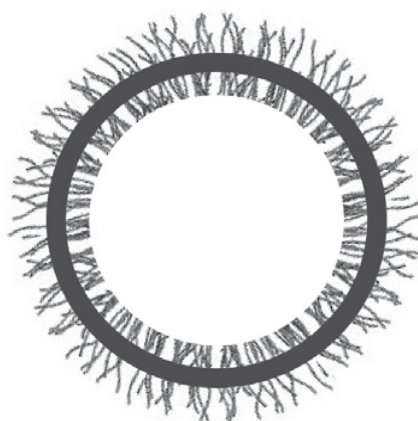


Figure 2.14 Schematic representation of a BCP vesicle.^{35a}

The first observation of simple BCP vesicles was done by Eisenberg and co-workers using PS-*b*-PAA BCP.¹¹⁶ Figure 2.14 shows a sketch of a polymer vesicle. Discher et al. investigated the physical properties of BCP vesicles and termed them as polymersomes.¹¹⁷ Vesicles from multi-BCPs in aqueous solution were first investigated by Nolte et al.¹¹⁸ In addition to the classical vesicles, large compound vesicles (LCVs) and multilamellar vesicles also exist in BCP mixtures.^{119,120} The formation of LCVs may be either from one lamella or from the fusion of many vesicles under kinetic control.¹²¹ LCV's can also found use in multiple encapsulating purposes for stepwise release.¹²²

2.8 Block copolymer blends and complexes

Blending or mixing of polymers have attained considerable attention for combining physical properties and significantly broadening the processing window for creating materials having desired characteristics that cannot be attained by a single polymer.¹²³ The homogeneous mixing of polymers can be performed in different ways including melt mixing as well as solution casting. In solutions, a blend or a complex precipitate can be formed between two polymers depending on the interaction between them. If a favourable intermolecular interaction exists between different polymers, a miscible polymer blend can be formed. And, if the interaction is sufficiently strong, i.e. the polymer-polymer interaction prevails over the polymer-solvent interaction, the two polymers co-precipitate to form highly associated mixtures known as polymer complexes. BCPs can be mixed with different complementary polymers to produce blends and complexes. These include blending di-BCP/homopolymer involving the same component of the blocks such as AB/A or AB/B.¹²⁴ Based on the molecular weight of A or B homopolymers, the phase behaviour of the blends exhibit wet brush¹²⁵ or dry brush characteristics.¹²⁶ In addition, BCP blending with low molecular weight molecules,¹²³ or homopolymer of C-type,^{116,117,127,128} other BCPs^{128,129} have been studied extensively. In this thesis, we mainly focus on BCP/homopolymer systems involving hydrogen bonding interactions.

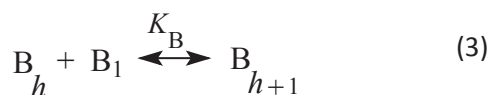
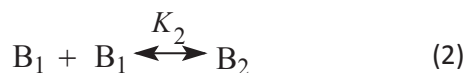
2.9 Hydrogen bonding in polymer mixtures

Hydrogen bonding, one of the major attractive forces, is an important key for function of making miscible polymer blends. Hydrogen bonding exists among the electron deficient [proton-donating group] H-atom and electron dense atom [proton-accepting groups] that accompanied by a considerable gain in interaction energy as well as a substantial loss in entropy as hydrogen bonding is directional.^{127,130} Typically, hydrogen bonds are expressed as A-H---B. Here A and B represents the high electronegative fluorine, oxygen and nitrogen atoms. There are principally two types of hydrogen bonding, self-associated bonds which exists within a single polymer component and inter-associated bonds which is between dissimilar polymer components. It is possible to obtain a homogeneous blend having suitable components via

specific inter-associated hydrogen bonding. Moreover, hydrogen bonding interactions are utilized to make various compatible polymer mixtures and thereby tune their properties.^{131,132}

Different experimental methods can be applied to characterise the hydrogen bonding in polymer blends. These include infrared spectroscopy (IR), Raman spectroscopy, nuclear magnetic resonance spectroscopy, gas phase microwave rotational spectroscopy, X-ray diffraction, neutron diffraction etc. Among these methods, IR is found to be the highly efficient technique to characterise the hydrogen bonding in blends. Generally, the hydrogen bond formation in a polymer mixture (A-H---B) involves the transferring of electron from B to A-H which makes the A-H bond weak as it begins to elongate. This will cause a lowering of frequency generally known as red-shift which is identified using IR spectroscopy.

The appropriate mixtures of proton-donors and proton-acceptors can make a strong or weak bond. When the hydrogen bond strength ranges from 60–170 kJ/mol, it is a strong bond, a moderate bond is at 15–60 range and weak bonds at 4–15 kJ/mol. The common proton-donating polymers include PVPh,¹³³ PVAL,¹³⁴ PAA,¹³⁵ their copolymers and analogues. The most common proton-accepting polymers are polyesters,¹³⁶ polyacrylates¹³⁷ and polyethers.¹³⁸ The strength of hydrogen bonds can also be determined by equilibrium constants. Painter and Coleman Association Model,¹³⁹⁻¹⁴¹ has been used to calculate the interactions in the hydrogen bonded systems in a blends containing three interacting components; one self-associating polymer (B) and two non-self-associating polymers (A and C), and B can interact with both A and C. Their corresponding equilibrium constants are K_B , K_A and K_C respectively and can be expressed by the following equations;^{140,141}





The equilibrium constants corresponding to above four equations can be expressed in terms of their volume fractions as follows,^{140,141}

$$\Phi_B = \Phi_{B1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \Phi_{B1})^2} \right) \right] \left[1 + \frac{K_A \Phi_{A1}}{r_A} + \frac{K_C \Phi_{C1}}{r_C} \right] \quad (6)$$

$$\Phi_C = \Phi_{C1} \left[1 + K_C \Phi_{B1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \Phi_{B1})} \right) \right] \right] \quad (7)$$

$$\Phi_A = \Phi_{A1} \left[1 + K_A \Phi_{B1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \Phi_{B1})} \right) \right] \right] \quad (8)$$

where Φ_B , Φ_A and Φ_C are the total volume fractions of the polymer units in the blends and Φ_{B1} , Φ_{A1} and Φ_{C1} are the volume fractions of isolated species in the mixture respectively; r is the segmental molar volume given as; $r_A = V_A/V_B$ and $r_C = V_C/V_B$. The predicted values of fraction of hydrogen bonding can be compared with the experimental values.

The degree of hydrogen bonding that are inter-associated is a key factor in polymer blends for inducing the compatibility or/and miscibility because it generally contributes significantly to the mixing free energy. Miscible polymer blends with hydrogen bonding interactions include, PVPh/PMMA,^{142,143} PVPh/PEO,^{144,145} PVPh/P4VP,¹⁴⁶ PVPh/PVAc,¹⁴⁷ PVPh/PHV,¹⁴⁸ PVPh/PVME,^{149,150} PVPh/PCL etc.¹⁵¹⁻¹⁵³ The hydrogen bonding has a major influence on polymer properties such as, thermal, crystallization behaviour, mechanical properties, etc. Generally, the polymer blends involving hydrogen bonding interactions are miscible and exhibit only one glass transition temperature (T_g). A large number of equations including Fox,¹⁵⁴ Gordon–Taylor,¹⁵⁵ Couchman–Karasz,¹⁵⁶ and Kwei.¹⁵⁷ etc., are utilized to calculate the T_g -composition dependence. The disparity between experimental and predicted T_g values

describe whether a polymer blend shows a positive or negative deviation. This can be taken in consideration in order to determine how strongly the polymer chains interact. For example, PVPh blended with PMMA,^{158,159} PVP,¹⁶⁰ and P4VP¹⁶¹ show a positive deviation, where the observed T_g value is higher than the T_g s calculated by a linear additivity law. A negative deviation in T_g is shown by PVPh/PCL¹⁶² epoxy/PEO¹⁶³ which is attributed to weak intermolecular interactions between the blended polymers. Most of the hydrogen-bonded blends exhibit melting point depressions when the blend is composed of at least one semicrystalline component.¹⁶⁴⁻¹⁶⁷ The miscibility induced by inter-associated bonds in polymer blends can suppress the crystallization of the crystalline component. For example, crystallization of PHB was hindered in its blends with 40 wt% of PVPh.¹⁶⁷ In some cases, the strong hydrogen bonds can even completely prohibit the crystallization of the crystalline component. Moreover, hydrogen bonding can also affect the surface enrichment in multicomponent polymer systems.^{168,169}

2.10 Self-assembled block copolymer blends and complexes by hydrogen bonding interactions in bulk

Self-assembled structures from BCP materials are attaining increasing interest both from a fundamental and applied point of view. The studies on nanostructured BCP have been emphasised on the synthesis and control the self-assembly by changing the parameters such as their molecular-weights, chemical-structure, volume-fraction, chain-flexibility, etc. The self-assembly of BCPs by blending is a convenient route for the development of new polymeric materials with property profiles superior to those of the individual components. This has been on the basis of the non-covalent physical interactions, such as ionic or electrostatic interactions, coordination bond and hydrogen bonding. The core advantage of this method is that it is possible to tune the behaviour of materials with various components at different concentrations.

The conventional AB/C systems involve blending an immiscible AB di-BCP with the homopolymer C, where C interacts favourably with block B, but is immiscible with A. Zhao et al.¹⁷⁰ studied the first AB/C system by blending an incompatible PS-*b*-PVPh di-BCP with PEO, P4VP and PBMA

homopolymers. Here, PEO, P4VP and PBMA are able to make hydrogen bonding interactions with PVPh whereas immiscible PS chains are phase separated.¹⁷⁰ The interactions and nanostructure morphologies formed by the hydrogen bonding between a small molecule and BCP were extensively investigated by Ikkala's group.¹⁷¹⁻¹⁷³ For example, the blending of immiscible PS-*b*-P4VP di-BCP with PDP, where PDP and P4VP can make hydrogen bonds and form an a homogeneous blend, however immiscible PS phase separates.¹⁷⁴ In other study, Ikkala and co-workers prepared blends of an incompatible PI-*b*-P2VP di-BCP and novolac resin. Here also resulted a blend of novolac with miscible P2VP and immiscible PI.¹⁷⁵

In AB/C BCP/homopolymer blends, χ_{AC} , χ_{BC} or χ_{AB} can be either positive or negative.¹⁷⁶ Generally, in such systems, two types of outcomes are possible when C is miscible with immiscible AB segments. The first case is C is miscible with B but immiscible with A i.e. with a negative χ_{BC} and positive χ_{AB} and χ_{AC} (A/B and A/C are immiscible). In such cases the immiscible A phase separates to form different ordered or disordered morphologies. Hashimoto et al., studied blending of PS-*b*-PI/PPO and PS-*b*-PB/PMVE systems, where the homopolymers exhibit negative χ parameters with polystyrene.^{177,178} Various nanostructures of PS-*b*-P2VP/PVPh blends with different blend compositions was reported by Matsushita and co-workers, where PVPh and P2VP form a miscible phase through strong hydrogen bonding interactions.^{179,180} The second case in AB/C systems is, the homopolymer C is miscible with both the blocks of the BCP i.e. A and B. For instance, Forster and co-workers investigated P2VP-*b*-PEO/PVPh blends where PVPh is miscible with both the BCP blocks.¹⁸¹ Moreover, PVPh-*b*-PMMA/PEO blends were investigated by Chang and co-workers.¹⁸² However, in these cases self-assembly or microphase separation was not detected. This is because of the non-selective bonding between the homopolymer and the BCP blocks to form a completely homogeneous system.

2.11 Self-assembled block copolymer complexes by hydrogen bonding interactions in solution

Recent studies in self-assembled systems have shown that interpolymer interactions other than covalent bonding can also create self-assembly in solutions. For immiscible polymer systems it is possible to induce miscibility by introducing interacting groups. The preparation of aggregates of complexes induced by secondary interactions has been extensively investigated.¹⁸⁰⁻¹⁸⁶ This includes electrostatic, hydrogen bonding, co-ordination bonding or polar-polar interactions. The foremost advantage of hydrogen bonded and polyelectrolytic mixtures is that they are simpler to process than to synthesize the covalent analogues. The most important features of hydrogen bonds are its thermoreversibility and stimuli-responsiveness and photochemical behaviour, so that it is easy to tune the material properties. The thermo-reversibility improves the equilibration through the phase separation process unlike if the bonds had been permanent. The combination of properties such as reversibility, easy control of composition, and concurrent self-assembly behaviour gives new opportunities for the tailoring of novel functional materials with new properties, such as improved processing, self-healing behaviour or stimuli responsiveness.

Hydrogen-bonding complexation in polymers was first reported by Dorby.¹⁸⁷ Later, in the 1960s, researchers at Union Carbide studied hydrogen-bonding complexation of PEO and PAA.^{188,189} Tsuchida et al.¹⁹⁰ and Jiang et al. have also given reviews about intermolecular complexations.¹⁹¹ As for hydrogen bonding interactions, micelles and other morphologies can be obtained either from complexation of by mixing AB with a homopolymer C, or AB and BC copolymers or by mixing AB and CD copolymers where A and C blocks can form hydrogen-bonded complexes.

The solvent plays a significant role in these systems as it controls the formation of complexes.¹⁹² Hence, it is possible to tune the aggregation behaviour of polymer complexes with hydrogen bonding interactions by the nature of the solvent used. Jiang et al. reported the first hydrogen-bonded micelles by blending PS-*b*-PMMA with hydroxyl containing modified polystyrene (PS(OH)) in toluene at the stoichiometric molar ratio.¹⁹³ The co-micellization of PEO-*b*-PAA/P4VP complexes in ethanol solution was investigated by Shi and co-workers.¹⁹⁴ There is a strong hydrogen bonding

interaction between PAA/P4VP blocks than PAA/PEO pair. Therefore PAA/P4VP forms the micellar corona and PEO block forms the core. Lee and co-workers studied the complex formation induced by the change in pH of PCL-*b*-PMAA/PEO in solution. The long-range-interconnected morphology was formed by the hydrogen bonding between PMAA and PEO.¹⁹⁵ Complexation of PEO-*b*-P2VP-*b*-PEO tri-BCP with PAA at small pH in aqueous media resulted in flowerlike micelles.¹⁹⁶ Chen et al. investigated the formation of controllable vesicles in the complexes of PEO-*b*-PB and PAA in a mixture of THF and n-dodecane.¹⁹⁷ Gohy and co-workers reported the aggregates formation in PS-*b*-P4VP and PAA mixtures in organic media.¹⁹⁸ Here complexes were formed by the bonding among the P4VP and PAA polymer segments. The P4VP/PAA bonded phase forms the core and the non-interacted PS form corona of the micellar aggregates. Zhang et al. studied a hydrogen bond-mediated adsorption of P4VP chains on the kinetically frozen PS-*b*-PAA aggregates in ethanol-DMF mixtures.¹⁹⁹

Shi and co-workers prepared multilayered micelles from PS-*b*-PAA and P4VP-*b*-PNIPAM copolymer mixture in ethanol. The complex structure comprised of non-interacting PS cores, hydrogen bonded PAA and P4VP shells and PNIPAM coronas.²⁰⁰ Those authors also prepared complex micelles from PtBA-*b*-PNIPAM with PtBA-*b*-P4VP.²⁰¹ Zhang group studied a hyper-branched structure formed from the complexation of PS-*b*-PAA and PMMA-*b*-PEO BCPs with respect to the molar-ratio of PAA/PEO. They obtained micellar clusters with a core of hydrogen bonded PAA/PEO pair and PS as the corona.²⁰²

2.12 Applications of self-assembled block copolymer systems

BCP self-assembly promises to create complex structures with domain sizes less than 20 nm which provides potential applications in electronic, biomedical, and optical devices. It has been reported that BCPs are extensively used for dispersion, wetting, emulsification, foam stabilization, flocculation, viscosity modification etc. A few applications of BCP self-assembly are detailed in the following section.

As BCPs can inhibit macrophase separation, they are widely used as TPEs. BCPs such as PS-*b*-PB-*b*-PS (eg., Kraton®), PU-*b*-PE etc. are chief commercial TPEs.^{203,204} These materials are used as bottle-stoppers, jelly-candles, exterior coatings for optical-fibres, and in artificial organ equipment. Some other BCPs are used in acoustic-barriers, airbag-doors, body-plugs, body-seals, damper-mounts, glazing-seals and wire and cable purposes.^{203,204} The surface activity of BCPs employs them to use as patterning templates. Self-assembled periodic and ordered BCP nanostructures can be controlled by a variety of factors, such as the interaction of the BCP molecules with the substrate, the film thickness and the post-deposition annealing procedures. Cheng et al. used an etch-mask of PS-*b*-PFS for fabricating a Co nanodot array.²⁰⁵ A high density mask from PS-*b*-PMMA BCPs was developed by Toshiba company.²⁰⁶ Self assembled BCP was used as templates for the preparation of nanomaterials through metal deposition or electro-deposition for lithography applications.²⁰⁷ The BCP micelle formation can be utilized for the elimination and retrieval of toxic components (for example halogenated and aromatic hydrocarbon materials) from polluted aqueous media. PCEMA-*b*-PAA,²⁰⁸ Pluronic (PEO-*b*-PPO-*b*-PEO)²⁰⁹ BCPs are more effective agents for this purpose.

The major application of amphiphilic BCPs by value and volume is obviously pharmaceutical industry, precisely drug-delivery, which has been extensively reviewed.²¹⁰⁻²¹² BCP micelles are suitable for drug-delivery, diagnostics and gene therapy since there are options of biocompatible and biodegradable BCPs.²¹³⁻²¹⁵ Micellar structures such as micelles and vesicles can encapsulate a variety of soluble solutes such as drugs, biopolymers (protein or DNA), cosmetic ingredients, or agrochemicals in their aqueous/organic core and these solutes can subsequently be released slowly and in a controlled manner through the vesicle bilayer.^{216,217} Actually the physical properties of micelles including size, size distribution and morphology impact their stability, loading and release characteristics, in vivo pharmacokinetics and biodistribution.²¹⁸

In another form of application, nanoparticles were synthesised in the presence of BCPs and these particles can be encapsulated within the core of the

micelles. Later, these particles were chemically treated and converted into fine metal-colloidal particles with attractive catalytic, conducting and magnetic behaviours.²¹⁹ Other important applications of self-assembled BCPs include their use in lubrication and surface treatment, stabilizer in latex technology, in polymer blends, activators phase transfer catalysts in some organic reactions.^{50,220} Some electroactive BCPs even used as nanoscale protonic conductors and nanoporous membranes, agricultural applications and emulsification.

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Competitive Hydrogen Bonding and Self-Assembly in P2VP-*b*-PMMA/Phenoxy) Blends

3.1 Abstract

Blends of P2VP-*b*-PMMA and phenoxy were prepared by solvent casting from chloroform solution. The specific interactions, phase behaviour and nanostructure morphologies of these blends were investigated by FTIR spectroscopy, DSC, DLS, AFM and TEM. In this BCP/homopolymer blend system, it is established that competitive hydrogen bonding exists as both blocks of the P2VP-*b*-PMMA are capable of forming intermolecular hydrogen bonds with phenoxy. It was observed that the interaction between phenoxy and P2VP is stronger than that between phenoxy and PMMA. This imbalance in the intermolecular interactions and the repulsions between the two blocks of the di-BCP lead to a variety of phase morphologies. At low phenoxy concentration, spherical micelles are observed. As the concentration increases, PMMA begins to interact with phenoxy, leading to the changes of morphology from spherical to wormlike micelles and finally forms a homogenous system. A model is proposed to describe the self-assembled nanostructures of the P2VP-*b*-PMMA/phenoxy blends, and the competitive hydrogen bonding is responsible for the morphological changes.

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3.2 Introduction

It is well known that blending is an expedient technique for the development of new polymeric materials with improved properties.^{1,2} There are various studies focused on di-BCP/homopolymer blends, mainly on A-*b*-B/C type systems. In particular, self-assembled nanostructures in blends of di-BCP with homopolymer involving specific interactions have attracted much interest in the past few decades because of their potential applications in various fields such as cosmetics, drug delivery, diagnostic agents, advanced materials formation, electronics, flocculants, viscosity modifiers, demulsifiers, etc., in many industrial and pharmaceutical preparations.^{1,3-8}

It has been shown that PS-*b*-PI/poly(2,6-dimethylphenylene oxide)⁹, PS-*b*-PS(OH)/PVME¹⁰ and PS-*b*-P4VP/PAA¹¹ can undergo aggregation and phase separation to yield nanoscale morphologies in selective solvents. The attachment of a homopolymer C to the di-BCP A-*b*-B depends on the composition and the strength of intermolecular hydrogen bonding between the homopolymer and BCP.¹² Hydrogen bonded polymer blends show macroscopic changes on their physical properties like melting temperature, glass transition temperature, surface properties, crystal structure and dielectric properties. So, it is a great challenge for constructing self-assembled nanostructures from polymeric building blocks through specific interactions.

In this paper, we report A-*b*-B/C type BCP/homopolymer blends of P2VP-*b*-PMMA and phenoxy. The BCP comprises of immiscible blocks A and B and the homopolymer C is miscible with both A and B. This indicates a positive χ_{AB} value, negative χ_{AC} and χ_{BC} , but χ_{BC} is more negative than χ_{AC} , which designates a competitive hydrogen bonding in this blend system. Moreover, phenoxy/PMMA blends¹³⁻¹⁷ and phenoxy/P2VP blends¹⁸ have been studied by different authors and it is known that hydrogen bonding is the driving force for their miscibility. The competitive hydrogen bonding interactions and phase behaviour of P2VP-*b*-PMMA/phenoxy blends were investigated using FTIR spectroscopy, DSC, DLS, AFM and TEM. The morphological changes and miscibility of this system are shown to be influenced by two factors: (1) intermolecular interaction between phenoxy and P2VP is stronger than that between phenoxy and PMMA which indicates the existence of competitive

hydrogen bonding, (2) formation of a homogenous phase of phenoxy/P2VP which excludes microdomains of PMMA. So, the morphology of blends changes upon swelling of phenoxy in the microphase of P2VP block. Self-assembled nanostructures form via microphase separation of PMMA blocks from phenoxy/P2VP phase driven by competitive hydrogen bonding.

3.3 Experimental section

3.3.1 Materials and preparation of samples

The polymers employed in this work were phenoxy and P2VP-*b*-PMMA. The phenoxy sample was a product of Aldrich Chemical Company, and it had a quoted average $M_w = 40,000$ and was used in our previous work.^{19,20} The P2VP-*b*-PMMA copolymer was from Polymer Source, with M_n (P2VP) = 56,000, M_n (PMMA) = 57,000, and $M_w/M_n = 1.09$. The polymers were used as received. The P2VP-*b*-PMMA/phenoxy blends were prepared by solution mixing. Chloroform solution containing 1% (w/v) of the polymer mixture was stirred well until a clear solution was obtained. The solvent was allowed to evaporate slowly at room temperature. The blend samples were dried in vacuum at 80 °C for 12 h before the measurements.

3.3.2 FTIR spectroscopy

Infrared spectra of P2VP-*b*-PMMA/phenoxy blends were obtained on a Bruker Vetex-70 FTIR spectrometer, and 32 scans were recorded with a resolution of 4 cm^{-1} . The spectra of all the samples were determined by using the conventional KBr disk method. Thin films of the blends were cast from chloroform solution onto KBr pellets and dried under vacuum in an oven to completely remove the solvent and then allowed to cool to room temperature.

3.3.3 DSC

The glass transition temperatures of the blends were determined by a TA Q200 differential scanning calorimeter using 5–10 mg of the sample under nitrogen atmosphere. A heating rate of 20 °C/min was employed. All the samples were first heated to 150 °C and kept at that temperature for 3 min; subsequently cooled to 0 °C at 20 °C/min, held for 5 min, and heating continued

from 0 to 200 °C. The midpoints of the second heating scan of the plot were taken as the glass transition temperatures (T_g s).

3.3.4 AFM

AFM analysis (DME type DS 45–40, Denmark) were performed to study the surface morphology of the blends. The thin films of the samples were prepared by casting dilute solution of complexes on glass slides using a Laurell model WS-400B spincoater operated at 3000 rpm. The samples were annealed under vacuum for 72 h before the measurements. The phase images and height were obtained by operating the instrument in the tapping mode.

3.3.5 TEM

TEM analysis was carried out on a JEOL JEM-2100 transmission electron microscope operating at an acceleration voltage of 100 kV. The chloroform sample solution was spread on a carbon coated TEM copper grid. After drying at room temperature, the samples were stained with ruthenium tetroxide (RuO_4).

3.3.6 DLS

DLS measurements were performed with a Malvern Zetasizer Nano ZS spectrometer equipped with He-Ne laser with a wavelength of 633 nm digital correlator. All measurements were carried out at 25 °C, with a detection angle of 173°. Solutions of 0.5% (w/v) blend aggregates in chloroform were used. The scattering intensity autocorrelation functions were analyzed using the methods of CONTIN and Cumulant which is based on an inverse-Laplace transformation of the data and gives access to a size distribution histogram for the analyzed solutions. The details were described previously.^{21,22}

3.4 Results and discussion

3.4.1 Hydrogen bonding interactions

FTIR analysis confirms the presence of specific interactions of hydrogen bonding in the blends under study. FTIR has been proven to be the most suitable technique for the observation of changes of hydrogen bonds in the

blends.²³ The possible hydrogen bonding interactions between P2VP-*b*-PMMA BCP and phenoxy homopolymer are schematically shown in Figure 3.1.

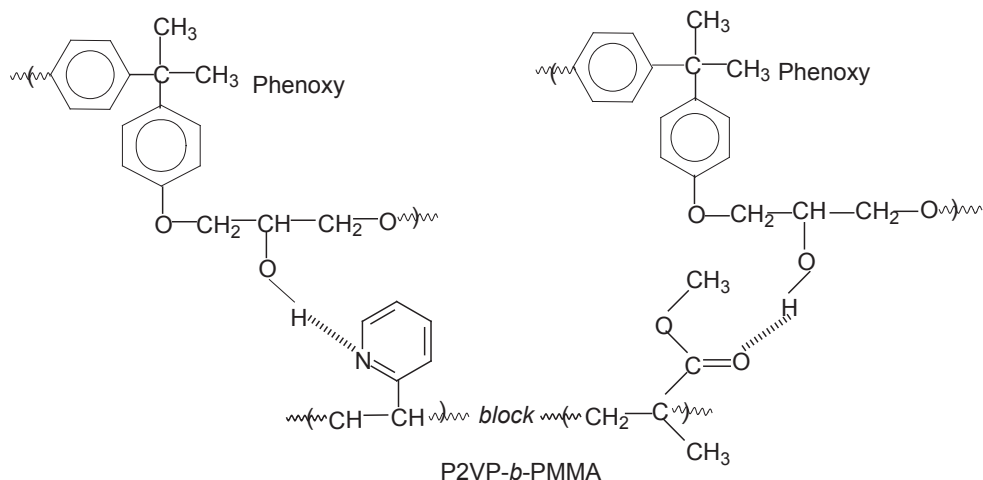


Figure 3.1 Schematic representation of possible hydrogen bonding interactions between P2VP-*b*-PMMA di-BCPs and phenoxy homopolymer.

Figure 3.2 shows the hydroxyl stretching region of P2VP-*b*-PMMA/phenoxy blends in the infrared spectra at room temperature. Phenoxy, in general is a selfassociated polymer²⁴ due to the presence of its pendent hydroxyl groups in the backbone. The spectrum of pure phenoxy exhibits a very broad band centered at 3435 cm^{-1} indicating the selfassociated hydrogen bonded hydroxyl groups. A shoulder band at 3564 cm^{-1} is assigned as a minor contribution which can be attributed to nonassociated hydroxyl groups. For P2VP-*b*-PMMA/phenoxy blends, the broad band appears to shift to lower frequencies as a function of BCP concentration, whilst the relative intensity of free hydroxyl band decreases and finally disappears. The observed shift of the hydrogen bonded hydroxyl region to lower wavenumber is due to the interactions of hydroxyl groups of phenoxy and pyridine and/or carbonyl groups of the BCP, which indicates the interassociated hydrogen bonds in the P2VP-*b*-PMMA/phenoxy is stronger than that of the self-association in pure phenoxy.

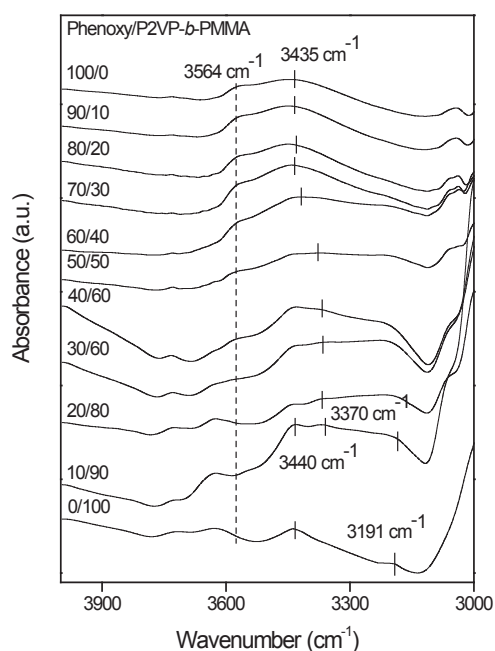


Figure 3.2 Hydroxyl region of P2VP-*b*-PMMA/phenoxy blends in the infrared spectra observed at room temperature

It is observed that a new band centered at 3191 cm^{-1} corresponds to the stretching vibration of the hydroxyl of phenoxy with pyridine nitrogen. This result can be compared with those obtained for phenoxy/P2VP by other authors.^{25–28} It is noticed that both P2VP and PMMA subchains of the BCP have unequal interactions with phenoxy. Moskala et al.²⁹ employed the shift of peak position ($\Delta\nu$) as a barometer for estimating the strength of hydrogen bonding interaction. Consequently, the average hydrogen bonding strength between the hydroxyl groups of phenoxy and nitrogen of P2VP ($\Delta\nu = 373\text{ cm}^{-1}$) is significantly greater than that of phenoxy/PMMA blend ($\Delta\nu = 24\text{ cm}^{-1}$)³⁰ and self-association of pure phenoxy ($\Delta\nu = 129\text{ cm}^{-1}$). From this point, it is clear that the hydroxyl-pyridine interassociation is more favorable than the hydroxyl-carbonyl interassociation. It is also noted that the band observed at 3440 cm^{-1} is due to the overtone of C=O stretching mode of pure PMMA.

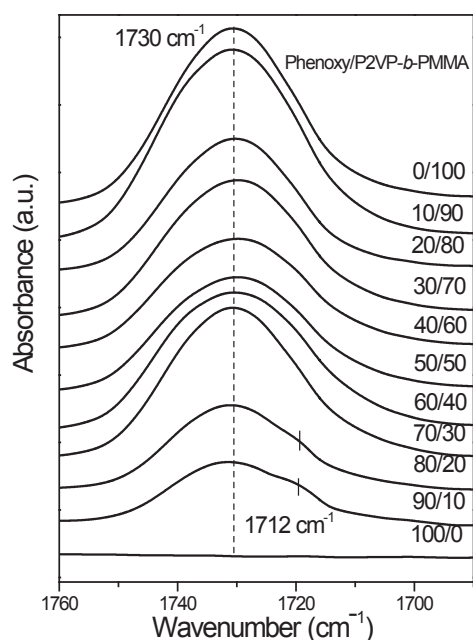


Figure 3.3 Infrared spectra corresponding to the carbonyl stretching region of P2VP-*b*-PMMA/phenoxy blends at room temperature

FTIR spectra in Figure 3.3 represent the carbonyl stretching vibrations ranging from 1760 to 1690 cm^{-1} of the blends at room temperature. The absorption at 1730 cm^{-1} represents the stretching of free carbonyl resembles a typical Gaussian type distribution. At higher concentration of phenoxy, a shoulder band is observed at low wave number region near 1712 cm^{-1} which is due to the hydrogen bonded carbonyl groups. It should be noted that only the blends of 80 and 90 wt% of phenoxy show this minor band indicating the weak intermolecular hydrogen bonding between phenoxy and PMMA. The spectra confirm that PMMA forms hydrogen bonds with phenoxy only when the phenoxy content is greater than 70 wt%.

FTIR spectra in the range of 1610-1550 cm^{-1} of P2VP-*b*-PMMA/phenoxy blends with different compositions are plotted in Figure 3.4. In this figure, the pyridine ring of P2VP shows intense bands at 1590 and 1568 cm^{-1} . But only 1590 cm^{-1} mode shows diverse behaviour when pyridine rings are hydrogen bonded which is attributed to an increase of the stiffness of pyridine ring by hydrogen bonding.²⁸ As a result the band at this region is shifted to higher

wave number regions. These results imply that the hydroxyl groups of phenoxy form hydrogen bonds with P2VP preferentially at all concentrations, whereas PMMA can take part in intermolecular interaction only at higher phenoxy content.

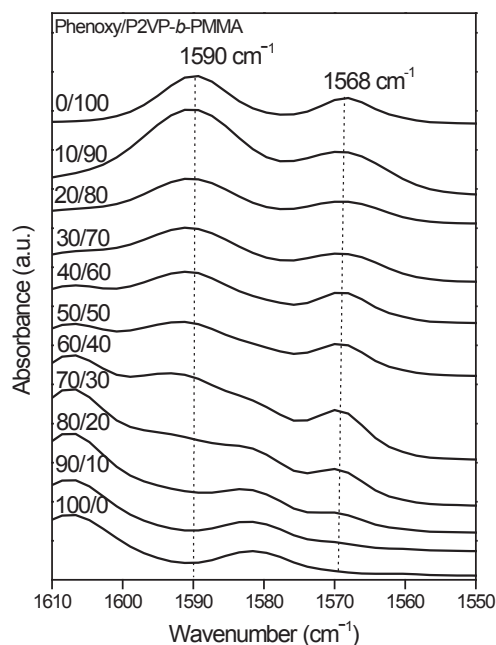


Figure 3.4 Infrared spectra in the region between 1550-1610 cm^{-1} of P2VP-*b*-PMMA/phenoxy blends at room temperature.

Again, a quantitative analysis of the fraction of free and hydrogen bonded carbonyl and pyridine groups can be conducted as the phenoxy content varies in the polymer blends. But in these blends, the hydrogen bonding between phenoxy and PMMA is found to be very weak; therefore the study of fraction of hydrogen bonded carbonyl groups is excluded. We use a least square curve fitting method for the pyridine bands located at 1590 and 1568 cm^{-1} region. It should be noticed that the fraction of hydrogen bonded pyridine groups can be determined from the following equation²⁷

$$f_b = \frac{A_b / a}{A_b / a + A_f} \quad (1)$$

where A_f and A_b are the areas (absorbances) under the peaks representing free and hydrogen bonded pyridine groups, and a is the conversion constant

corresponding to the ratio of the molar absorption coefficient of the above bands. Here, the value of a is taken as 1, is obtained from the literature where vinyl pyridines are blended with hydrogen donor polymers.²⁷

P2VP- <i>b</i> - PMMA/ phenoxy	Free pyridine group			Bonded pyridine group			f_b (%)
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b (%)	
10/90	1590	4.2	9.1	1595	14.1	90.9	90.9
20/80	1590	5.2	17.9	1595	13.8	82.1	82.1
30/70	1590	5.9	27.3	1595	14.2	72.7	72.7
40/60	1590	6.5	35.7	1595	10.9	64.3	64.3
50/50	1590	8.2	44.7	1595	8.4	55.3	55.3
60/40	1590	7.8	49.5	1595	9.3	50.5	50.5
70/30	1590	8.4	57.2	1595	9.1	42.8	42.8
80/20	1590	9.6	60.1	1595	10.2	39.9	39.9
90/10	1590	11.1	71.6	1595	8.8	28.4	28.4

Table 3.1 Curve fitting results of phenoxy hydroxyl and P2VP pyridine interactions in P2VP-*b*-PMMA/phenoxy blends at room temperature.

Table 3.1 shows the fraction of free and hydrogen bonded pyridine groups in the P2VP-*b*-PMMA/ phenoxy blends under study. The two bands of the free and interassociated pyridine groups were found to be well fit to a Gaussian function. In the present system, the band centered at 1568 cm^{-1} should be included in the fitting analysis, as this band remains unaffected by hydrogen bonding. However, this band is overlapped with the 1590 cm^{-1} band. For calculating the fraction of hydrogen bonded pyridine group, the band at 1568 cm^{-1} has been taken as internal standard as this pyridine mode not influenced by the presence of hydroxyl group. From the calculated results, it can be

noticed that the fraction of hydrogen bonding in pyridine groups increases with increase in the phenoxy content. The variation in half width values can be attributed to the sharp decrease in intensity of pyridine peak due strong interaction with phenoxy compared to PMMA.

In terms of the above results, FTIR spectra confirm that there is competitive hydrogen bonding interactions involved in P2VP-*b*-PMMA/phenoxy blends. Due to the strong hydrogen bonding between phenoxy and P2VP, the interaction between phenoxy and PMMA is observed to be mild. Only at higher phenoxy content, PMMA blocks form interassociated hydrogen bonding with phenoxy. Thus, we can conclude that competitive hydrogen bonding exists between phenoxy–phenoxy, phenoxy–P2VP, and phenoxy–PMMA, while the phenoxy–P2VP is observed to be most favorable.

3.4.2 Phase behaviour

We used DSC to assess the thermal properties of the BCP/homopolymer systems by measuring the T_g of all blend compositions. Figure 3.5 shows the DSC thermograms of the P2VP-*b*-PMMA/phenoxy blends. From the DSC curves, T_g of pure phenoxy is 86 °C whereas the BCP shows two glass transition temperatures revealing the presence of two immiscible blocks, namely P2VP and PMMA. The blends containing low phenoxy contents show two T_g s corresponding to the phenoxy/P2VP phase and non-hydrogen bonded PMMA blocks.

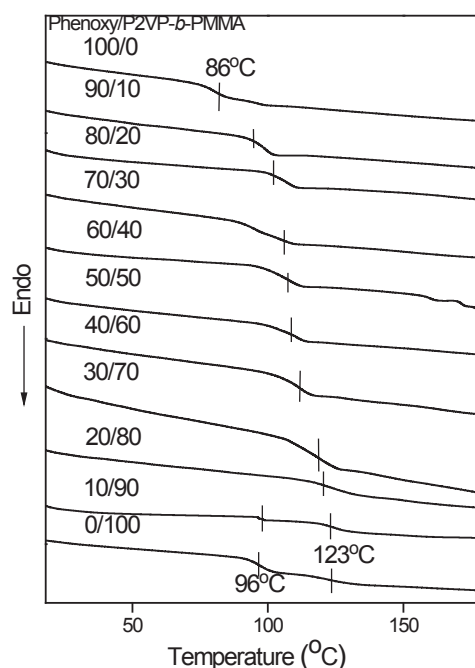


Figure 3.5 DSC thermograms of the second scan of P2VP-*b*-PMMA/phenoxy blends.

DSC thermograms in the temperature range of 80–130 °C of the blends containing 10–30 wt% of phenoxy are shown in Figure 3.6. It can be seen that PMMA exhibits T_g values at 10–30 wt% of phenoxy, however the intensity is reduced upon increase in phenoxy concentration. This is due to the increasing degree of hydrogen bonding interaction between phenoxy and PMMA at low phenoxy concentrations. However, the T_g of PMMA could not be distinguished in the blends containing 30 wt% or above phenoxy as the T_g value of phenoxy/P2VP meets that of PMMA. This could be due to the partial formation of hydrogen bonds between PMMA and phenoxy to form a phenoxy/P2VP phase and phenoxy/PMMA phase. At very high concentrations of phenoxy, PMMA also became miscible with phenoxy forming phenoxy/P2VP phase and phenoxy/PMMA phase. The miscibility can be identified by the formation of a single T_g value for the blends.

Based on the DSC results, it can be concluded that microphase separation exists only due to PMMA, which has weaker hydrogen bond interaction than P2VP. Also, at lower phenoxy contents, phenoxy concentration is insufficient

to form two hydrogen bonding integrations namely, phenoxy/PMMA and phenoxy/P2VP. Therefore PMMA has a higher chance to phase separate at these concentrations. This can be evidenced by TEM and AFM and will be discussed in the later part of this article.

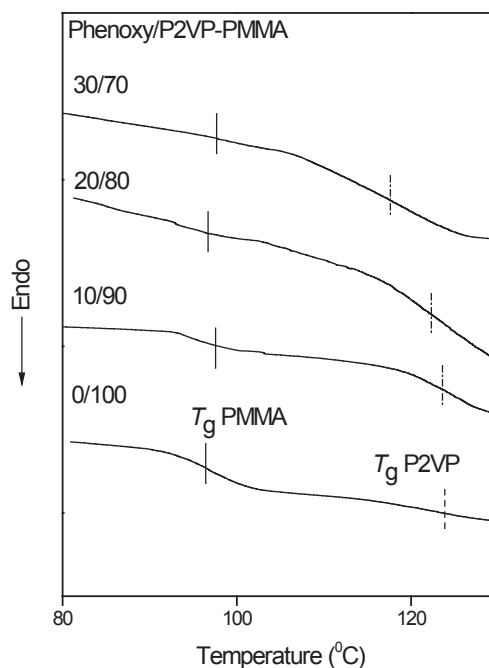


Figure 3.6 DSC thermograms of the second scan of P2VP-*b*-PMMA/phenoxy blends at 10-30 wt% of phenoxy.

3.4.3 Self-assembly and microphase separation in phenoxy/P2VP-*b*-PMMA blends

BCPs can self-assemble into micelles of varying sizes of nanometer scale. Addition of a homopolymer cause changes in the microdomain structure of the di-BCP. The micelles which are generally spherical undergo changes in their shape and size distribution under specific conditions to form various morphologies such as cylindrical, rods, lamellae and wormlike micelles. Morphological transitions due to hydrogen bonding interaction between homopolymer and BCP were studied by several groups including Hameed et al.^{19,21,22} Abetz et al.,³¹ Gohy et al.,³² and Chang et al.³³ By tuning the factors such as, stretching of the core-forming blocks, interfacial energy and intercoronal energy between the solvent and the micellar core, the forces

balancing the micellar structure can be disturbed, leading to the transformation of one morphology to other.

The morphology of self-assembled structures of P2VP-*b*-PMMA/phenoxy blends was observed by AFM. The AFM images of the blends containing 20–80 wt% of the homopolymer are presented in Figure 3.7.

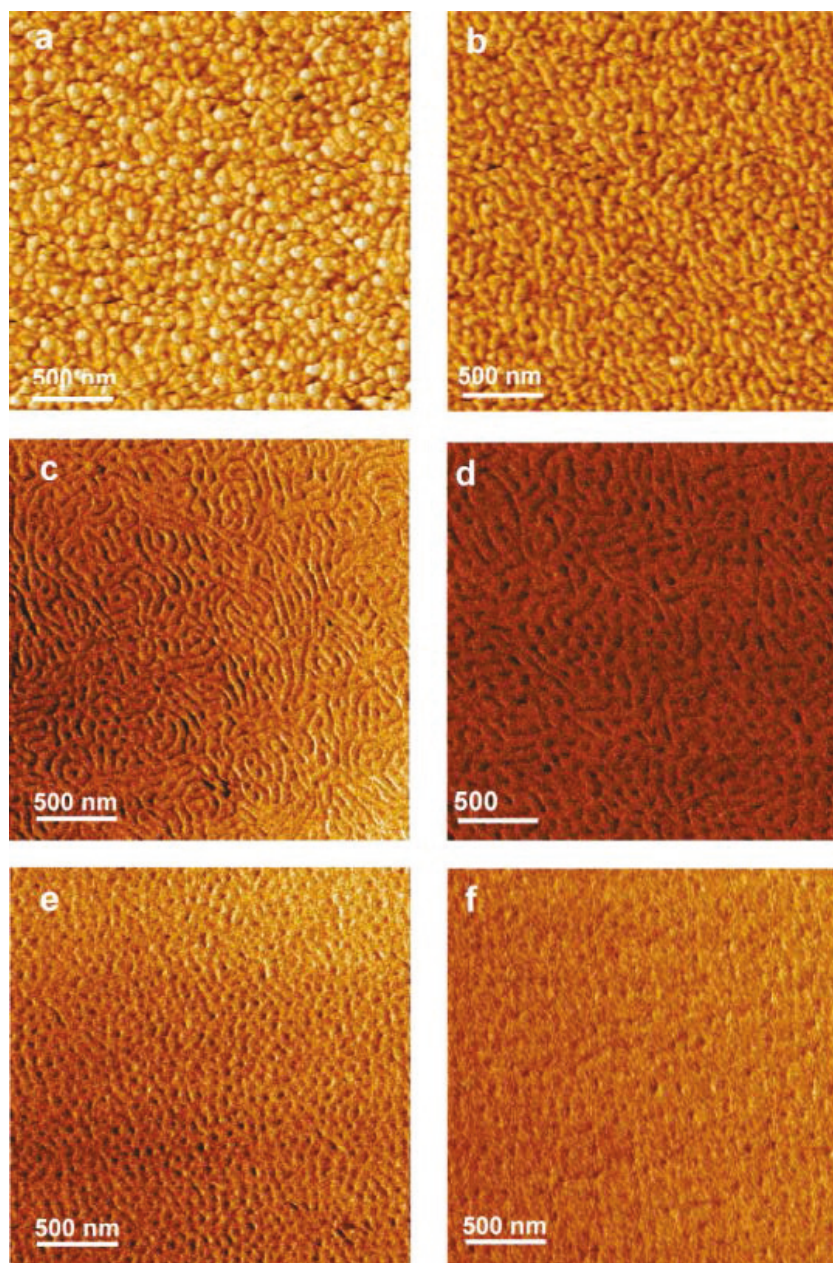


Figure 3.7 AFM images of P2VP-*b*-PMMA/phenoxy blends. P2VP-*b*-PMMA/phenoxy: (a) 80/20, (b) 60/40, (c) 40/60, (d) 30/70, (e) 20/80, and (f) 10/90.

The plain P2VP-*b*-PMMA BCP exhibited cylindrical lamellar morphology [as observed by TEM in Figure 3.8(a)]. The formation of cylindrical lamellar micellar via self-assembly of di-BCP is due to an entropy-driven association mechanism. When a homopolymer is added to a di-BCP involving competitive hydrogen bonding, the less hydrogen bonded block is excluded from the homogenous region due to the high entropic penalty for conformational distortion. When phenoxy is added to the P2VP-*b*-PMMA BCP, it selectively swells the blocks due to the competitive hydrogen bonding which results in phase separation. In the 20 wt% phenoxy blends, spherical micelles with an average diameter of 40–50 nm were obtained. As the concentration of phenoxy increases, the microphase morphology varies, displaying elongated spherical micelles in 40 wt% phenoxy blends, while wormlike morphology is obtained in 50–70 wt% phenoxy blends. The special feature of this morphology which should be noticed is that their diameters are very uniform and are orderly arranged. As the concentration reaches 90 wt% phenoxy, the interface between the microphases become less distinct. The AFM images clearly displays that morphologies transit from spherical to elongated spherical and worm like micelles by increasing the content of homopolymer. TEM imaging carried out for analyzing the morphologies of P2VP-*b*-PMMA/phenoxy blends at different phenoxy concentration is given in Figure 3.8. The P2VP-*b*-PMMA/phenoxy blend with 20 wt% phenoxy shows spherical micellar morphology as shown in Figure 3.8(b) and elongated micelles are observed in 40 wt% phenoxy blend [Figure 3.8(c)]. TEM images also confirm that wormlike morphology exists in 60 and 70 wt% phenoxy blends [Figure 3.8(d,e)] as observed in AFM experiments.

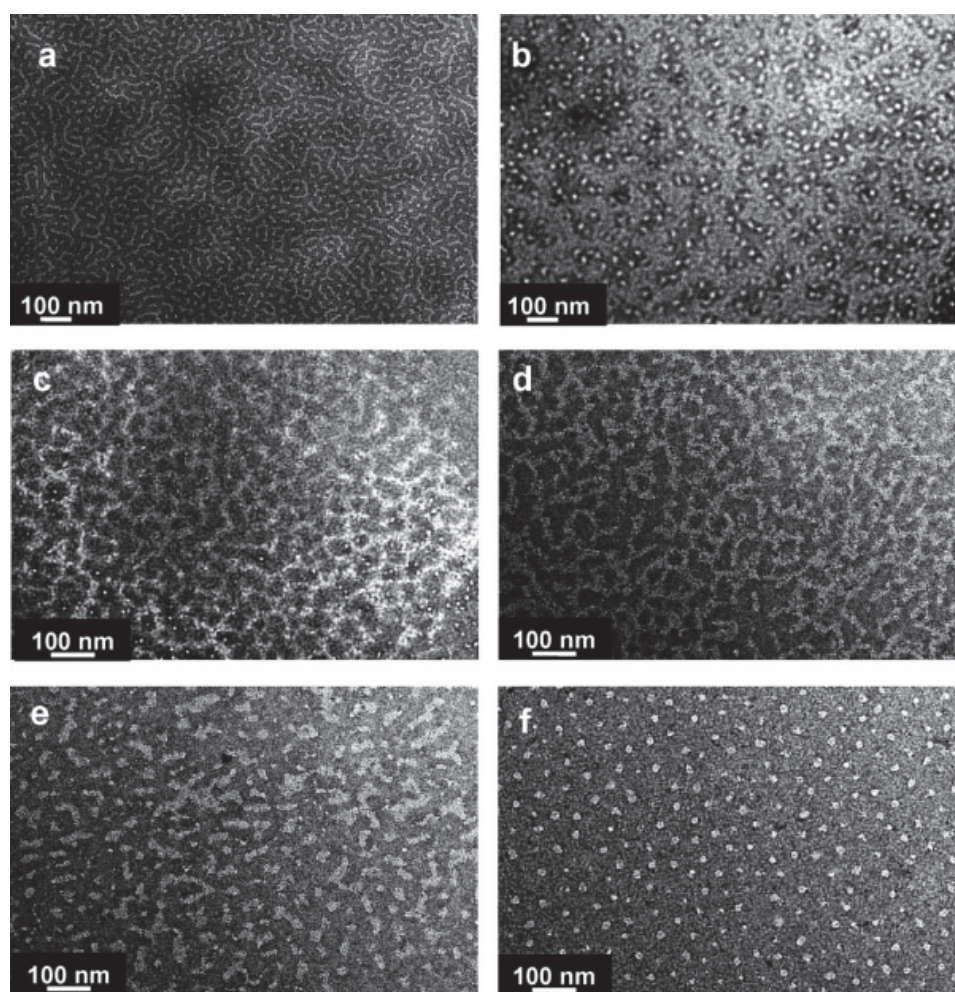


Figure 3.8 TEM micrographs of P2VP-*b*-PMMA/phenoxy blends. P2VP-*b*-PMMA/phenoxy: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 30/70, and (f) 20/80.

The appearance of spherical micellar morphology in 20 wt% phenoxy blend is due to the confinement of noninteracting PMMA blocks to the core of the micelles and the highly hydrogen bonded phenoxy/P2VP phase to the shell. The stretching of PMMA core as the homopolymer concentration increases resulting in the elongated micelles. The blends containing 60 and 70 wt% of phenoxy show wormlike micelles as observed by both AFM and TEM. This can be attributed to the beginning of phenoxy/PMMA interaction. Above 60 wt% phenoxy, PMMA starts forming hydrogen bonds with phenoxy since the homopolymer is available even after strong interaction with P2VP. Moreover,

at these compositions, molecular weights of the complementary components and the weight percentages are in such a way that the three components are in an identical state by weight. In fact, the competitive hydrogen bonding is supposed to occur with 60 wt% and more phenoxy content though it is not detected by FTIR. The transformation from spherical to wormlike morphology can be attributed to the competitive hydrogen bonding between phenoxy/P2VP and phenoxy/PMMA pairs. In 80 wt% phenoxy blend, spherical microdomains [the white areas in Figure 3.8(f)] form via microphase separation of PMMA blocks from phenoxy/P2VP phase, which is driven by competitive hydrogen bonding. However, it can be suggested that at very high concentrations of phenoxy (above 90 wt%), the blends will be homogeneous as phenoxy/PMMA hydrogen bonding becomes more prominent (as observed in the FTIR spectra).

3.4.4 Hydrodynamic size in solution

Figure 3.9 shows the D_h and its distribution of P2VP-*b*-PMMA/phenoxy blends in 0.5% (w/v) chloroform solutions determined by DLS experiments.

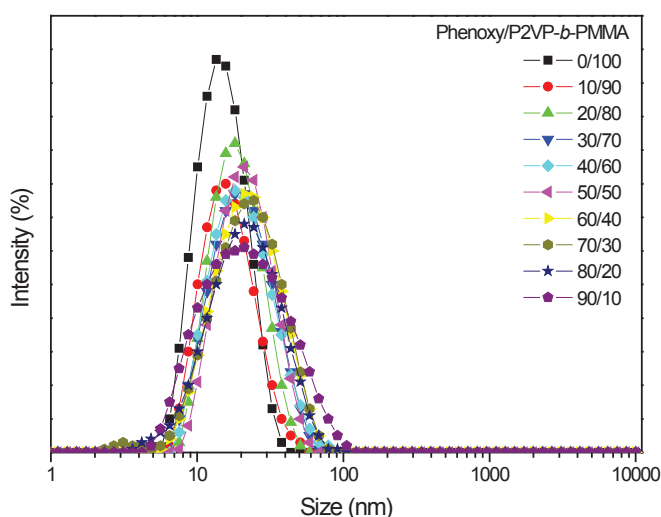


Figure 3.9 Hydrodynamic diameters from DLS measurements of phenoxy/P2VP-*b*-PMMA blends in 1% (w/v) chloroform solutions.

The blends all show a single peak, which indicates the uniformity in the hydrodynamic size. It can be seen that the blends below 50 wt% phenoxy show a sharper peak compared to those above 50 wt% phenoxy. This sharp peak

indicates the presence of spherical micelles, whereas broader peaks above 50 wt% phenoxy show the change in shape from spherical to nonspherical micelles in solution.

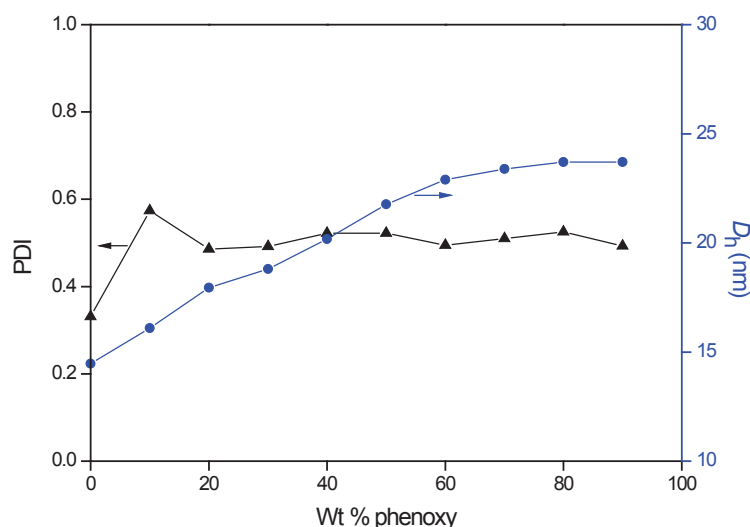


Figure 3.10 Hydrodynamic diameter (D_h) vs composition and polydispersity index (PDI) vs composition of P2VP-*b*-PMMA/phenoxy blends in 0.5% (w/v) chloroform solution.

The hydrodynamic size and PDI are given in Figure 3.10 as functions of blend composition. As can be seen, the pure BCP exhibits a hydrodynamic diameter of about 14 nm. The hydrodynamic size increases with increase in concentration of phenoxy and remains almost unchanged with 50 wt% and more phenoxy. After 50 wt% blends have nonspherical morphology and which possess similar hydrodynamic diameter. As we know, DLS measurements provide only apparent values of D_h and do not give information about the true shape of the micelles. As for the spherical micelles at very low phenoxy concentration, D_h is the value deduced from the unique relaxation mode and at higher phenoxy concentrations, it is the average of the multimodal distribution. This is justified since the AFM experiments have shown polydisperse micellar morphologies. It is noted that the size of the micelles obtained by DLS and microscopic measurements cannot be compared directly. This is because D_h from DLS, in principle is applicable to hypothetical spherical objects and not to anisotropic objects. Moreover, the D_h value derived from the cumulant analysis

represents the average dimensions (equivalent sphere) of the P2VP-*b*-PMMA/phenoxy micelles (wormlike). In this work, DLS, TEM and AFM results were found to be in good agreement, indicating the strong evolution of the micellar morphology as a function of composition due to the competitive interactions in the blends.

3.4.5 Mechanism of microphase separation

It is established that several factors influence the phase transitions of BCP aggregates.^{34,35} In our system, phenoxy is capable of forming hydrogen bonding which plays an important role in the variation in morphology of the micelles. In addition, the BCP comprising P2VP and PMMA can form intermolecular hydrogen bonding with phenoxy. However, only P2VP is able to form strong intermolecular interaction with phenoxy, when compared to PMMA. This competitive hydrogen bonding interaction and the repulsive forces between the two blocks are responsible for the self-assembled nanostructures of P2VP-*b*-PMMA/phenoxy blends.

The mechanism of formation of different microphases in P2VP-*b*-PMMA/phenoxy blends is shown in Figure 3.11.

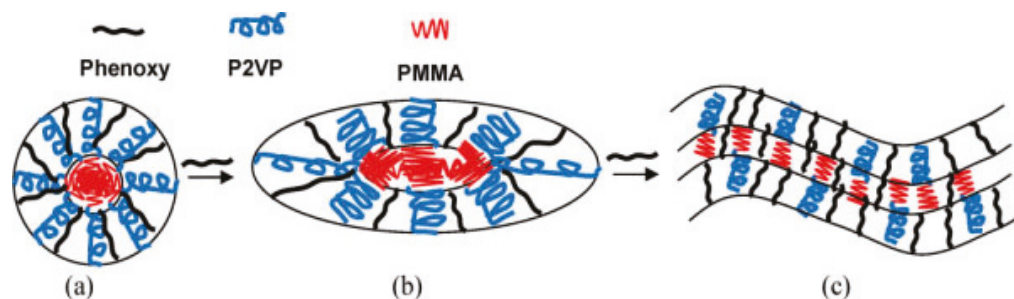


Figure 3.11 Schematic representation of phase morphologies in P2VP-*b*-PMMA/phenoxy blends: (a) Spherical micelles at 20 wt% phenoxy concentration, (b) elongated spherical micelles at 40 wt% phenoxy concentration, and (c) wormlike micelles at 50-70 wt% phenoxy concentration.

From the TEM images, the pure BCP shows cylindrical lamellar structure. Upon the addition of homopolymer, the microphase separation takes place to form spherical micelles. The schematic representation of spherical micelles

formed in 20 wt% phenoxy blends is shown in Figure 3.11(a). Here, phenoxy and the P2VP blocks form a single phase due to strong hydrogen bonding while the PMMA blocks separate from the homogenous phenoxy/P2VP phase, resulting in the two phase structure in the blends. At lower phenoxy contents (20 wt%), hydrogen bonding is predominantly between phenoxy and P2VP and the PMMA phase had been excluded from the mixed phase because of its significantly weaker ability to form hydrogen bonds with phenoxy. This spherical structure is easily evident from Figure 3.8(b) as the dark region (shell) corresponds to a mixed phase of phenoxy and P2VP; the bright region (core) corresponds to the PMMA phase that has been confined within the mixed phenoxy/P2VP phase. The phase which looks black can be considered as the phenoxy and P2VP rich phase, which is preferentially stained with RuO₄ due to the aromatic moieties in the main chain.²⁰ Moreover it has been proven that PMMA cannot be stained by RuO₄ and appears bright.^{36,37}

In other words, the incorporation of phenoxy in the P2VP-*b*-PMMA BCP may increase the interaction parameter difference between phenoxy/ P2VP and PMMA phases because of the difference in the intermolecular interaction between them. Therefore, phenoxy forms hydrogen bonding with P2VP selectively, and PMMA phase separates. Therefore it can be concluded that in A-*b*-B/ C systems, the strongly hydrogen bonded phase form one phase and the nonhydrogen bonded or less hydrogen bonded phase excluded from or confined in to the other phase. Similar microphases separated structures have been observed in hydrogen bonded BCP/homopolymer systems by many authors.^{19,21,22,37} In the blends containing 20–70 wt% phenoxy, the PMMA blocks, which are repelled by P2VP, only have weak interaction with the hydroxyl groups of phenoxy, resulting in different nanostructures such as elongated spherical micelles [Figure 3.11(b)] and wormlike micelles [Figure 3.11(c)]. As the concentration of phenoxy increases above 70 wt%, the internal domains segregate to form featureless microstructures. This is assumed to be due to the increased intermolecular interaction between PMMA and phenoxy which was confirmed by FTIR spectra. At higher phenoxy compositions availability of free hydroxyl group is more, so phenoxy can form hydrogen

bonds with both P2VP and PMMA. Here, it is understood that phenoxy can act as a nonselective solvent for the two blocks, resulting in a homogenous system.

3.4.6 Conclusions

We have investigated the competitive hydrogen bonding interactions of A-B/C type P2VP-*b*-PMMA/phenoxy blends. FTIR study confirms that the pyridine groups are stronger hydrogen bond acceptors than the PMMA carbonyl groups, which is responsible for the existence of competition in hydrogen bonding. Only P2VP can form strong interassociated hydrogen bonds with phenoxy when the phenoxy content is low. At moderate and higher compositions, PMMA is also capable of making hydrogen bonds with phenoxy. By DSC characterization, miscible blends are found due to the interactions between homopolymer and di-BCP blocks. The AFM and TEM results clearly revealed that the self-assembled nanostructures of a matrix with a homogenous phenoxy/P2VP phase and micellar domains of excluded PMMA. The competitive hydrogen bonding plays an important role in the self-assembly and microphase morphology of the P2VP-*b*-PMMA/phenoxy blends.

3.5 References

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Microphase Separation through Competitive Hydrogen Bonding in Double Crystalline Diblock Copolymer/Homopolymer Blends

4.1 Abstract

Microphase separation induced by competitive hydrogen bonding interactions in double crystalline di-BCP/homopolymer blends was studied for the first time. PEO-*b*-PCL/PVPh blends were prepared in THF. The di-BCP PEO-*b*-PCL consists of two immiscible crystallizable blocks where both PEO and PCL blocks can form hydrogen bonds with PVPh. In these A-*b*-B/C di-BCP/homopolymer blends, microphase separation takes place due to the disparity in intermolecular interactions; specifically PVPh and PEO block interact strongly whereas PVPh and PCL block interact weakly. The TEM and SAXS results show that the cubic PEO-*b*-PCL di-BCP changes into ordered hexagonal cylindrical morphology upon addition of 20 wt% PVPh followed by disordered bicontinuous phase in the blend with 40 wt% PVPh and then to homogenous phase at 60 wt% PVPh and above blends. Up to 40 wt% PVPh there is only weak interaction between PVPh and PCL due to the selective hydrogen bonding between PVPh and PEO. However, with higher PVPh concentration, the blends become homogeneous since a sufficient amount of PVPh is available to form hydrogen bonds with both PEO and PCL. A structural model was proposed to explain the self-assembly and microphase morphology of these blends based on the experimental results obtained.

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4.2 Introduction

The morphology of BCPs and development of self-assembled nanostructures have been intensively studied during the last decades, and highly ordered structures such as spheres, cylinders packed in a hexagonal lattice, worm like micelles, lamellae, and hierarchical nanostructures have been revealed.¹⁻⁵ A binary mixture of self-assembled mixture comprises a di-BCP and a homopolymer can also exhibit well-defined morphologies; these nanostructures are currently being used for diverse applications.⁶⁻¹⁶

There is a considerable interest on polymer blends with secondary interactions, like ionic or electrostatic and hydrogen bonding interactions.¹⁷ Among these, hydrogen bonds in the BCP mixtures can promote nanostructure formation and different phase transitions that allows the development of materials with high functionality. Morphological changes due to hydrogen bonding between amphiphilic BCPs and a homopolymer were studied by several groups.¹⁸⁻²⁰ The hydrogen bonding and nanostructure morphologies formed by the hydrogen bonding interaction between a small molecule and BCP were extensively investigated by Ikkala's group.²¹

Guo et al.²² and Chang et al.²³ recently reported the self-assembled BCP blends and complexes involving competitive hydrogen bonding interactions between different BCP blocks and the homopolymer. This new strategy for the design of nanostructures is based on the competition between different blocks of the BCP forming more than one kind of intermolecular interactions with the complementary polymer, leading to a highly stable blend or complex compared to analogous systems which involve elaborate syntheses and multistep preparation protocols. It is proven that careful selection of the polymers, specifically the BCP, molecular weight, and the experimental conditions, can lead to self-assembled structures in blends and complexes. Such self-assembled blends involving selective hydrogen bonding could be used for the fabrication of hierarchical and functional materials.

The interaction between different chains in A-*b*-B/C di-BCP/homopolymer mixtures can be characterized by Flory-Huggins interaction parameter (χ).^{24,25} Various studies have been conducted in such systems, wherein χ between the interacting polymers (χ_{AC} , χ_{BC} or χ_{AB}) are either positive or negative and can

provide more interesting combinations for blending. The interaction of homopolymer C to the BCP depends on the chemical composition and strength of hydrogen bonding between BCP and homopolymer. There are many theories regarding the microphase separation in BCP/homopolymer systems. One of them is random phase approximation (RPA), where χ denotes repulsive (bad) interactions ($\chi > 0$) and ξ represents attractive (good) interactions ($\xi < 0$) are the two interaction parameters using for characterizing such systems. Hellmann et al.²⁵ studied that there is always a repulsive interaction between the homopolymer and one block of the BCP ($\chi > 0$) which induces the microphase separation avoiding the homogeneous state or macrophase separation. In di-BCP blends, a homopolymer with high molecular weights can induce phase separation with a disordered phase containing homopolymer and ordered phase containing BCP.²⁶

Very recently, Guo and co-workers²⁷ have investigated microphase separation induced by competitive hydrogen bonding in A-*b*-B/C di-BCP/homopolymer complexes where the di-BCP A-*b*-B is immiscible and the homopolymer C can interact unequally with both A and B blocks through hydrogen bonding. The hydrogen bonding interactions were analyzed in terms of the difference in inter-association constants (K), i.e., interaction parameters of each blocks of the BCP to the homopolymer and according to the random phase approximation. It has been established how hydrogen bonding determines the self-assembly and causes morphological transitions in different A-*b*-B/C di-BCP/homopolymer systems with respect to the K values. The A-*b*-B/C systems involving competitive hydrogen bonding investigated so far consist of BCP with two amorphous blocks^{22c, 23a,b} or amorphous-crystalline blocks.^{30,31} Nevertheless, blends in which both components of the di-BCP are crystalline (double crystalline) have never been studied to our knowledge. In BCPs containing crystallizable components, the relationship between crystallization and phase separation can affect the structure, phase behavior functional application of these materials. If there are two crystallizable segments in a BCP, it is possible to create different conditions to examine the structure and phase behavior of such systems.

In the current study the competitive hydrogen bonding and nanostructure formation in self-assembled double-crystalline BCP/homopolymer mixture are detailed. In particular, the self-assembly, crystallization, phase behaviour and morphology of PEO-*b*-PCL/PVPh blends are investigated. The di-BCP PEO-*b*-PCL is immiscible and PVPh can hydrogen bond with both PEO and PCL components. However, there is an unequal competitive hydrogen bonding interaction between the PVPh/PEO and PVPh/PCL sets. The results are correlated with the phase behaviour of the blends experimentally obtained with SAXS and TEM. This work for the first time demonstrates how the competitive hydrogen bonding determines the self-assembly and causes morphological transitions in A-*b*-B/C double crystalline di-BCP/homopolymer blends.

4.3 Experimental section

4.3.1 Materials and preparation of samples.

PVPh with $M_w = 20,000$ and $M_w/M_n = 1.70$ was obtained from Aldrich Chemical Co., Inc. The BCP used in the present study, PEO-*b*-PCL was purchased from Polymer Source Inc. with $M_n(\text{PEO}) = 15,000$, $M_n(\text{PCL}) = 25,000$ and $M_w/M_n = 1.17$. All these polymers were used as received. The blends of PEO-*b*-PCL/PVPh were prepared by solution mixing. THF solution containing 1% (w/v) of the individual polymers were mixed and stirred well until a clear solution was obtained. The solvent was allowed to evaporate slowly at room temperature. The blends were dried under vacuum for 72 h before the measurements in order to reach equilibrium.

4.3.2 FTIR spectroscopy

The IR measurements were performed on a Bruker Vetex 70 spectrometer. The THF samples were cast onto KBr pellets and dried in-vacuo (80 °C) to completely remove the solvent and then allowed to cool to room temperature. The spectra were recorded at the average of 32 scans at 4 cm^{-1} resolution.

4.3.3 DSC

The glass transition temperatures of the blends were determined by a TA Q200 differential scanning calorimeter using 5–10 mg of the sample under nitrogen atmosphere. A heating rate of 10 °C/min was employed. All the samples were first heated to 150 °C and kept at that temperature for 3 min; subsequently cooled to -70 °C at 10 °C/min, held for 5 min, and heating continued from -70 to 200 °C. The midpoints of the second heating scan of the plot were taken as the glass transition temperatures (T_g s).

4.3.4 POM

Spherulite growth was studied using a POM with the Nikon Digital Sight DS 5M U1 system. The polymer sample sandwiched between two glass slides. All samples were vacuum-dried at 50 °C (48 h), then melted at 100 °C (5 min), finally quenched and annealed at 25 °C for 4h.

4.3.5 TEM

TEM experiments were performed on a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 100 kV. The samples were cut into ultrathin sections of approximately 70 nm thickness at room temperature with a diamond knife using a Leica EM UC6 ultra microtome machine. The bulk samples were annealed at 180 °C for about 48 hrs before microtoming. The thin sections were stained by ruthenium tetroxide (RuO_4) before TEM observation.

4.3.6 WAXS

WAXS analyses were carried out on a Panalytical XPert Pro XRD machine. The scanning angle 2θ , from 5° to 35° was swept at a speed of 0.02/s. The polymer thin films were fixed on the equipment, and the data were collected with every 0.02°.

4.3.7 SAXS

The SAXS experiments were performed on a Bruker NanoStar 3 pin-hole instrument using Cu $K\alpha$ radiation ($\lambda=1.54 \text{ \AA}$, wavelength). Annealed samples having 1mm thickness were prepared for SAXS measurements. The intensity

profiles were interpreted as scattering intensity (I) vs vector, $q = (4/\lambda) \sin (\theta/2)$ (θ = scattering angle).

4.4 Results and discussion

4.4.1 Hydrogen bonding interactions.

FTIR technique provides information on specific interaction between PEO-*b*-PCL/PVPh blends.²⁸ Figure 4.1 shows the possible specific interaction in the PEO-*b*-PCL/PVPh blends. PVPh has an excellent potential as a proton donor because the hydroxyl groups are simply acceptable at the fourth location of every aromatic ring.

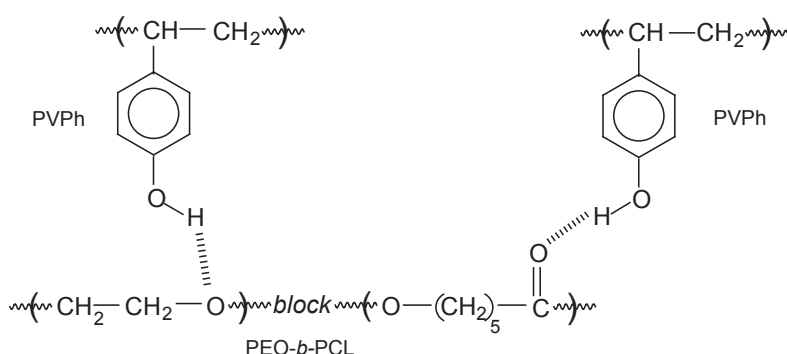


Figure 4.1 Schematic representation of possible hydrogen bonding interactions between PEO-*b*-PCL di-BCPs and PVPh homopolymer.

As shown in Figure 4.2, PVPh displays two absorption peaks in the OH region. The first absorption is at 3352 cm⁻¹ that represents self-associated hydroxyl groups. The other absorption observed at 3525 cm⁻¹ indicates the free hydroxyl region, but the intensity of this band reduces and finally disappears with increase in BCP content in the blends. This implies the hydrogen bonds of PVPh/PEO and PVPh/PCL pairs. Meanwhile, the self-associated hydroxyl groups of PVPh at 3352 cm⁻¹ shift towards low frequencies with increasing PEO-*b*-PCL content. The peak at 3325 cm⁻¹ in 90/10 PEO-*b*-PCL/PVPh blends represents the intermolecular interactions between PVPh with PEO/PCL blocks.

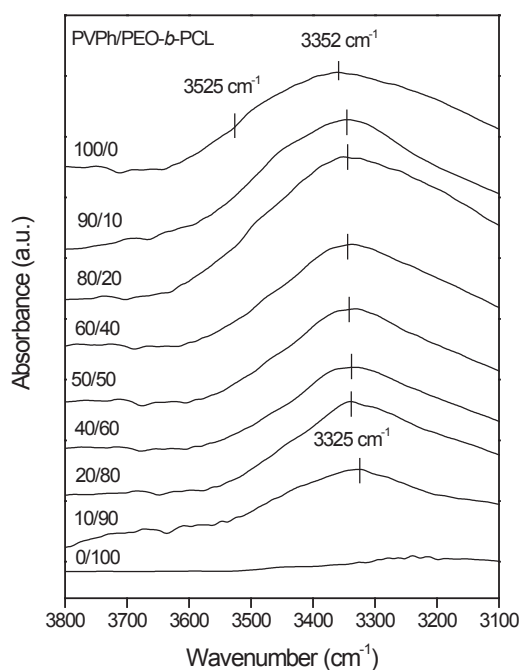


Figure 4.2 Hydroxyl region of PEO-*b*-PCL/PVPh blends in the infrared spectra observed at room temperature.

Table 4.1 shows the difference in frequencies ($\Delta\nu$) among the free OH region to that of the bonded components.²⁹ The $\Delta\nu$ values of PVPh/PCL (105 cm^{-1})³⁰ and PVPh/PEO (295 cm^{-1})³¹ binary blends are also given for comparison. This observation implies that the average strength of the bond among PVPh hydroxyl group and PEO-*b*-PCL BCP (200 cm^{-1}) is higher than that between hydroxyls in PVPh (173 cm^{-1}) homopolymer.

System	$\Delta\nu\text{ (cm}^{-1}\text{)}$
PVPh	173
PVPh/PEO	295 ^a
PVPh/PCL	105 ^b
PEO- <i>b</i> -PCL/PVPh	200

a. Ref. [31], *b.* Ref. [30]

Table 4.1 Wave number shift of hydroxyl region in PEO-*b*-PCL containing PVPh

However, this value is less than the interassociation between PVPh and PEO (295 cm^{-1}). This method also reveals the hydrogen bonding strength of PEO-*b*-PCL/PVPh blends. The analysis of the $\Delta\nu$ values of pure PVPh, PVPh/PEO, and PVPh/PCL reflects that PEO and PCL are both capable of making hydrogen bond with PVPh, although the resulting bond strengths are unequal. The above results denote that the hydrogen bonds among PVPh/PEO are stronger compared to PVPh/PVPh and PVPh/PCL hydrogen bonds.

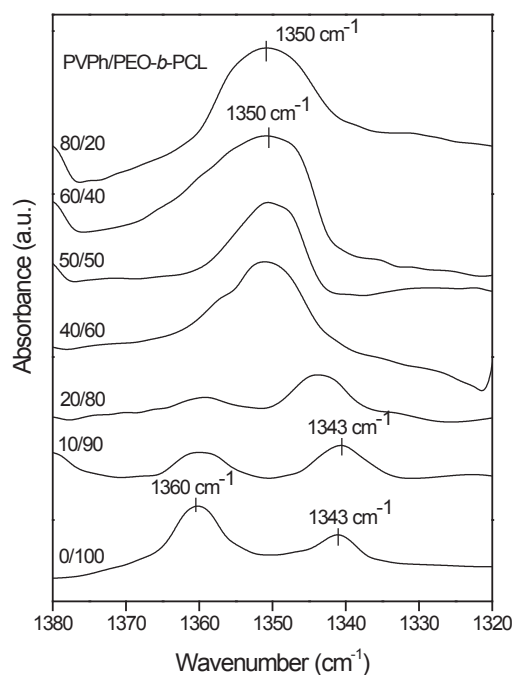


Figure 4.3 FTIR spectra corresponding to the ether region of PEO-*b*-PCL/PVPh blends at room temperature.

Figure 4.3 represents the FTIR spectra of CH₂ wagging of PEO from 1380 to 1320 cm^{-1} . The PEO spectra show absorptions at 1360 and 1343 cm^{-1} corresponding to its crystalline phases.³² Upon blending, retardation of PEO crystallization takes place which can be observed in Figure 4.3. When the PVPh concentration increases in PEO-*b*-PCL/PVPh blends, a new band is formed at 1350 cm^{-1} which represents the amorphous state of PEO. This result designates that the interactions between PVPh/PEO is very strong and exists at all compositions of PVPh.

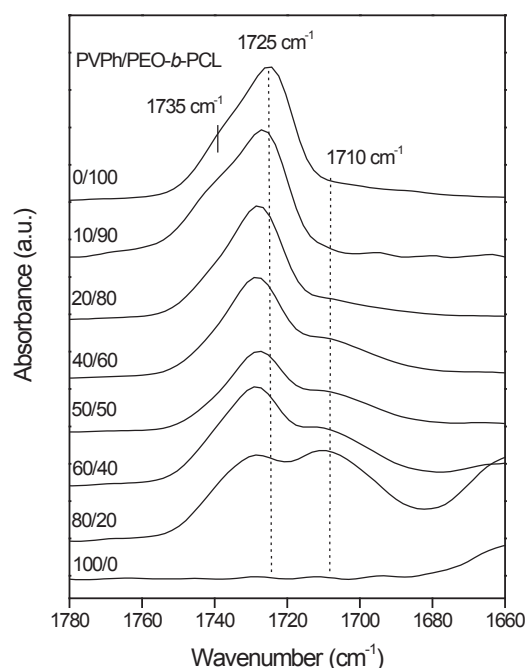


Figure 4.4 FTIR spectra in the carbonyl region of PEO-*b*-PCL/PVPh blends

Figure 4.4 shows the carbonyl (C=O) spectrum in region of 1660-1780 cm^{-1} . The IR spectra of pure PCL exhibits two peaks: a sharp absorption at 1725 cm^{-1} corresponds to PCL in its crystalline-phase conformation, and another weak absorption at 1735 cm^{-1} implying the amorphous-phase of PCL.³³ When the PVPh concentration is above 20 wt%, another band contribution is observed at 1710 cm^{-1} confirming the absorption of bonded C=O groups. This implies that the interaction among PVPh and PCL starts when the PVPh concentration is above 20 wt%. Here the intensity increases very slowly with increase in PVPh concentration compared to the free carbonyl band. This signifies that the fraction of bonded C=O group in PEO-*b*-PCL/PVPh blends are less at lower PVPh concentrations. This is due to the strong hydrogen interacting ability of PEO with PVPh compared to PCL.

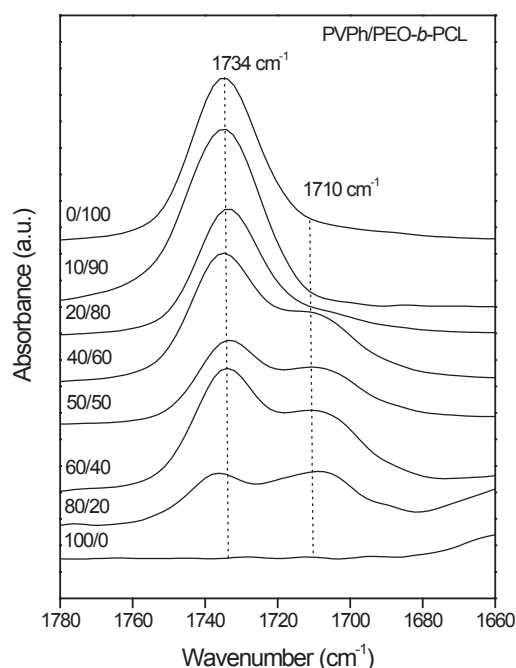


Figure 4.5 Carbonyl stretching region of PEO-*b*-PCL/PVPh blends at 75 °C.

The hydrogen bonding interaction of PVPh and PCL was also examined at higher temperature. Figure 4.5 displays spectral changes of PEO-*b*-PCL/PVPh blends in the carbonyl stretching region at 75 °C. The crystalline peak of PCL centered at 1725 cm⁻¹ has vanished here because of the melting of crystalline-phase of PCL blocks. It is to be noted that the intensity of 1710 cm⁻¹ absorption increases with increasing concentration of PVPh. Again, quantitative determination of the fraction of free and bonded C=O groups was calculated based on the equation below;

$$f_b = \frac{A_b/a}{A_b/a + A_f}$$

where A_f and A_b are the areas (absorbances) under the peaks representing free and hydrogen bonded C=O group, respectively. The conversion factor ' a ' is the specific absorption ratio of the free and bonded bands. The value of $a = 1.5$ for the PVPh/PCL system was determined previously.³⁴ The results of room temperature curve fitting are given in Table 4.2.

PEO- <i>b</i> - PCL/PVPh	Amorphous C=O			Bonded C=O			
	ν (cm^{-1})	$\overline{W_{1/2}}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$\overline{W_{1/2}}$ (cm^{-1})	A_b (%)	f_b (%)
80/20	1735.5	15.57	28.82	1704.5	26.98	71.18	62.21
60/40	1735.1	17.81	58.2	1710.9	29.27	41.8	32.37
50/50	1735.3	16.39	64.9	1709.9	29.25	35.1	26.5
40/60	1735.6	17.26	81.26	1710.1	26.63	18.74	13.32
20/80	1735.8	18.89	94.75	1711.2	27.36	5.25	3.52
10/90	1735.4	17.82	98.28	1712.8	28.36	1.72	1.14

Table 4.2 Curve fitting results of PVPh hydroxyl and PCL carbonyl interactions in PEO-*b*-PCL/PVPh blends at room temperature.

These results indicate that the fraction of bonded carbonyl group is very less at low PVPh concentrations and also the value increases as the concentration of PVPh increases. From the FTIR data given in Figure 4.1- 4.5 and Table 4.2, up to 40 wt% of PVPh, the peak intensity and fraction of the bonded carbonyl group are relatively less compared to the free carbonyl peak. It is assumed that the C=O groups are less involved in bonding in the present BCP blend system compared with the PVPh/PCL homopolymer binary blends investigated by other authors.³⁵

In the present PEO-*b*-PCL/PVPh blends, PCL block also forms hydrogen bonds with PVPh, and the average strength of these bonds increases with increasing PVPh concentration. The PCL block exhibits extensive hydrogen bonding with PVPh only when PVPh content reaches 40 wt% or above. This is due to the competitive hydrogen-bonding interaction between PVPh/PEO blocks and PVPh/PCL blocks. Since the ability of PEO to form hydrogen bonds with PVPh is relatively high compared with PCL, the PEO blocks preferentially form high degree of hydrogen bonding with PVPh first.

It can be concluded from the FTIR results that strong hydrogen bonding between PEO and PVPh was observed in all the compositions. However, the carbonyl groups of PCL form less hydrogen bonding with PVPh hydroxyl groups at very low PVPh concentrations and PCL interacts more strongly with PVPh at higher PVPh blends. In PEO-*b*-PCL/PVPh blends, competitive hydrogen bonding exists between PVPh/PEO pair and PVPh/PCL pair at all the compositions. Since the PVPh/PEO pair is relatively much stronger, PVPh/PCL hydrogen bonded pair exists weakly at lower PVPh concentration.

4.4.2 Phase behaviour and crystallization.

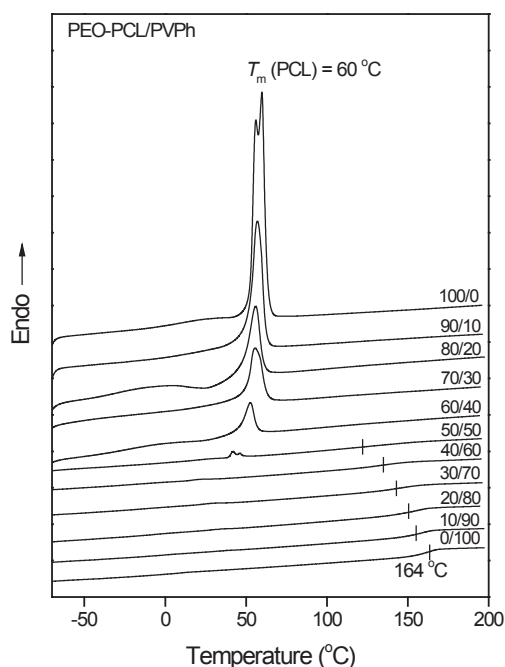


Figure 4.6 DSC thermograms of the second scan of PEO-*b*-PCL/PVPh blends.

DSC experiments were conducted to investigate the phase behaviour of PEO-*b*-PCL/PVPh blends. Figures 4.6 and 4.8 show the DSC traces of PVPh, PEO-*b*-PCL, and PEO-*b*-PCL/PVPh blends measured during heating and cooling, respectively. The pure BCP PEO-*b*-PCL should exhibit two T_g s corresponding to two immiscible blocks such as PEO and PCL. However, the T_g s of pure BCP components were not detectable under the present experimental conditions. It is noticeable that during heating and cooling run of

DSC, the crystallization and melting peaks were overlapped for samples with PEO-*b*-PCL due to the quite near (cooling) T_c and (melting) T_m of both blocks. In fact, PVPh/PEO³¹ and PVPh/PCL³⁶ blends are completely miscible through all composition range; however the T_g s of the blends PEO-*b*-PCL/PVPh show variations. The pure PVPh exhibits a T_g at 164 °C, which becomes broad and shifted down to lower temperatures in the blends as the BCP content was increased. This is due to the miscibility between PVPh/PEO and PVPh/PCL components indicating strong hydrogen bonds between them.

Melting point depression is a major characteristic feature of a miscible blend involving hydrogen bonding interactions. The pure PEO-*b*-PCL di-BCP shows two melting points, T_m (PEO) = 60 °C and T_m (PCL) = 56 °C, corresponding to that of PEO and PCL, respectively. Figure 4.6 shows the heating scan of PEO-*b*-PCL/PVPh blends. As the concentration of PVPh increases, the T_m of PEO disappears (or overlaps with the T_m of PCL), whereas that of PCL significantly moves to low temperature region. At low PVPh content, there is no variation in the melting of PCL segments in PEO-*b*-PCL/PVPh blends. This represents that a good level of miscibility was not achieved between PCL and PVPh at low PVPh contents. The T_m of crystalline PCL phase decreases in its intensity and finally vanishes at 50-60 wt% PVPh, due to the miscibility of PCL and PEO with PVPh at higher PVPh contents.

The values of ΔH_f and crystallization ΔH_c for PEO-*b*-PCL/PVPh blends are represented with respect to the composition in Figure 4.7. These graphs indicate that at higher BCP concentration the heat of crystallization and melting temperature are very high, whereas the values go to zero when the PVPh content in the blends increases. This is because the overall crystallinity decreases due to the miscibility of PVPh with the BCP components. This is due to the interaction of PEO and PCL components with PVPh. ΔH_f decrease is the indication of decreased crystallinity in the blends. But PEO-*b*-PCL/PVPh blends show a superposed T_m and T_c peak in the second heating as well as cooling; that is, both PCL and PEO chains exhibit comparable T_m and T_c .³⁷ Therefore, it is difficult to calculate the individual degrees of crystallinity of

PCL and PEO. However, overall crystallinity of the BCP keeps decreasing with increase in PVPh concentration.

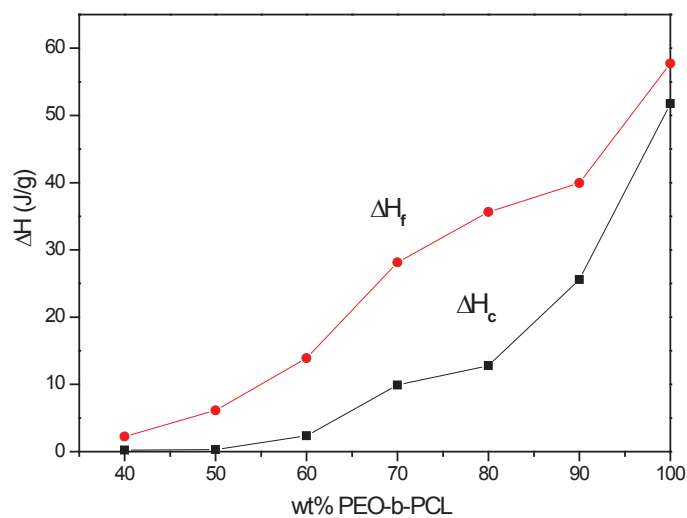


Figure 4.7 ΔH_f and ΔH_c of PEO-*b*-PCL/PVPh blends.

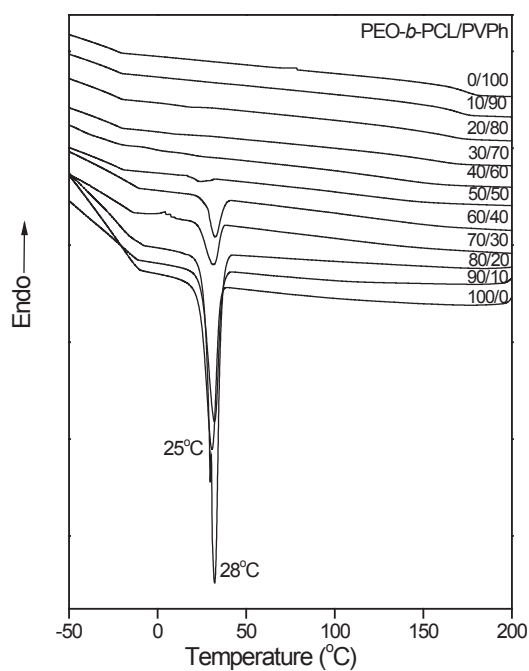


Figure 4.8 Crystallization curves of PEO-*b*-PCL/PVPh blends during cooling.

Figure 4.8 represents the cooling scan of PEO-*b*-PCL/PVPh blends. The neat BCP shows two T_c s at 25 and 28 °C. However the T_c of the blends

increases slightly by the addition of PVPh which is due to the PCL chain relaxation. Moreover there is a better bond formation between PVPh and PEO rather than PVPh and PCL which also facilitate the T_c shift.

WAXS patterns of PEO-*b*-PCL/PVPh blends are given in Figure 4.9. It is noted that PEO and PCL show monoclinic and orthorhombic crystal systems, respectively. [120] peak of PEO and [200] of PCL were observed for neat BCP. This indicates that both segments are crystallizable and form distinct crystalline phases. The PEO crystallization peak is dropped with increase in PVPh in the blends, indicating the deterioration of the PEO crystalline structure [Figure 4.9]. The addition of PVPh resulted in the change of crystal alignment for the development of the inter-associated bonds between PEO and PVPh. At 40 wt% PVPh, the blends show a relative intensity of the [032] plane and minor to [120] plane. The crystalline order of PEO declines designates that the hydrogen bonding interactions of PEO with PVPh prevents its crystallization, which also agrees with DSC data in Figures 4.6 and 4.8. Moreover, in PEO-*b*-PCL di-BCPs, the capacity of PEO to crystallize is constrained by PCL blocks, which is covalently coupled to the other end of the PEO block. This indicates that two separated crystalline domains comprising of PEO and PCL segments in these di-BCPs. This crystalline order of PCL also decreases once the PCL block starts to make hydrogen bonds with PVPh. Further increasing the PVPh content to 60-70 wt%, the crystallization peak of PCL disappears and results in amorphous halos in the WAXS because a large number of hydroxyl groups of PVPh form hydrogen bonds with carbonyl groups of PCL which inhibits the crystallization. In other words, the blend becomes miscible, and the crystalline structures of the PEO and PCL are destroyed. Further increasing the PVPh content, abundant PVPh becomes available to interact with both PEO and PCL through hydrogen bonding. By blending 70 wt% PVPh, the blends become miscible, and PVPh acts like a common solvent in this blend system. The WAXS results also show decreased crystallinity in the blends for PCL and PEO as in agreement with DSC results.

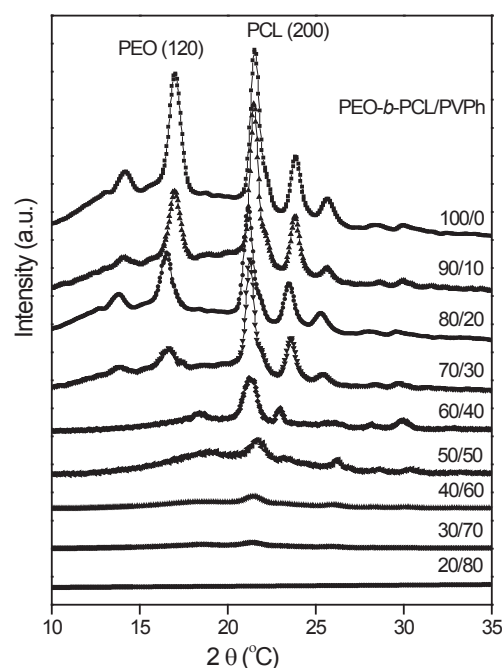


Figure 4.9 WAXD profile of PEO-*b*-PCL/PVPh blends.

Blending of crystalline polymers with amorphous polymers induces changes in the crystallization such as depression in equilibrium melting temperature, decrease of crystallinity, and changes in semicrystalline morphology.³⁸ The POM images of neat BCP and the blends are shown in Figure 4.10. The samples were observed at various magnifications. Spherulite attains diverse crystalline orientations as the concentration of PEO-*b*-PCL changes in the blends. In PEO-*b*-PCL/PVPh blends, as the concentration of PVPh increases, the size of spherulite becomes small. The POM picture of the neat BCP is given in Figure 4.10(a). A Maltese cross birefringence pattern was observed for BCP with an even shape and distinct boundaries. On the other hand, the blends exhibit a smaller amount of even spherulitic pattern.

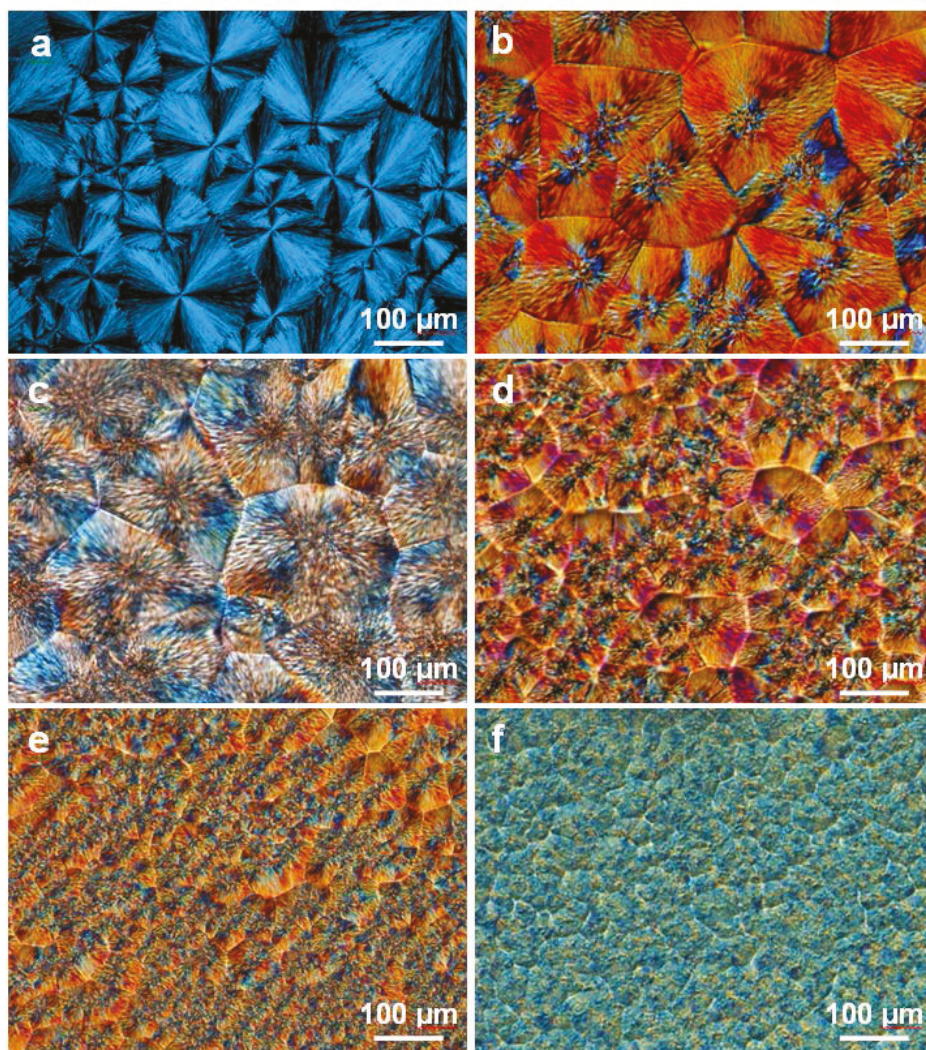


Figure 4.10 POM images of different PEO-*b*-PCL/PVPh blends at room temperature; (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40, and (f) 50/50 PEO-*b*-PCL/PVPh.

This is because the region in the blend comprising PVPh and the amorphous phases of PEO/PCL can interfere in the spherulite formation and merged with the lamellae during crystal formation process. This in turn interrupts the radial alignment and the lamellar region finally coarsens.²⁵ Figure 4.10(b) shows the spherulite morphology of 10 wt% PVPh blends, where the spherulite appears quite different to that of PEO-*b*-PCL BCP. Apparently, PVPh significantly dampens the crystallization of PEO blocks due to stronger hydrogen bonding or miscibility, whereas PCL has no strong interactions at lower PVPh concentrations. As the content of PVPh reaches 60

wt% (not given), there is no indication of crystalline structure; this specifies the miscibility of PCL blocks with PVPh, which restricts PCL from crystallization in these compositions. The morphologies obtained from POM seem to be a result of changes in the hydrogen bonding interactions between PVPh/PEO and PVPh/PCL. The degree of crystallinity was found to be lowered in blends where both chains are crystallized, which was speculated to be due to crystallization of one component reducing crystallization of the other within the same molecule.²⁵ Furthermore, the presence of PVPh in the blends having high glass transition reduces the degree of crystallization of PEO and PCL, thereby reducing the spherulite growth.

4.4.3 Self-assembly and nanostructures in PEO-*b*-PCL/PVPh blends.

BCPs can self-assemble into a variety of ordered nanostructures due to microphase separation. This is driven by the enthalpy of demixing of the constituents of the BCP.³⁹ Since the BCPs have covalent bond between them, they have a general tendency to separate, which results in microphase separated structures. When a homopolymer is added to a di-BCP involving competitive hydrogen bonding, the less hydrogen bonded block is excluded from the homogeneous region due to the entropic penalty for conformational distortion.

Figure 4.11(a) displays the structure of double crystalline PEO-*b*-PCL BCP observed by TEM. The plain BCP shows an ordered cubic structure in which spherical PEO nanophases are arranged in cubic lattices. The morphology of the PEO-*b*-PCL changes after the addition of homopolymer. Blends containing 20 wt% PVPh exhibit hexagonal cylindrical morphology with size in the order of ~40 nm [Figure 4.11(b)]. Thus, it is obvious that the addition of PVPh can induce morphological transition in PEO-*b*-PCL selfassemblies. The nanostructures in blends was observed to change from hexagonal cylindrical to disordered bicontinuous phase as the PVPh concentration reaches 40 wt% [Figure 4.11(c)], which is a result of segregation of PCL blocks. At 60 wt% PVPh, the polymer blend adopts a miscible or near-homogeneous morphology with no evidence of phase separation, illustrated in Figure 4.11(d). As the content of PVPh is increasing further, the blends show completely homogeneous phase.

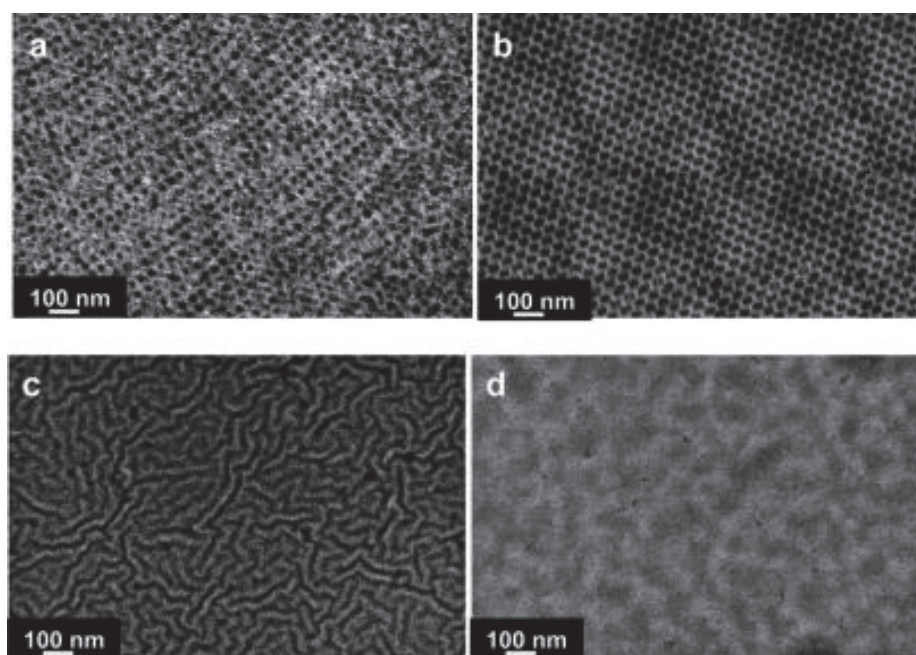


Figure 4.11 TEM micrographs of PEO-*b*-PCL/PVPh blends. (a) 100/0, (b) 80/20, (c) 60/40, and (d) 40/60; PEO-*b*-PCL/PVPh

The self-assembled morphology of PEO-*b*-PCL/PVPh blends was again studied using SAXS and the patterns are given in Figure 4.12. The microphase separated morphology of the blends is clearly seen in the SAXS profiles. It is evident that the PEO-*b*-PCL BCP exhibits a scattering profile characteristic of ordered cubic phase having period of 35 nm represents the distance between adjacent PEO and PCL microdomains. The SAXS peaks of the BCP at q values of $1: \sqrt{3}: \sqrt{6}: \sqrt{9}: \sqrt{16}$ relative to q^* are apparent. This can be attributed to the scattering of spheres (or cylinders) dispersed in cubical lattice for example BCC, FCC or simple cubic. Moreover, the cubic morphology of the pure BCP was already revealed in TEM observations. The 20 wt% PVPh blend shows a well ordered hexagonally packed cylindrical profile ($q/q^* = 1: \sqrt{3}: \sqrt{4}: \sqrt{7}: \sqrt{12}$) and is also in consistent with the TEM images. The blends with 40 wt% PVPh give broad peaks, and the broadening of the peak indicates the deterioration of long-range ordered structures. The average spacing between the neighboring micro domains is 38, and 41 nm for 20, and 40 wt% PVPh blends, respectively. This result shows that there is a systematic increase in the size of the phase

separated domain which implies the progressive incorporation of PVPh. Above 40wt% PVPh, the blends show only weak and broad peaks indicating a near-homogeneous morphology as observed in 60 and 80wt% PVPh blends in Figure 4.12.

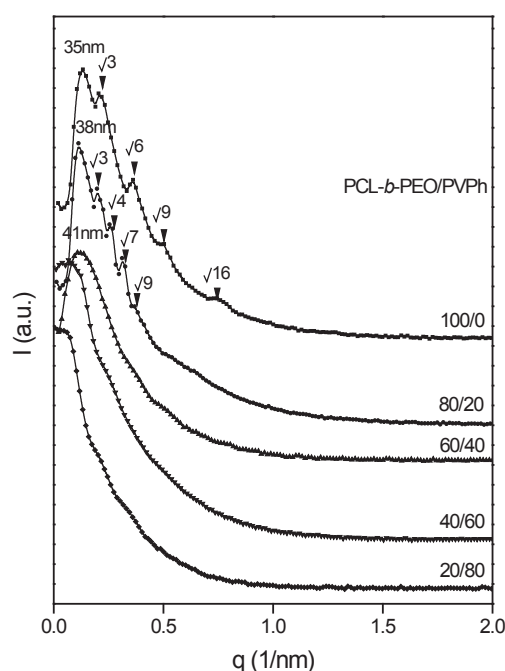


Figure 4.12 SAXS profiles of PEO-*b*-PCL/PVPh blends at room temperature.

Figure 4.13 displays the SAXS measurements of the blends performed at 100 °C. At 100 °C, where both PCL and PEO blocks are amorphous, broad scattering peaks are observed, indicating that there are no ordered structures; i.e., neither crystalline lamellae nor ordered microphases existed in the melts. Therefore PVPh can be located in both the PEO and PCL domains. Moreover, an ordered-to-disordered transition of the microphase morphology took place upon heating, and the order-disorder transition temperature is lower than 100 °C. This is revealed by disappearance of the ordered cubic phase for the pure BCP and the hexagonal cylindrical morphology for the blend with 20 wt% PVPh. The blends all display disordered microphase morphology at 100 °C. It is observed in Figure 4.13 that the primary scattering peak of all the blends moves to higher q -values with broadening of some peaks which indicating a reduction in the domains distance.

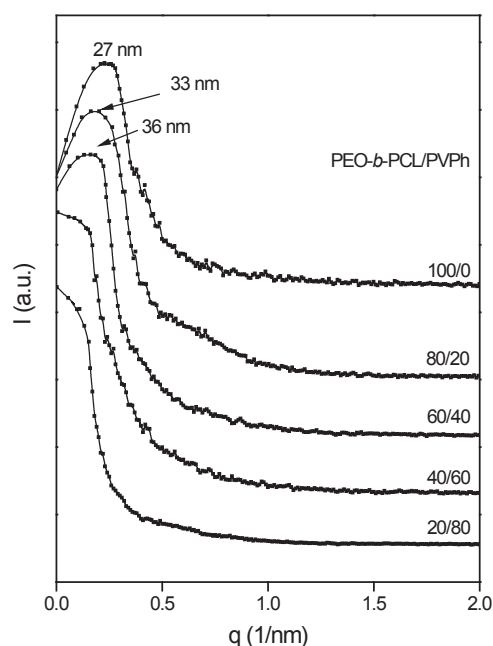


Figure 4.13 SAXS profiles of PEO-*b*-PCL/PVPh blends at 100 °C.

4.4.4 Mechanism of microphase separation.

The formation of nanostructures in PEO-*b*-PCL/PVPh blends at various compositions is schematically summarized in Figure 4.14. The blends include an immiscible BCP PEO-*b*-PCL and a homopolymer PVPh, which is miscible with both PEO and PCL blocks depending on the concentration. The pure di-BCP exhibits a cubic structure. The BCPs have the general tendency to separate. They exhibit amphiphilic characteristic which is caused by the restriction due to the presence of a covalent bond between the chemically different blocks, resulting in microphase separated structures.

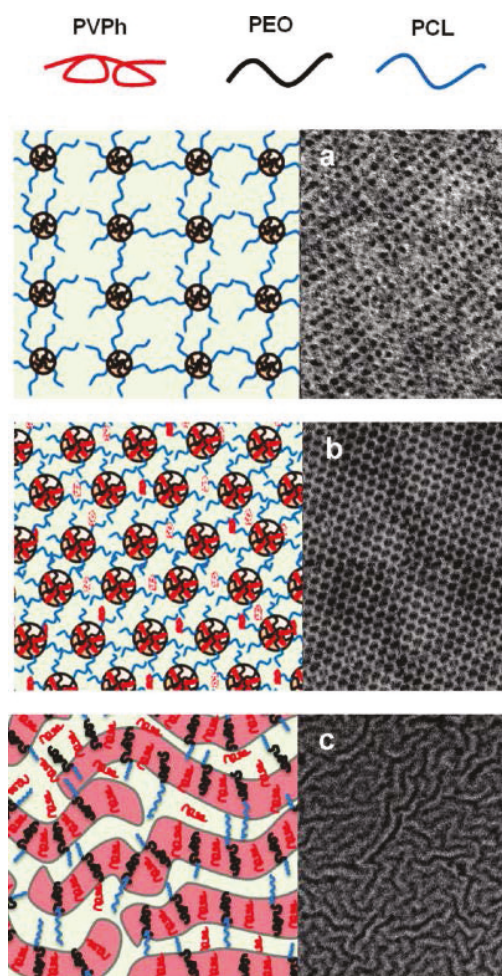


Figure 4.14 Schematic representation of phase morphologies in PEO-*b*-PCL/PVPh blends: (a) Cubical micelles of PEO-*b*-PCL BCP, (b) hexagonal cylindrical micelles at 20 wt% PVPh concentration, and (c) disordered lamellae at 40 wt% PVPh concentration.

The 20 wt% PVPh blends show a cylindrical morphology. At 20 wt%, the added PVPh and PEO interact very strongly, whereas PCL blocks, which are repelled by PEO, have a weak association with PVPh. The added PVPh which strongly hydrogen bonded with PEO form PVPh/PEO single phase cylinders inside, whereas the weakly interacting PVPh/PCL phase separates, as shown in Figure 4.14(b). At very low concentration, PVPh selectively interacts only with PEO. For the pure BCP, which is originally in the cubical phase, the addition of PVPh is thus expected to induce structural transformations, in analogy with BCP selective solvent systems.³² In 40 wt% PVPh blends, the concentration of

homopolymer, as well as PVPh/PEO single phase, increases, whereas PCL also forms hydrogen bonds with PVPh. This competitive hydrogen bonding destroys the ordered structure of the BCP. This leads to the decrease in the interfacial area, which results in the planar interfaces and thereby the formation of disordered bicontinuous phase, as shown in Figure 4.14(c). At 60 wt% or above PVPh blends, more PCL forms hydrogen bonds with PVPh, or in other words, both BCP blocks are miscible with PVPh to form homogeneous morphology. At high PVPh contents, hydrogen bonding interactions with PCL also occurs because extra free hydroxyl groups are available for bonding which finally results in homogeneous morphology. Here, hydrogen bonds clearly form the dominant interaction in the blend where PVPh/PEO hydrogen bonds are found to be stronger than PVPh/PVPh and PVPh/PCL hydrogen bonds.

The hydrogen bonding interactions in PEO-*b*-PCL/PVPh blends are detailed in this study. Here, the value of χ_{AB} is positive, and χ_{AC} and χ_{BC} are negative, but χ_{AC} is more negative than χ_{BC} . The variation in morphologies in PEO-*b*-PCL/PVPh blends is affected by two factors: (1) intermolecular interaction between PVPh and PEO is stronger than that between PVPh and PCL, which indicates the existence of competitive hydrogen bonding, and (2) formation of a homogeneous phase of PVPh/PEO excludes the microdomains of weakly interacted PCL. So the geometry of the structures formed in the blends is decided by the competition among PEO and PCL blocks in regards to hydrogen bonding with PVPh. Moreover, it is also established that adding a homopolymer to a BCP can alter the microphase structure.

4.5 Conclusions

The microphase separation facilitated by competitive hydrogen bonding in PEO-*b*-PCL/PVPh double crystalline di-BCP/homopolymer blends was investigated. The hydroxyl groups of PVPh can selectively interact with both PEO-ether and PCL-carbonyl, which results in the development of composition-dependent nanostructures in these blends. The disparity of weakly associated PVPh/PCL pairs and strongly associated PVPh/PEO pairs results in microphase separation and the formation of cubic, hexagonal cylindrical morphologies at lower PVPh concentrations. The PVPh acts like a common-

solvent for both blocks at higher concentrations which results in disordered and homogeneous blends at high PVPh contents. The formation of various composition-dependent microphase-separated morphologies in the PEO-*b*-PCL/PVPh blends can be explained on the basis of relative strength of interactions among different pairs in the system.

4.6 References

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Microphase Separation Induced by Competitive Hydrogen Bonding Interactions in Semicrystalline Triblock Copolymer/Homopolymer Complexes

5.1 Abstract

In this study, we have investigated that self-assembled nanostructures can be obtained in the bulk by the complexation of a semicrystalline SVPEO tri-BCP with a PVPh homopolymer in THF. In these complexes, microphase separation takes place due to the disparity in intermolecular interactions; specifically PVPh and P4VP blocks interact strongly compared to PVPh and PEO. At low PVPh concentrations, PEO interacts relatively weak with PVPh, whereas in the complexes containing more than 30 wt% PVPh, PEO block began to interact considerably with PVPh, leading to the formation of composition-dependent morphologies. SAXS and TEM results indicate that the cylindrical morphology of SVPEO BCP changes in to twisted lamellae structures at 20 wt% of PVPh then to disordered bicontinuous phase with 40 wt% PVPh. Wormlike structures were obtained in the complex with 50 wt% PVPh, followed by spherical microdomains with the size range of 40-50 nm in the complexes with 60-80 wt% PVPh. Also when the content of PVPh increases to 80 wt%, the complexes show a completely homogenous phase of PVPh/P4VP and PVPh/PEO with phase separated spherical PS domains. Moreover, we have examined the fractional crystallization behaviour in SVPEO and complexes with lower PVPh content. A structural model was proposed to explain the microphase separation and self-assembled morphologies of these polymer complexes according to the experiment results. The formation of nanostructures and changes in morphologies depend on the relative strength of hydrogen bonding interaction between each block of the BCP and the homopolymer.

5.2 Introduction

BCPs belong to the category of soft materials and they can self-assemble to form various nanostructures.¹ The repulsive and attractive interactions within and between the blocks as well as their covalent linkage are the driving force for producing self-assembled nanostructures. In di-BCP, the microphase behaviour is governed by two factors: χ and N . When the values of χN exceed a critical value, the BCPs microphase separates into a periodically ordered structure with a length scale varying from a few nanometers to several hundred nanometers. Blending of BCP with a homopolymer is a convenient technique that offers rich variety of self-organized nanostructures with diverse applications.²⁻⁶ There are many theoretical as well as experimental analyses investigated extensively regarding the microphase separation in BCP/homopolymer systems.^{7,8} Unlike di-BCP, the microphase separation in ABC tri-BCPs results in a rich variety of nanostructures because of the three different components A, B and C. Tri-BCP systems have revealed a wide range of well-ordered complex micro domain morphologies.^{9,10} In ABC tri-BCPs with one or more crystallizable block, a much more complex behaviour can be expected because of the crystallization process which, either disturb an already organized structure and microphase separation, or induce a transition between two different morphologies.¹¹

In recent years, more attention has focused on blending BCPs of different compositions or adding homopolymer to a BCP involving secondary interactions, though there were a few reports which have dealt with the influence of association on nanophase separated structures. In many polymer blends, hydrogen bonding is an important secondary interaction, where the strength of this interaction depends on the relative affinities between hydrogen bond acceptors and donors.¹² When the hydrogen bonding interaction among polymers is strong, a miscible polymer blend can be formed. And, if the interaction is sufficiently strong i.e., polymer-polymer interaction prevails over the polymer-solvent interaction, the two polymers co-precipitate to form highly associated mixtures known as polymer complexes. Very recently, Guo et al.¹³⁻¹⁶ and Chang et al.¹⁷⁻¹⁹ have reported a facile way for the self-assembly of nanostructured BCP blends^{13,14,17-9} and complexes^{15,16} through competitive

hydrogen bonding interactions. The concept is based on the competition between different blocks of the BCP to form more than one kind of intermolecular interaction with the complimentary polymer in the complex. This important advance directs to a new strategy for the design of self-assembled nanostructures for diverse applications.

In this study, for the first time we have investigated the microphase separation induced by competitive hydrogen bonding in self-assembled semicrystalline tri-BCP/homopolymer complexes in THF. The self-assembly, hydrogen bonding interaction, phase behaviour and crystallization of SVPEO/PVPh complexes have been studied. The tri-BCP ABC is immiscible and the homopolymer D can interact with both B and C blocks, but unequally due to the competitive hydrogen bonding interaction between the B/D and C/D pairs, while the A block has no interactions with D and gets phase separated in the entire compositions. Here χ_{AB} and χ_{BC} are positive, but the value of χ_{BD} and χ_{CD} are negative, however the value of χ_{BD} is more negative than χ_{CD} . There is an unequal hydrogen bonding interactions of PVPh with both P4VP and PEO, whereas, the unreacted PS phase separated which altogether leads to form various nanostructures in PVPh/SVPEO complexes. The strength of hydrogen bonding interaction between PVPh/P4VP, PVPh/PEO pairs and self-associated PVPh/PVPh leads to the nanoscale organization of the complexes via competitive distribution of PVPh chains in the SVPEO BCP. This will further enhance the miscibility of the blocks; facilitate the phase separation which in turn affects the properties of the complexes. The phase behaviour of the complexes is correlated with the results obtained from SAXS and TEM. This work, for the first time, demonstrates how the competitive hydrogen bonding determines the self-assembly and causes morphological transitions in ABC/D tri-BCP/homopolymer complexes.

5.3 Experimental section

5.3.1 Materials and preparation of samples

PVPh with an average $M_w = 20,000$ and $M_w/M_n = 1.70$, was a product of Aldrich Chemical Company. The tri-BCP, SVPEO was purchased from Polymer Source Inc., with $M_n(PS) = 60,000$, $M_n(P4VP) = 32,000$, $M_n(PEO) =$

39,500 and $M_w/M_n = 1.2$. All these polymers were used as received. The complexes of PVPh/SVPEO were prepared by solution mixing. THF solution containing 1% (w/v) of the individual polymers were mixed and stirred well until the complexes were precipitated. The solvent was allowed to evaporate slowly at room temperature. The complexes were dried under vacuum for 72 h before the measurements in order to reach equilibrium.

5.3.2 FTIR spectroscopy

Infrared measurements were obtained from a Bruker Vetex-70 FTIR spectrometer and 32 scans were recorded with a resolution of 4 cm^{-1} . Thin films of the blends were cast from THF solution onto KBr pellets and dried under vacuum at $80\text{ }^{\circ}\text{C}$ to completely remove the solvent and then allowed to cool to room temperature.

5.3.3 DSC

The glass transition temperatures of the complexes were determined by a TA Q200 differential scanning calorimeter using 5–10 mg of the sample under nitrogen atmosphere. A heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ was employed. All the samples were first heated to $150\text{ }^{\circ}\text{C}$ and kept at that temperature for 3 min; subsequently cooled to $-70\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$, held for 5 min, and heating continued from -70 to $200\text{ }^{\circ}\text{C}$. The midpoints of the second heating scan of the plot were taken as the glass transition temperatures (T_g).

5.3.4 SAXS

The SAXS measurements were taken on a Bruker NanoStar 3 pin-hole instrument using $\text{Cu K}\alpha$ radiation ($\lambda=1.54\text{ \AA}$, wavelength). Annealed samples having 1mm thickness were prepared for SAXS measurements. The intensity profiles were interpreted as the plot of scattering intensity (I) versus scattering vector, $q = (4/\lambda) \sin (\theta/2)$ (θ = scattering angle).

5.3.5 TEM

TEM experiments were performed on a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 100 kV. The samples were

cut into ultrathin sections of approximately 70 nm thickness at room temperature with a diamond knife using a Leica EM UC6 ultra microtome machine. The bulk samples were annealed at 180 °C for about 72 hrs before microtoming. The thin sections were stained by ruthenium tetroxide (RuO₄) before TEM observation.

5.4 Results and discussion

5.4.1 Hydrogen bonding interactions

FTIR spectroscopy is an excellent tool for providing information on specific interaction between various components in PVPh/SVPEO complexes by detecting hydroxyl, pyridine and ether regions.²⁰⁻²² Figure 5.1 shows the possible hydrogen bonding interaction in the PVPh/SVPEO complexes.

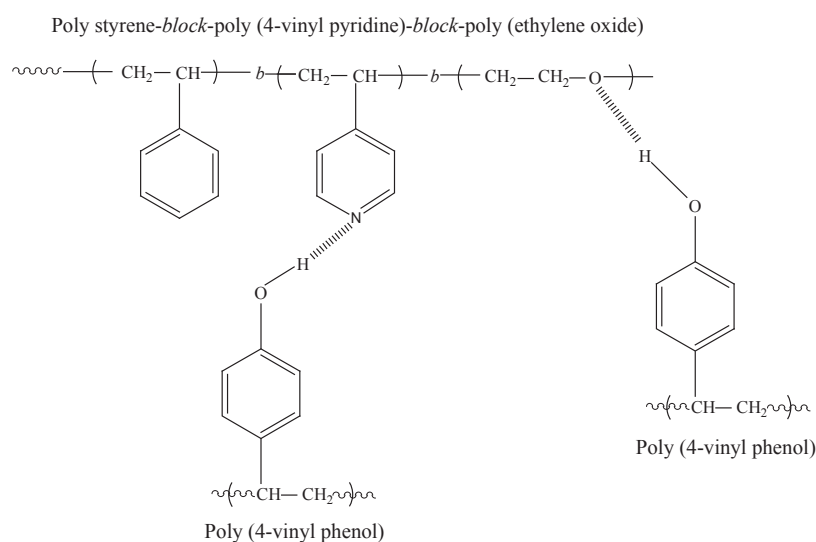


Figure 5.1 Schematic representation of possible hydrogen bonding interactions between SVPEO tri-BCP and PVPh homopolymer.

The hydroxyl stretching region in the infrared spectra of PVPh/SVPEO complexes is given in Figure 5.2. It can be noticed that the hydroxyl region of pure PVPh consists of two bands; the absorption at 3354 cm⁻¹ represents the self-associated hydroxyl groups. The other absorption at 3525 cm⁻¹ featured the free hydroxyl groups.²³ In this figure the free hydroxyl absorption band observed as a shoulder indicating that relatively smaller amount of free

hydroxyl groups compared with the extensively distributed self-associated ones. When the SVPEO complexed with PVPh, the intensity of the free hydroxyl decreases and ultimately vanishes. But the 3354 cm^{-1} region shifts to a low wavenumber area with increasing SVPEO concentration. The absorption of 20 wt% PVPh at 3159 cm^{-1} is corresponding to the hydrogen bonding of PVPh with P4VP and/or PEO blocks of SVPEO.

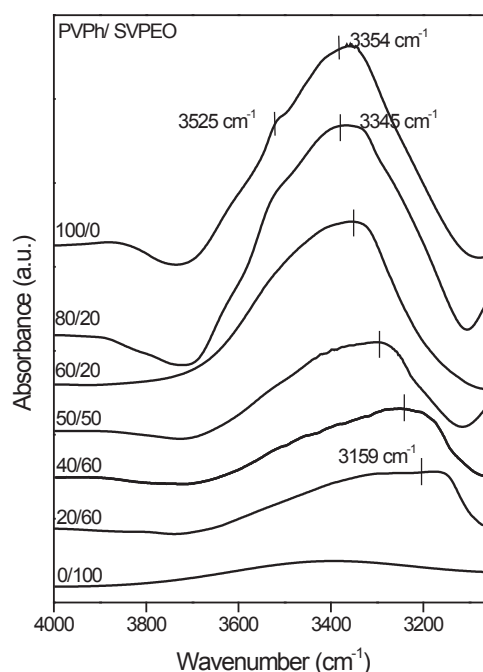


Figure 5.2 The hydroxyl region of PVPh/SVPEO complexes in the infrared spectra observed at room temperature.

Coleman et al²⁴ have explained the average strength of the hydrogen bonding ($\Delta\nu$) between the free hydroxyl region and those of the hydrogen bonded species in polymer blends. Table 5.1 summarizes the $\Delta\nu$ values of the complexes and the results imply that hydrogen bonding strength of PVPh/SVPEO complexes is in-between the values for PVPh/P4VP and PVPh/PEO binary systems. By analysing $\Delta\nu$ values, it can be observed that the average strength of interaction between PVPh and PEO is less than that occurring between PVPh and P4VP, which reflects that both these blocks can interact with PVPh, but with unequal strengths.

System	$\Delta\nu$
PVPh	171
PVPh/P4VP	400 ¹
PVPh/P2VP	390 ²
PVPh/SVPEO	366
PVPh/PEO	325 ³

¹Ref. 25, ²Ref. 26, ³Ref. 24

Table 5.1 Wavenumber shift of hydroxyl region in PVPh/SVEPO complexes containing PVPh.

The hydrogen bonding interactions between PVPh and P4VP can be identified by examining the pyridine region in the spectra of the complexes. The characteristics bands of pyridine ring at 1590, 1050, 993, and 625 cm^{-1} are sensitive to hydrogen-bonding interaction.^{26,27} However, the bands at 1590 cm^{-1} for P4VP are difficult to analyse as it overlaps with the band of PVPh (1600 cm^{-1} region). Therefore the absorption at 993 cm^{-1} is taken to detect the presence of hydrogen bonding between the PVPh hydroxyl group and P4VP pyridine group. FTIR spectra in the range of 1030-960 cm^{-1} of PVPh/SVPEO complexes with different compositions are plotted in Figure 5.3. The bands at 993 and 1013 cm^{-1} represent the aryl CH bending of pure pyridine ring and PVPh phenol ring. Another band observed in the complexes at 1005 cm^{-1} is attributed to the hydrogen-bonding interaction between pyridine ring of P4VP and phenol group of PVPh. The spectral changes in both wave number regions suggest that strong hydrogen bonding interaction exist between pendant pyridine groups of P4VP and phenol group of PVPh in all the complex compositions. This interaction is very significant in the formation of a stable complex.

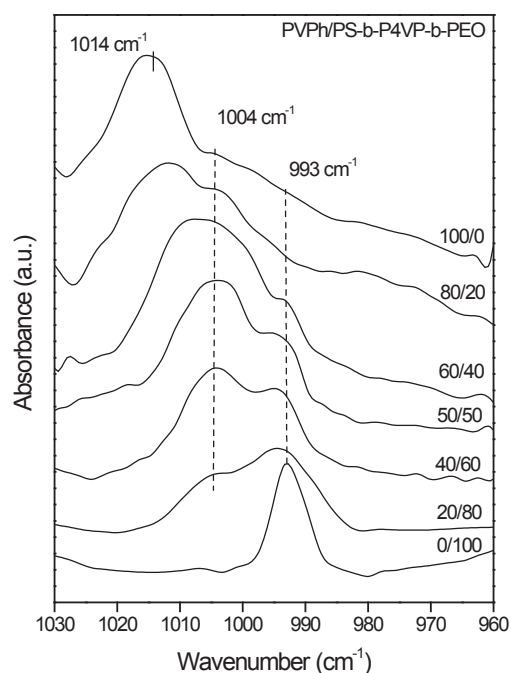


Figure 5.3 The FTIR spectra corresponding to the pyridine region of PVPh/SVPEO complexes at room temperature.

Figure 5.4 represents the FTIR spectra of CH_2 wagging region of PEO in SVEPO and its complexes with PVPh ranging from 1380 to 1320 cm^{-1} . PEO shows two absorption regions corresponds to crystalline-phase at 1360 and 1343 cm^{-1} .²⁸ As the PVPh concentration in the complexes increases, these bands are substituted with another band around 1350 cm^{-1} which represents the amorphous-phase, which suggests a retardation of PEO crystallization by the addition of PVPh. From Figure 5.4 it can be seen that the retardation of PEO crystallization peaks begins in complexes with 40 wt% of PVPh. That means a considerably strong interaction between PVPh and PEO starts when the PVPh concentration is ~ 40 wt%. Therefore it can be assumed that PEO ether groups have only weak interaction with PVPh hydroxyl groups at concentrations below 40 wt% of PVPh. This is due to the strong hydrogen bonding interaction between pyridine groups of P4VP with all the available hydroxyl groups of PVPh at low PVPh concentrations.

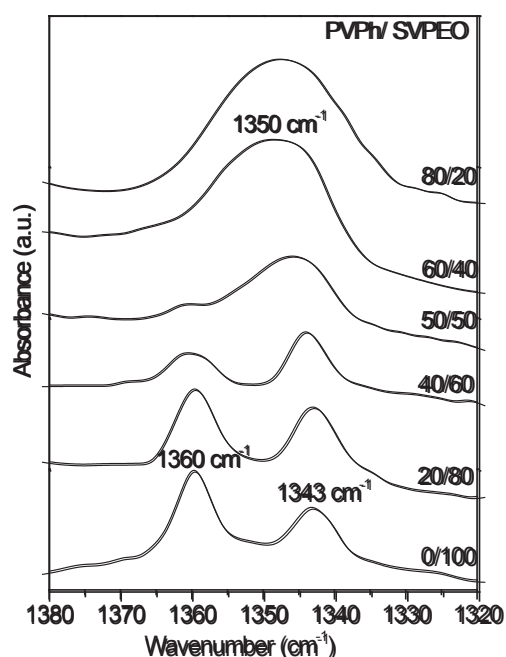


Figure 5.4 Ether region of PVPh/SVPEO complexes at room temperature

5.4.2 Phase behaviour

Figure 5.5 and 5.6 show DSC heating as well as cooling thermograms of neat BCP and their complexes with PVPh. Pure PVPh show a T_g at 164 °C whereas BCP exhibit two distinct T_g s at 107 °C, and 150 °C corresponding to immiscible PS and P4VP blocks. The T_g of PEO block could not be observed under the current experimental conditions. The melting temperature (T_m) of the PEO block can be observed at 50 °C. There is no change in the T_g of PS blocks since they have no interactions with PVPh at entire compositions. It is already proven that the binary complexes of PVPh/P4VP²⁹ and PVPh/PEO³⁰ form homogenous blend at all compositions due to the intermolecular hydrogen bonding interactions. In PVPh/SVPEO complexes, since PVPh is miscible with P4VP blocks, a single T_g was detected. Figure 5.5 shows the T_g of P4VP/PVPh phase is substantially higher than the T_g of P4VP at lower PVPh content (20 wt% PVPh complexes). This positive deviation is due to the formation of strong intermolecular interactions between P4VP/PVPh which enhances the mixing free energy and thereby from miscible blends. Above 40 wt% of PVPh,

there is a reduction in the T_g value of the complexes which is due to the considerable miscibility of PEO blocks with PVPh at these compositions.

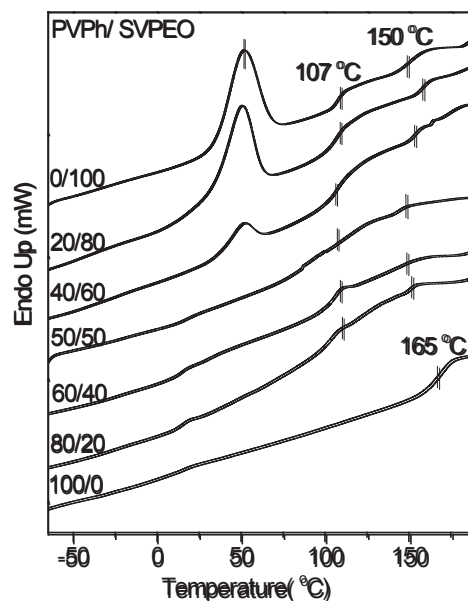


Figure 5.5 DSC thermograms of the second scan of PVPh/SVPEO complexes.

The reductions of melting temperature of the crystalline components in the mixtures provide major information regarding miscibility and intermolecular interaction behaviour. Figure 5.5 illustrates all the thermal transition temperatures of the heating scan of the PVPh/SVPEO complexes. The crystalline PEO component in SVPEO shows a melting temperature at 50 °C. It is clearly displayed that the T_m of PEO blocks in PVPh/SVPEO complexes remains almost unchanged with very low PVPh concentration. This implies a weak interaction between PEO/PVPh pair at low PVPh content. There is a decrease in intensity and final vanishing of T_m observed at 30-40 wt% PVPh complexes. This is due to the miscibility of PEO with PVPh at higher PVPh contents. The intensity of melting peak decreases at 30-40 wt% PVPh complexes and are unable to see at higher PVPh contents which is due to the miscibility of PEO with PVPh at higher PVPh contents.

Figure 5.6 shows the conventional cooling scan of PVPh/SVPEO complexes. The crystalline peaks of pure SVPEO and PVPh/SVPEO

complexes show a remarkable example of fractionated crystallization with increase of PVPh content. The existence of more than one crystallization exotherm is termed as fractionated crystallization.^{31,32} This behaviour was previously observed in other semicrystalline BCPs.³³⁻³⁵ Fractionated crystallization of a pure BCP takes place either due to morphological heterogeneity i.e., heterogeneous-nucleation and homogeneous-nucleation or a slow crystallization rate. Usually, homogeneous-nucleation is observed in confined or unconnected crystalline domains and that preserves the spherulite morphology. However in connected domains, heterogeneous-nucleation takes place and form mixed morphologies. The peak of the crystallization exotherm is termed as T_f . In pure SVPEO BCP, at low cooling rate, a large part of the PEO block crystallizes at 40 °C whereas a minor fraction of the PEO can only crystallize at much lower temperatures (30 °C and below). In such cases fractionated crystallization results in a lamellar morphology, where the PEO is dispersed into droplets in an immiscible matrix.^{36,37} The exotherm at -27 °C can be explained as the crystallization of the PEO block originated from the homogeneous nucleation.

The fractionated crystallization behaviour can also be observed in PVPh/SVPEO complexes up to 40 wt% of PVPh. From FTIR analyses it was confirmed that PVPh interacts weakly with PEO compared to the strong interaction between PVPh and P4VP. Therefore the appearance of two exotherms can be explained by two different crystallization behaviour of PEO domains within the PVPh/P4VP mixed phase. The high temperature exotherm is from first crystallization process due to heterogeneous nucleation of the continuous domains and the low temperature exotherm is produced by the homogeneous nucleation (non-connecting) PEO domains in PVPh/P4VP mixed phase.

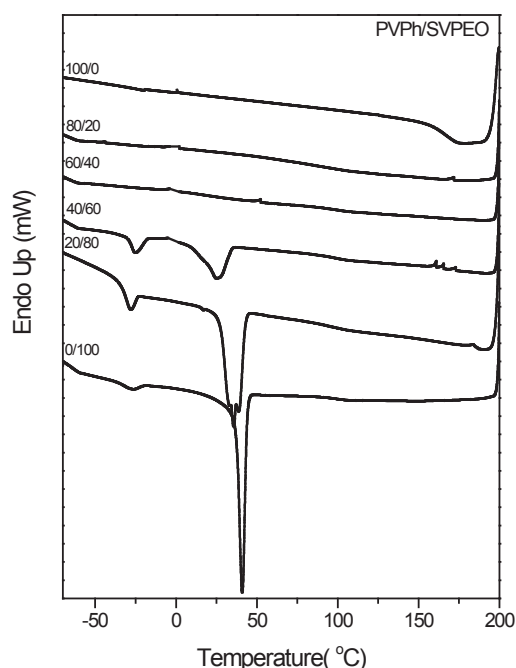


Figure 5.6 Crystallization curves of PVPh/SVPEO complexes during cooling.

5.4.3 Nanostructured morphology of PVPh/SVPEO complexes

The morphologies of PVPh/SVPEO complexes were investigated by SAXS and their profiles are shown in Figure 5.7. For pure BCP, the first scattering (q^*) has a Bragg spacing of 35 nm. The scattering peak positions of SVEPO in the SAXS profile indicate cylindrical profile, situated at q values of $1: \sqrt{3}: \sqrt{4}: \sqrt{7}...$ (where q^* denotes the position of the first-order scattering maximum).³⁸ The complexes with 10-40 wt% of PVPh show multiple scattering peaks, denotes that they possess long-range ordered nanostructures to some extent. The SAXS profile of 20 wt% PVPh complex situated at q values of $1: 2: 3$ relative to q^* are apparent, which are characteristics of twisted lamellae. At 40 wt% PVPh, complexes show another small peak around 2 and 3, respectively, owing to the incomplete disordering of the twisted lamellae present in the complexes and the average spacing between the neighboring micro domains is 51 nm. Complexes with high content of PVPh exhibit disordered structures, which are revealed by the disappearance of higher order reflections in the SAXS profiles. This result shows that there is a systematic increase in the size of the phase separated domain with the progressive

incorporation of PVPh. Above 40 wt% PVPh, the complexes show only weak and broad peaks and display a disordered morphology as observed in 60 and 80 wt% PVPh complexes in later part of this paper [Figure 5.8(e, f)]

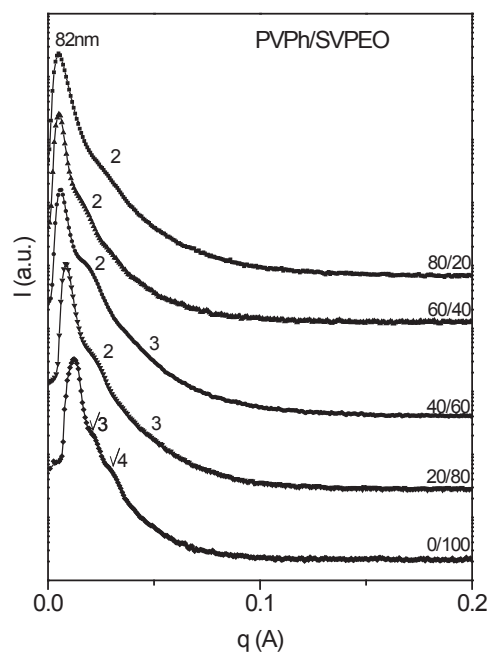


Figure 5.7 SAXS profiles of PVPh/SVPEO complexes.

TEM examination provided further insight into the morphology of PVPh/SVPEO complexes. Based on the electron density of various groups, PS, P4VP, PVPh and PEO appear as deep, intermediate, light, and very-light contrasts when stained with RuO_4 . The morphological transformations of PVPh/SVPEO complexes with 20 to 80 wt% of PVPh compositions are given in Figure 5.8. It is seen that all the complexes exhibit heterogeneous morphology at the nanoscale.

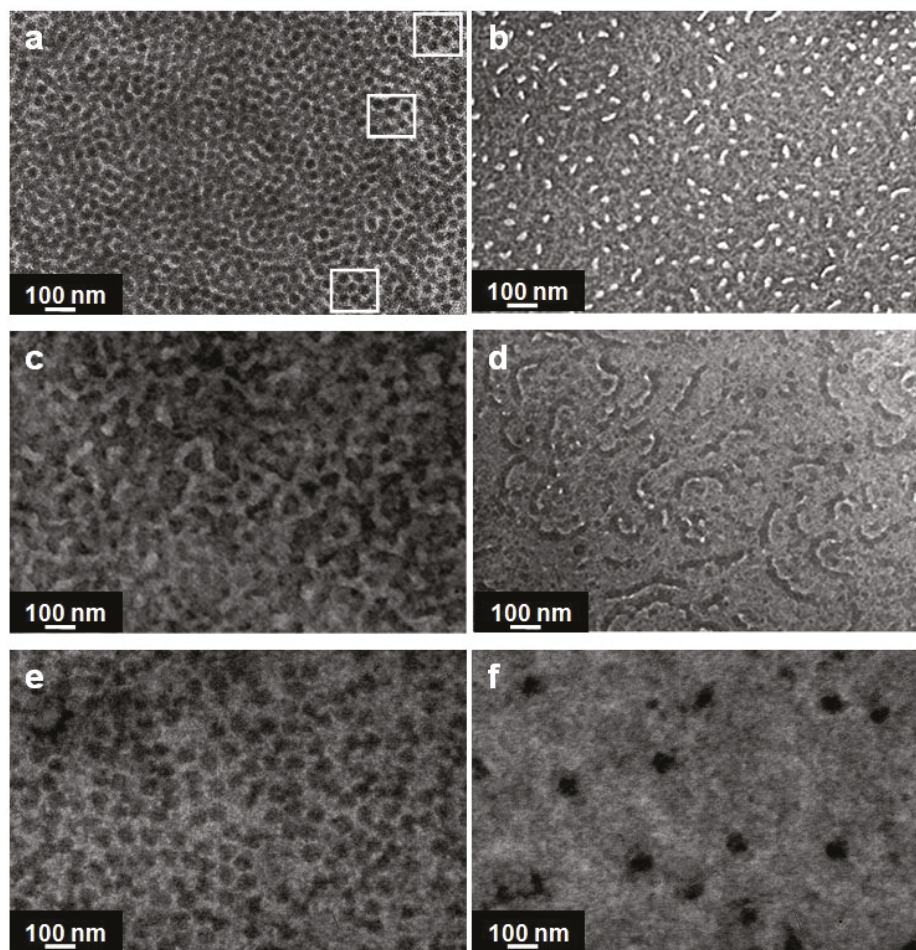


Figure 5.8 TEM micrographs of PVPh/SVPEO complexes. (a) 0/100, (b) 20/80, (c) 40/60, (d) 50/50, (e) 60/40, and (f) 80/20 PVPh/SVPEO.

The pure BCP shows a cylindrical morphology [Figure 5.8(a)]. In fact, a pseudo “hexagonally packed cylinders” was observed for the SVPEO BCP, where some percolated microdomains coexist with this cylindrical structure in some areas [inset Figure 5.8(a)]. The SAXS experiments also prove the existence of cylindrical morphology in SVPEO BCP [Figure 5.7], though a lateral view of these cylinders was not observed by TEM. A similar cylindrical morphology has observed for PS-*b*-P2VP-*b*-PtBMA tri-BCP as reported by Liedel et al.³⁹

The 20 wt% PVPh complexes exhibit a twisted lamellar structure as shown in Figure 5.8(b). Here, the very dark region corresponds to PS and a mixed phase of PVPh and P4VP appears as grey and the PEO blocks appears as bright.⁴⁰ At this composition, the concentration of PVPh is very less compared

to the BCP. Hence the added PVPh strongly hydrogen bonded to P4VP and formed a single phase whereas the less-interacting PEO block, phase separates within the matrix as spherical or elongated microdomains [Figure 5.8(b)]. At 40 wt% PVPh complexes, PEO also forms hydrogen-bonding interaction with PVPh since a higher number of hydroxyl units are available even after strong interaction with P4VP. This induces a bicontinuous structure for 40 wt% PVPh complexes as shown in Figure 5.8(c). This competitive hydrogen bonding destroys the ordered structure of the system and leads to the decrease in the interfacial area, which results in the planar interfaces and thereby the formation of disordered bicontinuous phase. Further increasing the PVPh content to 50 wt%, the complexes adopt a highly disordered morphology with some wormlike structures dispersed in the matrix as given in Figure 5.8(d). The PVPh/SVPEO complexes containing 60 wt% PVPh display spherical nanostructures [Figure 5.8(e)]. Here, PS segments are dispersed in the hydrogen bonded PVPh/P4VP and PVPh/PEO matrix. As the content of PVPh increases to 80 wt%, the complexes show a completely homogenous phase of PVPh/P4VP and PVPh/PEO with phase separated spherical PS domains [Figure 5.8(f)]. Previously, Lee et al.,⁴¹ have investigated the miscibility and morphologies of P2VP-*b*-PEO/PVPh blends. No self-assembly was observed and the blends were homogenous at all compositions though the interactions between PVPh/P2VP and PVPh/PEO were different. The complete miscibility observed in this system was obviously due to the very low molecular weight of the blocks compared to the homopolymer. If the molecular weights of the homopolymer and each block were comparable or higher, self-assembled structures have been formed through competitive hydrogen bonding interactions.

5.4.4 Mechanism of microphase separation

The formation mechanism of different self-assembled nanostructures in PVPh/SVPEO complexes at different compositions is schematically shown in Figure 5.9. The complexes comprise an immiscible SVPEO tri-BCP and a homopolymer PVPh, which is miscible with both P4VP and PEO blocks depending on the concentration. Pure tri-BCP exhibited cylindrical

nanostructures as observed using TEM in Figure 5.9(a). Since the blocks in the tri-BCPs have the general tendency to separate, they exhibit amphiphilic characteristic which is caused by the restriction due to the presence of a covalent bond between the chemically different blocks, resulting in microphase separated structures. When a homopolymer is complexed with a tri-BCP, involving competitive hydrogen bonding interactions, the weakly hydrogen bonded block is excluded from the homogenous region due to the high entropic penalty for conformational distortion. Here, by addition of homopolymer, microphase separation takes place due to the self-assembly of the elementary BCP i.e.; it selectively swells the blocks due to the competitive hydrogen bonding which results in phase separation.

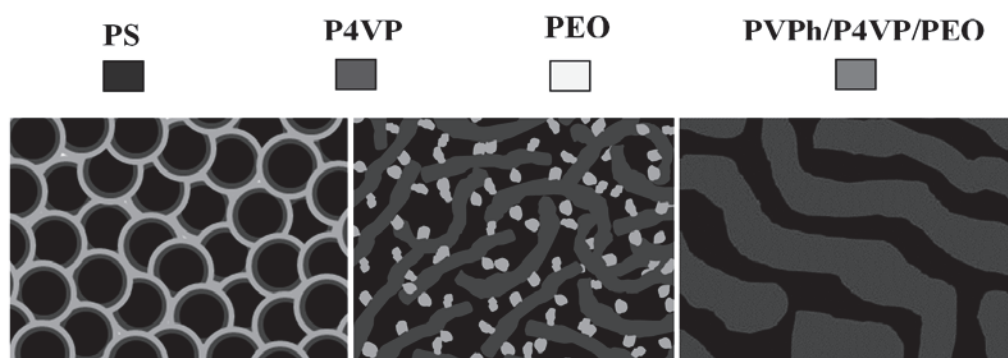


Figure 5.9 Schematic representation of phase morphologies in PVPh/SVPEO complexes: (a) cylindrical morphology of SVPEO tri-BCP, (b) twisted lamellae at 20 wt% PVPh concentration, and (c) bicontinuous phase at 40 wt% PVPh concentration.

In 20 wt% of PVPh complexes, twisted lamellae with an average diameter of 40-50 nm were obtained which is schematically shown in Figure 5.9(b). At 20 wt%, the added PVPh and P4VP interacts very strongly whereas PEO blocks, which are repelled by P4VP, have relatively weak hydrogen bonding with PVPh. In other words, PVPh acts as a selective amphiphilic solvent for the P4VP blocks of the SVPEO tri-BCP. Therefore the added PVPh form PVPh/P4VP single phase layers whereas the weakly interacting PEO phase separates as spherical or elongated microdomains. For the pure BCP, which is originally in the cylindrical phase, the addition of PVPh is thus expected to induce structural transformations, in analogy with BCP selective solvent

systems. As the concentration of PVPh increases again, the microphase morphology varies, displaying bicontinuous structure in 40 wt% PVPh complexes [Figure 5.9(c)], whereas matrix-dispersed wormlike morphology is obtained in 50 wt% of PVPh. As the concentration reaches 60-80 wt% PVPh, the interface between the PVPh/P4VP and PVPh/PEO microphases become less distinct. The interaction of PVPh between P4VP and PEO together with non-interacting PS blocks form spherical microdomains. The appearance of spherical morphology at high PVPh concentrations is due to the confinement of non-interacting PS blocks within the highly hydrogen bonded PVPh/P4VP and PVPh/PEO phases form the homogenous matrix. This is due to the hydrogen bonding interactions of PVPh with PEO along with P4VP because free hydroxyl groups are easily available. Or in other words PVPh behaves as the common-solvent for both P4VP and PEO polymer segments. The morphological variations of this system is shown to be influenced by the following factors; (1) intermolecular interaction between PVPh and P4VP is stronger than that between PVPh and PEO which indicates the existence of competitive hydrogen bonding, (2) strong interaction of PVPh/P4VP excludes microdomains of PEO at lower PVPh content, (3) formation of a homogenous phase of PVPh/P4VP and PVPh/PEO excludes microdomains of non-interacted PS at high PVPh content. So the geometry of the structures formed in the complexes is determined to a large extent by the competition between P4VP and PEO blocks in regards to hydrogen bonding with PVPh. Moreover it is also established that the addition of a homopolymer into to an ordered BCP will cause changes in the microdomain structure.

5.5 Conclusions

We have studied the microphase separation mediated by competitive hydrogen bonding in PVPh/SVPEO tri-BCP/homopolymer complexes. The hydroxyl groups of PVPh can selectively interact with both pyridine group of P4VP and ether groups of PEO and can form various nanostructures. The disparity of weakly associated PVPh/PEO pairs and strongly associated PVPh/P4VP pairs results in microphase separation and the formation of cylindrical, twisted lamellae, disordered bicontinuous and wormlike

morphologies at lower PVPh concentrations. At higher concentrations, PVPh acts like a common-solvent for P4VP and PEO blocks. That results in a homogeneous phase with PS as the only phase separated domain. The formation of various composition-dependent microphase separated morphologies in the PVPh/SVPEO complexes can be explained based on the relative strength of hydrogen bonding between the different pairs in the system.

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Multiple Vesicular Morphologies in AB/AC Diblock Copolymer Complexes through Hydrogen Bonding Interactions

6.1 Abstract

We report for the first time multiple vesicular morphologies in BCP complexes formed in aqueous media via hydrogen bonding interactions. A model AB/AC di-BCP system consisting of PS-*b*-PAA and PS-*b*-PEO was examined using TEM, SAXS and DLS. The complexation and morphological transitions were determined via the hydrogen bonding among PAA/PEO chains of two di-BCPs. Upon the addition of PS-*b*-PEO, a variety of bilayer aggregates were formed in PS-*b*-PAA/PS-*b*-PEO complexes including vesicles, MLVs, TWVs, ICCVs, and IAs. Among these aggregates, ICCVs were observed as a new morphology. The morphology of aggregates was correlated with respect to the molar ratio of PEO to PAA. At $[EO]/[AA] = 0.5$, vesicles were observed, while MLVs were obtained at $[EO]/[AA] = 1$. TWVs and ICCVs were formed at $[EO]/[AA] = 2$ and 6, respectively. When $[EO]/[AA]$ reached 8 and above, only irregular aggregates appeared. These findings suggest that complexation between two amphiphilic di-BCPs is a viable approach to prepare polymer vesicles in aqueous media.

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6.2 Introduction

The self-assembly of BCPs in aqueous solutions including micellization is of great interest due to their various possible applications.¹⁻⁷ By taking advantage of interpolymer complexation, it is possible to manipulate novel ordered and disordered nanostructures for diverse applications. Complexation between two polymers in solution can be driven by electrostatic interactions,⁸ hydrogen bonding,⁹ etc. As an important intermolecular interaction, hydrogen bonding plays a fundamental role to create a higher level of hierarchy in structure formation of BCPs.¹⁰ The moderate bonding energy of hydrogen bonds offers the flexibility for association and dissociation in the self-assembly process. Most of the studies so far reported have shown that the self-assembly of micelles via hydrogen bonding interactions are capable of forming hierarchical two-dimensional nanostructures.¹¹⁻¹³

Some complicated aggregate structures such as helical superstructures and multicompartiment micelles are reported by the self-assembling behaviour of tri and multi- BCPs in solvents.¹⁴ Self-assembly and formation of ordered nanostructures such as lamellar and gyroid morphology in BCP blends with hydrogen bonding interactions were investigated by Matsushita et al.¹⁵ and by Abetz et al.¹⁶ Chang et al. studied the self-assembled BCP mixtures in solution mediated by hydrogen bonding.¹⁷ Other authors have reported the micellization of two BCPs in solutions driven by hydrogen bonding interactions.¹⁸ The complexation of di-BCP mixtures reported previously cannot be strictly compared with our results for different polymer pairs because the molecular weights and concentration of polymers are different. We have recently reported the self-assembled BCP blends and complexes through competitive hydrogen bonding interactions between different BCP blocks and the homopolymer.¹⁹ These studies have shown that hydrogen bonding interactions are crucial in the self-assembling process of BCP blends and complexes and also in the formation of aggregate structures.

To date, little work has involved vesicles in di-BCP mixtures in solutions.²⁰ In the present study, the complexation and aggregate morphologies in a model AB/AC di-BCP system consisting of PS-*b*-PAA and PS-*b*-PEO in water was studied. Varying the relative amounts of the two BCPs, a range of

bilayer aggregates were formed, including vesicles, MLVs, TWVs, ICCVs, and IAs. The hydrophobic PS blocks were segregated as the cores while the hydrogen bonded PEO and PAA blocks formed the coronae of bilayer aggregates. We also investigate how the incorporation of PS-*b*-PEO into PS-*b*-PAA solutions influences the aggregate morphology of the resulting complexes. This work introduces a viable route to multicompartment vesicles in aqueous solutions. The formation of BCP vesicles in water is of particular importance due to their numerous applications.

6.3 Experimental section

6.3.1 Materials and preparation of complex aggregates.

The BCPs PS-*b*-PAA and PS-*b*-PEO were purchased from Polymer Source, Inc. The PS-*b*-PAA was with a $M_n(\text{PS}) = 61,000$, $M_n(\text{PAA}) = 4000$, and $M_w/M_n = 1.05$ while the PS-*b*-PEO had $M_n(\text{PS}) = 190,000$, $M_n(\text{PEO}) = 48,000$ and $M_w/M_n = 1.07$. The BCPs were first dissolved individually in DMF to prepare a 1% (w/v) of polymer mixture solution. Then PS-*b*-PEO/DMF mixture was added dropwise into the PS-*b*-PAA mixture to get a series of solutions with molar ratio ($[\text{EO}]/[\text{AA}]$) ranging from 0.5 to 12, i.e., corresponding to the weight ratio ($W_{\text{SEO}}/W_{\text{SAA}}$) ranging from 0.1 to 1.5. Then 3-6 wt% of deionized water was added into the mixture followed by stirring for 1 day to allow polymer chains for exchange. Finally, the mixture solution was quenched by adding extra water (25 wt%). This allows the kinetic freezing of morphology in the solution. Finally, dialyse the solution against deionized water for removing DMF. The solution was maintained at a particular pH (~ 4) to induce the hydrogen bonding among PAA and PEO blocks. This is because PAA is a weak polyanion, and its ionization degree is strongly pH-dependent, with a $\text{pK}_a \sim 5.6$. The hydrogen bonding complexation between PAA and PEO occurs only at low pH values.²⁰ At higher pH, the complexation-level is less because PAA ionizes in aqueous environment. The presence of opacity indicates the aggregation. The obtained complexes were used for further experiments.

In amphiphilic BCP systems, the aggregates are created by first solubilizing the BCP in a solvent appropriate for all polymer segments. The

non-solvent is then added that is good for one polymer-block and bad for the other one.²¹ This method was adopted in the preparation of the BCP complexes in this study. In PS-*b*-PAA/PS-*b*-PEO complexes, the hydrogen bonding interactions are relatively strong and interpolymer complexation may occur.²² Both the BCPs were first dissolved in DMF, which is the common solvent for all blocks used here. The complexes were made by adding excess H₂O dropwise into the polymer solution to kinetically freeze the morphology and stirred for 1 day. By this process a thermodynamically stable morphology can be obtained because the PS blocks are not in their glassy state. According to Eisenberg and co-workers,²¹ a thermodynamic equilibrium is operative in the beginning of complexation and aggregation of the BCP mixtures. It was suggested that the indirect way as employed here is a practical method to prepare equilibrium aggregates of copolymer in solution.²³ With increasing water, the solvent becomes bad for the core-forming PS block, the interfacial-tension increases, while the corona repulsion may not change much because both the solvents are very good for the corona forming PAA and PEO blocks. However, during the process of the core enlargement the stretching of polymer chains in the core enhances. This causes an increase in the component of the free energy that reflects core chain stretching. The aggregates change to another geometry when the stretching is too high, and therefore the total free energy is minimized. Overall, the morphological change of the aggregates is always in a direction that decreases the overall free energy, which is from vesicles to spheres in the present system.

6.3.2 FTIR spectroscopy.

Infrared spectra of P2VP-*b*-PMMA/phenoxy blends were obtained on a Bruker Vetex-70 FTIR spectrometer, and 32 scans were recorded with a resolution of 4 cm⁻¹. The spectra of all the samples were determined by using the conventional KBr disk method. The complex powder was mixed with KBr and powdered to form the disk. The samples were kept to dry in-vacuo for 72 hours before the experiments.

6.3.3 TEM

TEM analysis was carried out on a JEOL JEM- 2100 transmission electron microscope operating at an acceleration voltage of 100 kV. The sample solution was spread on a carbon coated TEM copper grid. After drying at room temperature, the samples were stained with ruthenium tetroxide (RuO₄).

6.3.4 SAXS

The SAXS experiments were performed on a Bruker NanoStar 3 pin-hole instrument with Cu K α radiation ($\lambda=1.54$ Å, wavelength). Annealed samples having 1mm thickness were prepared for SAXS measurements. The scattering profiles were interpreted as intensity (I) vs scattering vector, $q = (4/\lambda) \sin (\theta/2)$ (θ = scattering angle).

6.3.5 DLS

The hydrodynamic diameter of the complex aggregates was measured on a Zetasizer Nano instrument. The temperature stability inside DLS sample holder was controlled at 25 °C, and the measurements were carried out at detection angle of 173°. Solutions of 0.5% (w/v) complex aggregates in water/DMF were used. The scattering intensity autocorrelation functions were analyzed by using the methods of CONTIN and Cumulant, which are based on an inverse-Laplace transformation of data, this gives access to a size distribution histogram for the analysed complex solutions.

6.4 Results and discussion

6.4.1 Hydrogen bonding interactions.

The hydrogen bonding interactions of the complexes were examined using FTIR spectroscopy. The pH dependent micellization and hydrogen bonding interactions of BCP containing PAA segments was discussed in detail elsewhere.²⁴ For the present complexes two absorption bands, the C=O stretching near 1700 cm⁻¹ and the OH stretching near 3000-3500 cm⁻¹ are particularly sensitive to form bonds. Figure 6.1 shows the IR spectra of OH regions in PS-*b*-PAA/PS-*b*-PEO complexes. It can be noticed that the OH region of PAA shows a broad peak related to the overlapping elements at 3560 and 3172 cm⁻¹, respectively. These peaks correspond to the nonassociated OH

groups and self-associated OH groups of PAA.²⁴ When PS-*b*-PEO BCP is added, the free OH peak reduces in its intensity. On the other hand, hydrogen bonded peak moves toward low wavenumber area. This shift can be attributed to the intermolecular interaction among PAA/PEO pair that is stronger than the self-associated OH groups.²⁵

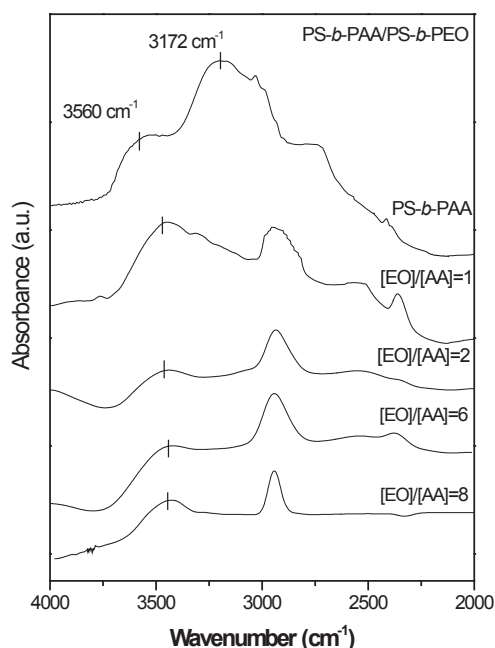


Figure 6.1 IR in the OH region of the complexes

The FTIR spectra of complexes in the range 1700-1750 cm^{-1} are shown in Figure 6.2. The absorption at 1710 cm^{-1} corresponding to its C=O stretching of PAA. Given the work of Coleman and Painter et al.,²⁶ the lower frequency region is corresponding (1710 cm^{-1}) to the intramolecular hydrogen bonding of PAA, where two carboxylic acid groups form a dimer and the higher frequency one (1724 cm^{-1}) is due to free C=O region. However, upon the addition of PS-*b*-PEO BCPs, the band associated with the intramolecular dimers decreases significantly, and the free C=O band increases in intensity. This indicates the release of C=O when bonds are generated among PEO ether and acid OH group.²⁶ There is a high level of hydrogen bonding interaction among PS-*b*-PAA and PS-*b*-PEO BCPs. Also, a band occurs at 1955 cm^{-1} in the complexes and its intensity grows when PEO concentration increases. This new band

region is an indication of strong hydrogen bonds, which is a satellite band of a hydrogen bonded OH group.²⁶

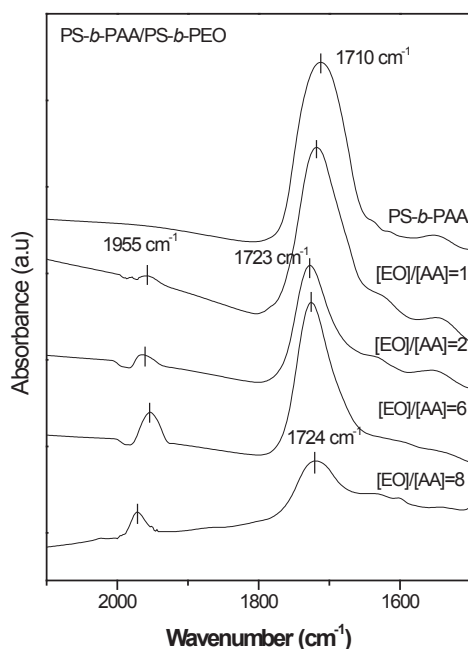
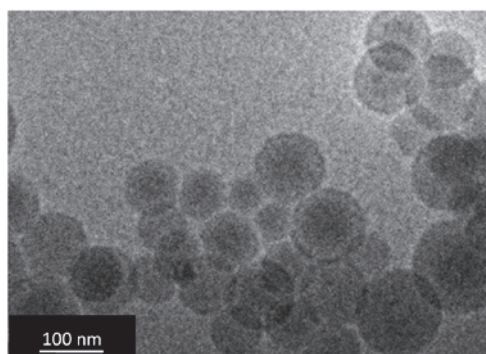


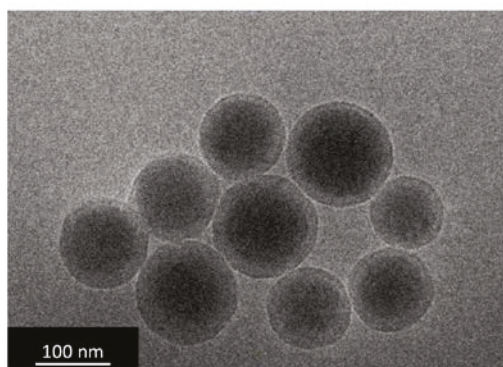
Figure 6.2 FTIR spectra of PS-*b*-PAA/PS-*b*-PEO complexes in the carbonyl region at room temperature.

6.4.2 Morphology of PS-*b*-PAA/PS-*b*-PEO complexes in water.

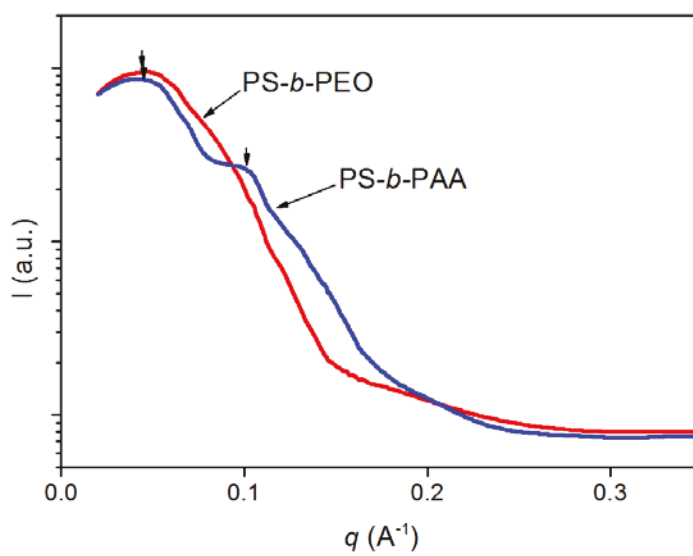
Various morphologies of complex BCP aggregates have been intensively investigated by Eisenberg and co-workers.²⁷ They detailed about the factors influencing the morphological transitions in BCPs such as BCP concentration, composition, solvent interaction, etc. In this study, a combination of micellization and interpolymer complexation is taking place in these BCP mixtures. A thermodynamic analysis of these combinations is usually difficult because they are composed of multiple components such as BCPs, common solvent, and selective solvent.



(a)



(b)



(c)

Figure 6.3 TEM images of (a) PS-*b*-PAA and (b) PS-*b*-PEO di-BCP. (c) SAXS patterns of PS-*b*-PAA and PS-*b*-PEO di-BCPs in aqueous solution.

TEM observation was performed with the complexes formed in water. It can be seen from the TEM images that PS-*b*-PAA BCP showed vesicular morphology [Figure 6.3(a)] whereas spherical micelles were observed for PS-*b*-PEO [Figure 6.3(b)]. The PS-*b*-PEO micelle comprises hydrophobic PS core surrounded by hydrophilic PEO corona [Figure 6.3(b)]. In PS-*b*-PAA vesicles, the PS blocks are pointed toward the center of the vesicle membrane and the PAA blocks toward the solvent [Figure 6.3(a)]. The vesicles can be identified by the high electron transmissions or the lighter areas in the middle of the structures than the boundary. The SAXS patterns of PS-*b*-PAA and PS-*b*-PEO are presented in Figure 6.3(c), distinguishably showing the scattering features of spheres and vesicles, respectively. The SAXS pattern of PS-*b*-PEO exhibits a broad scattering peak that is characteristic of spherical micelles. Meanwhile, a secondary scattering peak is observed for PS-*b*-PAA, indicative of vesicles. The DLS experiment was conducted to calculate the hydrodynamic sizes of the pure BCPs and the complexes in water.

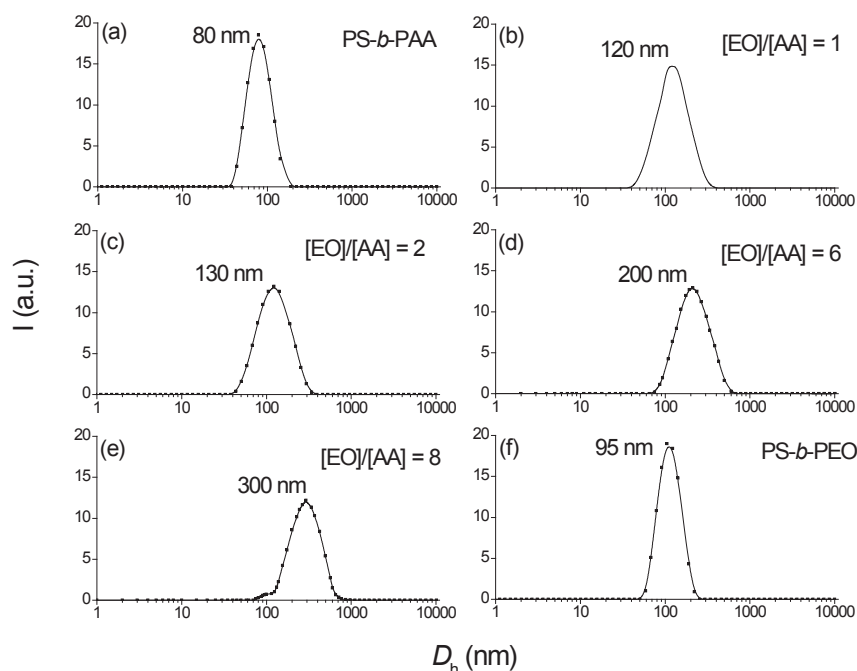


Figure 6.4 Hydrodynamic diameter (D_h) distribution of (a) pure PS-*b*-PAA di-BCP and (f) PS-*b*-PEO di-BCP and PS-*b*-PAA/PS-*b*-PEO complexes measured by DLS. [EO]/[AA]: (b) 1, (c) 2, (d) 6, and (e) 8.

The D_h of PS-*b*-PAA vesicles and PS-*b*-PEO micelles is about 80 nm [Figure 6.4(a)] and 95 nm [Figure 6.4(f)], respectively. It is interesting to see that size of PS-*b*-PEO micelles is bigger than that of PS-*b*-PAA vesicles. This is due to the high molecular weight of PS-*b*-PEO ($M_n = 238,000$) compared to PS-*b*-PAA ($M_n = 65,000$). Similar morphology was obtained for Eisenberg et al.²⁸ with slightly different molecular weights of the PS-*b*-PAA BCP.

[EO]/[AA] molar ratio	Morphology	Average Hydrodynamic diameter (D_h) (nm)
Pure PS- <i>b</i> -PAA	V	80
0.5	V	105
1	MLV	120
2	TWV	130
6	ICCV	200
8	IA	300
12	IA	310
Pure PS- <i>b</i> -PEO	SM	95

V = vesicle, MLV = multilamellar vesicle, TWV = thick-walled vesicle, ICCV = interconnected compound vesicle, IA = irregular aggregate, and SM = spherical micelle.

Table 6.1 Aggregate morphologies formed in PS-*b*-PAA/PS-*b*-PEO di-BCP complexes at different compositions in water.

The TEM images of the PS-*b*-PAA/PS-*b*-PEO complexes are presented in Figures 6.5-6.8. The morphology of complexes was investigated with increasing PS-*b*-PEO content. The TEM study showed that vesicles were the only morphology (not presented here for brevity) when the PS-*b*-PEO content was very low in the complexes, i.e., at $[EO]/[AA] = 0.5$. That means at this molar ratio, the PS-*b*-PEO content was very low and the complex aggregates resemble the pure PS-*b*-PAA di-BCP. Thus, PS-*b*-PAA, which is the major component in complexes, dominated their structure and PS-*b*-PEO was

introduced as the spherical domains in the solution. In other words, the intrinsic microphase of each diblock-copolymer was independently formed. TEM images in Figures 6.5-6.8 show that, with again increasing PS-*b*-PEO content, the aggregate morphology changes from vesicles to irregular spherical micelles through a variety of complex morphologies. This is due to the intermolecular hydrogen bonding interaction between PAA and PEO which is proven in the FTIR experiments. The morphologies of complexes at different molar ratios of [EO]/[AA] were studied and the results are summarized in Table 6.1.

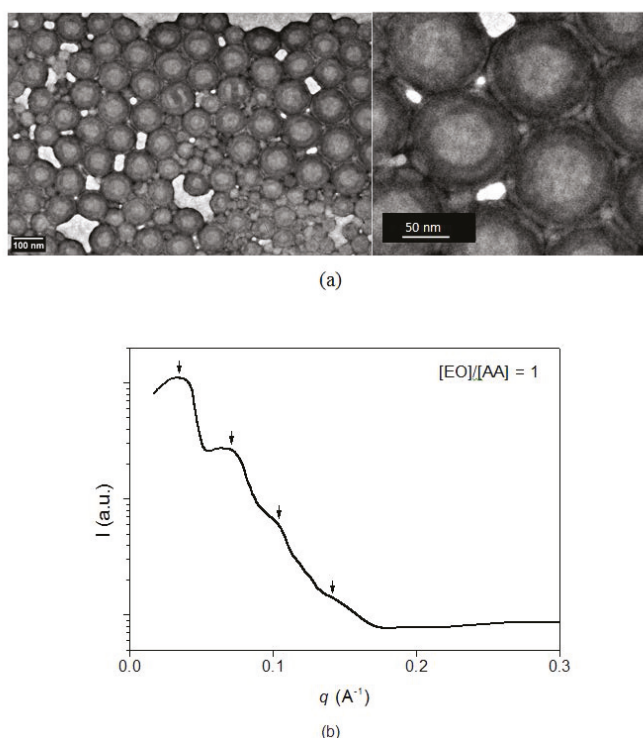
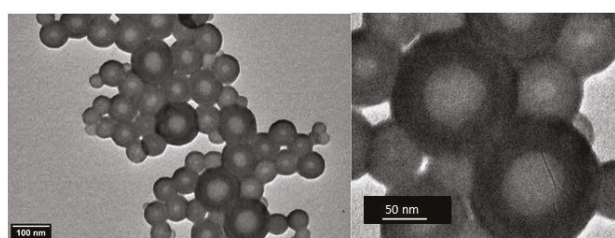


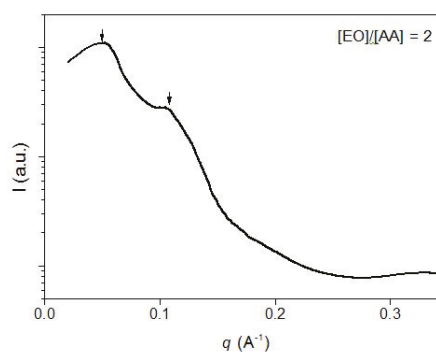
Figure 6.5(a) TEM images of MLVs formed in PS-*b*-PAA/PS-*b*-PEO complex in water at [EO]/[AA] = 1, showing multilamellar layers in the vesicle walls at both low and high magnifications; (b) SAXS pattern of the MLVs, showing the periodic peak characteristics of multilamellar layers.

Figure 6.5(a) shows the TEM image of multilamellar vesicles (MLVs) formed from self-assembly of the PS-*b*-PAA/PS-*b*-PEO complexes when the molar ratio is [EO]/[AA] = 1 in water. The MLVs formation can be identified from the presence of different lamellar layers in the vesicle walls of TEM image. We assumed that the multilamellar vesicles are formed as a consequence of spontaneous reorganization of the PS-*b*-PAA/PS-*b*-PEO

fragments induced by the hydrogen bonds in the complexes. The vesicle wall possesses an overall thickness (L_{MLV}) of approximately 45-50 nm measured from TEM image [Figure 6.5(a)]. The DLS measurement shows a sharp peak indicating the homogeneity of the size of these MLVs, and their D_h is evaluated from the peak position as 120 nm [Figure 6.4(b)]. The SAXS pattern of MLVs is given in Figure 6.5(b). This has a typical SAXS pattern of vesicle dispersion associated with lamellae. The multiple peaks (structure peak and form factors) present in the graph show the multilamellar nature of the vesicles. The TEM image of the aggregates at concentration $[EO]/[AA] = 2$ is given in Figure 6.6(a).



(a)

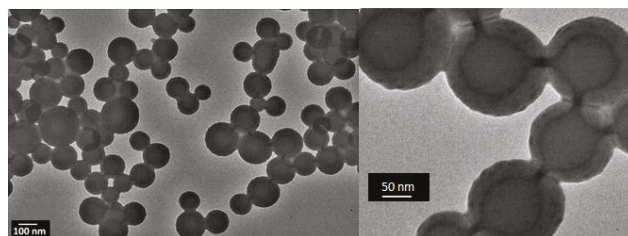


(b)

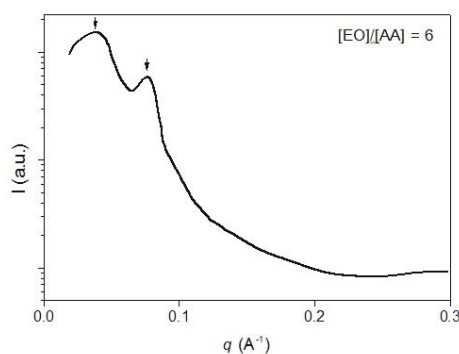
Figure 6.6(a) TEM images of TWVs formed in PS-*b*-PAA/PS-*b*-PEO complex at $[EO]/[AA] = 2$. The dense nature of the vesicle is due to the highly accumulated PS chains in the vesicle wall; (b) SAXS pattern of the TWVs.

It is clear that the multilamellar layers in the wall of the vesicles transformed into a rather thick wall. That means MLVs have changed into TWVs at this concentration. Figure 6.6(a) shows the SAXS pattern of TWVs that confirms the lamellar dispersion of a vesicle. However, these vesicles are more inhomogeneous compared to the MLVs and this can be identified by the

broad DLS peak displayed in Figure 6.4(c). The D_h of the TWVs is 130 nm, which is comparable to that of MLVs. Figure 6.6(a) shows that the overall wall thickness of these TWVs is slightly decreased ($L_{TWV} \sim 35\text{-}40$ nm). At the even higher concentration, $[\text{EO}]/[\text{AA}] = 6$, interconnected compound vesicles (ICCVs) were found as shown in Figure 6.7(a).



(a)

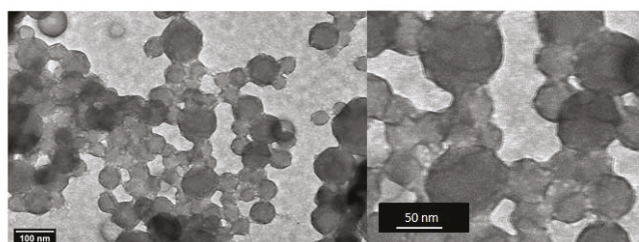


(b)

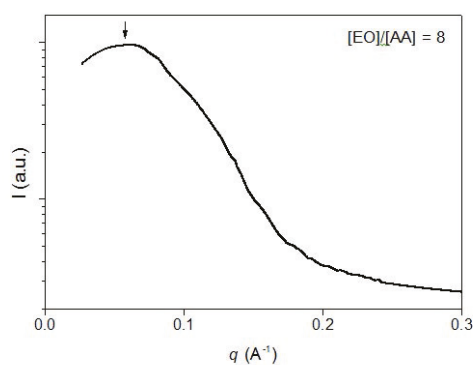
Figure 6.7(a) TEM images of ICCVs formed in PS-*b*-PAA/PS-*b*-PEO complex at $[\text{EO}]/[\text{AA}] = 6$, showing a structure of vesicles linked via a tube-like bilayer; (b) SAXS pattern of the ICCVs.

It is interesting to point out that ICCV is a new morphology observed for the first time. Here, more PEO blocks combine with the PAA in the corona, while the remaining PS-*b*-PEO may act as the channels for ICCVs. This in turn leads to the association of vesicles, which grow in fusion and transform into new interconnected bilayer structures. Zhang and Eisenberg²⁷ suggested a fusion/fission process for PS-*b*-PAA blocks in various dioxane/water solutions when two vesicles share a common membrane. The TEM images show a structure of vesicles connected via a tubelike bilayer that could be due to the stretching of the vesicle structures. The connections between the vesicles are seen in the magnified TEM image shown in Figure 6.7(a) (the right side

image). These ICCVs are polydispersed, as evidenced by the appearance of a wide DLS peak [Figure 6.4(d)] with an average D_h value of 200 nm. The SAXS pattern of ICCVs is shown in Figure 6.7(b), which represents results from two independently scattering structures. The two peaks in the SAXS pattern are due to two different form factors (the vesicles and the tubelike interconnections).²⁹ At $[EO]/[AA] = 8$ and above, irregular aggregates (IAs) were observed with TEM and SAXS (Figure 6.8(a) and (b), respectively).



(a)



(b)

Figure 6.8(a) IAs of PS-*b*-PAA/PS-*b*-PEO complex at $[EO]/[AA] = 8$; (b) SAXS pattern of the irregular aggregates.

6.4.3 Formation of various aggregates morphologies.

The morphologies observed in this study are fundamentally different at each molar ratio as the total structure and size of aggregates changes with the range of composition of the BCPs. Here intermolecular bonding among PAA and PEO play a crucial part in the complexation and formation of various morphologies, which is different from the other BCP mixture solutions without specific interactions where the morphology transition is only composition-dependent. When secondary interactions occur between different polymer chains in a solution, interpolymer complexation can lead to coaggregation in

blend solution.³⁰ Such aggregates are completely different from the original blocks in terms of their morphology and structure.³¹

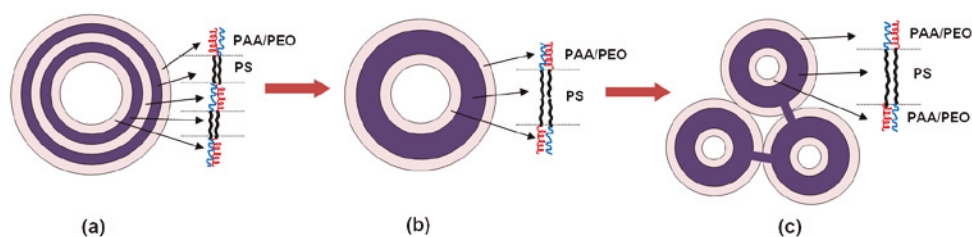


Figure 6.9 Schematic representation of morphological transitions in PS-*b*-PAA/PS-*b*-PEO di-BCP complexes; (a) MLVs at $[EO]/[AA] = 1$, (b) TWVs at $[EO]/[AA] = 2$, and (c) ICCVs at $[EO]/[AA] = 6$.

The formation of various complex aggregates observed in TEM is schematically shown in Figure 6.9, and the morphological transitions can be explained as follows. The specific final morphology of any aggregates of BCP complex including vesicles is a result of an equilibrium between three thermodynamic contributions to the free energy, which include core-chain stretching, corona-chain repulsion, and interfacial energy.³² In complexes, vesicles are formed at molar ratio $[EO]/[AA]=0.5$. The balance of the above explained thermodynamic contributions is changed at the interface by the favorable hydrogen bonding interaction of the PEO/PAA blocks. This would facilitate the formation of vesicles at minor PS-*b*-PEO content presumably by increasing the core chain stretching and reducing the corona chain repulsion. When the ratio $[EO]/[AA] = 1$, the complexes show MLVs. MLVs consist of lamellae like multiple bilayers in the vesicle wall. Here, the PS blocks from the two copolymers may interpenetrate to form intermediate layers of the multilamellar core. Meanwhile, PEO is segregated to the outermost layer where it forms hydrogen bonds with PAA and the remaining PAA blocks form multilamellar corona. The aggregates comprise two different layers; an insoluble PS as core and PAA/PEO bonded pair as corona. Note at this concentration that the molar ratio of hydrogen bonded components is stoichiometric, i.e., 1:1. For such systems, an elongated in line series of bonds between the polymer segments may result in a lamellar structure [Figure

6.9(a)]. This would rather resist the inter-conformation and results in parallel arrangement, which facilitates the formation of MLVs.³¹ TWVs are observed at $[EO]/[AA] = 2$. Here with increased PSb-PEO content, more PS blocks move toward the interior. This caused a high level of PS chains in the vesicle-core, resulting in the formation of vesicles with thick walls (TWVs) as schematically illustrated in Figure 6.9(b). In other words, the increasing thickness of vesicles is due to the progressive accumulation of the random PS blocks at the interface. The term “thick wall” is used because it has a high amount of hydrophobic PS blocks, which is in fact more dense compared to hydrophilic PEO and PAA.

A new morphology (ICCVs) is formed in the case of PS-*b*-PAA/PS-*b*-PEO complexes at $[EO]/[AA] = 6$. When PS-*b*-PEO BCP is the main constituent in the mixtures, they form ICCVs [Figure 6.9(c)]. At given water content in the complexes, as the amount of PS-*b*-PEO increases, the corona-repulsion around PAA reduces with increase in hydrophilic chain-length due to the hydrogen bonded PAA/PEO. The mechanism of this morphological change is, most likely, the partial building up of the segments in the middle, decreasing the core chain-stretching.³² Specifically, from Figure 6.7(a), the ICCVs with an average size of 200 nm are formed in water at $[EO]/[AA] = 6$. The formation of connection between the vesicles could be due to the aggregation of individual vesicles and a subsequent fusion process. Moreover, the bonding among PAA and PEO in the corona can also contribute toward the interconnection. Theoretically, ICCVs are formed from vesicles by gaining of conformation entropy.³³ The localization of the PEO blocks at the interface for making complexation with PAA actually decreases the corona-chain repulsion and increases the core-chain stretching so that the vesicular morphology is maintained. The formation of ICCVs normally requires a reduced repulsion of PAA blocks by complexation with PEO and thereby increasing the effective collisions of the individual vesicles.

With PEO content is at $[EO]/[AA] = 8$ and above, irregular aggregates were mainly observed but with evidence of some spherical micelles. Because the amount of PEO blocks is much higher than the amount of PAA blocks at this concentration, only part of the PEO chain can take part in bonding with the PAA blocks. Therefore, the remaining PEO blocks are dissolved in the solution

while the PS blocks formed the core. Based on these results, it is proposed that with an increase in the hydrophobicity of PS blocks, the large ICCVs transform to the irregular aggregates to decrease the interfacial energy between the blocks and solvents.

It should be noted that the general trend in variation of the schematic morphology shown in Figure 6.9 is not directly dependent on the block-length as in pure BCP, but on the molar ratio $[EO]/[AA]$ of two blocks. The current AB/AC di-BCP system consists of three chemically different polymeric chains but can be separated into two phases. That is, the PS blocks segregate into an isolated microphase while PEO and PAA blocks are miscible due to the favorable hydrogen bonding interaction, forming one single phase. An additional advantage of the present system in comparison with conventional BCP systems is the ease of morphology design. To tune nanostructures in PS-*b*-PAA/PS-*b*-PEO complexes simply requires different ratios of the two asymmetric BCPs without involving elaborated synthetic efforts.

6.5 Conclusions

Multiple vesicular morphologies were formed in AB/AC di-BCP complexes of PS-*b*-PAA and PS-*b*-PEO in water. The formation of complexes is due to the favorable bonding among the PAA and PEO blocks of the two di-BCPs. A variety of aggregated nanostructures, including vesicles, MLVs, TWVs, ICCVs, and IAs were documented in the complexes. Interestingly, ICCVs were observed for the first time as a new morphology, which may open up various opportunities for nanotechnology applications. The aggregate morphologies of the complexes can be correlated to the molar ratios $[EO]/[AA]$. When $[EO]/[AA] = 0.5$, only vesicles were found, whereas the MLVs appeared as $[EO]/[AA]$ reached 1. When $[EO]/[AA]$ was increased to 2 and 6, the TWV's and ICCVs were formed, respectively. Finally, IAs were obtained with $[EO]/[AA] = 8$ and above. It is clear from the present study that complexation of two amphiphilic di-BCPs provides a viable approach to vesicles in aqueous media.

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A Simple and Effective Approach to Vesicles and Large Compound Vesicles via Complexation of Amphiphilic Block Copolymer with Polyelectrolyte in Water

7.1 Abstract

In this study, vesicles and large compound vesicles were prepared via complexation of PS-*b*-PEO and PAA in water and directly visualized using cryo-TEM. Upon addition of PAA homopolymer into PS-*b*-PEO, a variety of bilayer morphologies were formed in the PS-*b*-PEO/PAA complexes. The morphology of aggregates was correlated with respect to the molar ratio of PAA to PEO. At $[AA]/[EO] = 0.2$ spherical micelles were observed, while a mixture of micelles and vesicles were obtained at $[AA]/[EO] = 0.5$. Vesicles were formed at $[AA]/[EO] = 1$. When the $[AA]/[EO]$ ratio increases further to 4 compound vesicular morphology starts to appear and at very high concentration of PAA ($[AA]/[EO] = 8$), LCVs appeared. The findings in this work suggest that complexation between amphiphilic BCP and polyelectrolyte is a viable approach to vesicles and LCVs in aqueous media.

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7.2 Introduction

Vesicles, formed from polymers are often known as ‘polymersomes’¹⁻³ and show increased stability and robustness plus reduced membrane permeability in aqueous solutions. Most importantly, the physical, chemical and biological behaviours of polymer-vesicles can be tuned by varying the composition and length of the constituting polymers. Moreover, BCPs having similar architecture of lipids can mimic the lipid amphiphilicity and the unilamellar structure of a vesicle mimics the cell membrane.³ Therefore, these vesicles have been widely used as model systems for *in vitro* explorations such as the study of membrane proteins, as well as in the development of drug delivery systems.⁴

Vesicle formation and morphological transition in asymmetric amphiphilic BCPs have been comprehensively reported by Eisenberg et al.⁵ Since BCP vesicles have the potential for many interesting applications, they have been extensively studied over the years.⁶⁻¹¹ The findings emphasise the requirement of BCP synthesis for achieving a particular type of micelles or vesicles. In principle, this can be avoided, to some extent, by developing the mixtures of BCPs or BCP with a homopolymer. The formation of vesicles has been observed in the solid-state of BCP/homopolymer systems such as in PS/PS-*b*-PB blends,¹² epoxy/BCP blends,¹³ reactive BCP blends,¹⁴ as well as BCP/homopolymer in organic solvents.¹⁵

In this communication, we report a simple, effective approach to trigger a sphere-to-vesicle morphological transition in PS-*b*-PEO/PAA complexes in aqueous solution. Here we present the creation of vesicles in water by complexation of an amphiphilic BCP (PS-*b*-PEO) and a polyelectrolyte (PAA). A variety of vesicular aggregate structures involving small vesicles and LCVs, were obtained and directly visualized in PS-*b*-PEO/PAA complexes in aqueous solutions using cryo-TEM. The plain PS-*b*-PEO BCP forms only spherical micelles in water. However, the mixture of PS-*b*-PEO BCP and the polyelectrolyte PAA form self-assembled complexes through bonding between the PAA and the PEO block of the BCP, which leads to morphological transitions from spherical micelles to vesicles, and further to complex compound vesicles with the increase of the amount of polyelectrolyte PAA.

7.3 Experimental section

7.3.1 Materials and preparation of complex aggregates

The polymer materials in this study were PAA and PS-*b*-PEO. The PS-*b*-PEO BCP was purchased from Polymer Source, Inc., with $M_n(\text{PS}) = 190,000$, $M_n(\text{PEO}) = 48,000$, and $M_w/M_n = 1.07$. The PAA sample with a $M_w = 1,800$ was the product of Aldrich Chemical Company, Inc. The BCP PS-*b*-PEO was first dissolved in THF ($c = 1 \text{ mg/ml}$) solution. Then a specific amount of deionized water was added (25 wt%) into the solutions and stirred again for 1 day to allow the system to reach equilibrium. Then the PAA solution (1 mg/ml in an identical solvent mixture) was gradually mixed to the PS-*b*-PEO solution. The weight-ratio of the PAA/PEO-*b*-PS (W_A/W_{ES}) was from 0.3 to 2.61. Or in other words the ratio $[AA]/[EO]$ is 0.2 to 8 ($[AA]/[EO] \approx (W_A/72)/(0.2 \times W_{ES}/44)$). Here the values 72 and 44 are the molar-masses of the repeat-units of PAA and PEO and 0.2 is the weight-fraction of PEO). Finally, additional amount of water was added to the mixture for quenching and kinetic-freezing of the structure of the aggregates. The final solution was dialysed with respect to water to remove THF. The pH values were adjusted by dilution with hydrochloric acid and monitored by a pH meter (Mettler Toledo). The solution was maintained at a particular pH (~ 4.8) so as to induce the intermolecular bonding between PAA and PEO blocks. The obtained complexes were used for further experiments.

7.3.2 FTIR spectroscopy.

Infrared spectra of the samples were obtained on a Bruker Vetex-70 FTIR spectrometer, and 32 scans were recorded with a resolution of 4 cm^{-1} . The spectra of all the samples were determined by using the conventional KBr disk method. The complex powder was mixed with KBr and ground well to form the disk. The samples were kept to dry in-vacuo for 72 hours before the experiments.

7.3.3 Cryo-TEM

A laboratory-built humidity-controlled vitrification system was used to prepare the sample for imaging in a thin layer of vitrified ice using cryo-TEM. Humidity was kept close to 80% for all experiments, and the temperature was 22 °C. 200-mesh copper grids coated with perforated carbon film (Lacey carbon film: ProSciTech, Qld, Australia) were used for all experiments. 4μL aliquots of the sample were pipetted onto each grid prior to plunging. After an interval of 30 sec to allow adsorption; the grid was blotted manually using Whatman 541 filter paper for approximately 2 sec. The blotting time was optimized for each sample. The grid was then plunged into liquid ethane cooled by liquid nitrogen. Frozen grids were stored in liquid nitrogen until required for cryo-TEM observation. The samples were examined using a Gatan 626 cryoholder (Gatan, Pleasanton, CA, USA) and Tecnai 12 transmission electron microscope (FEI, Eindhoven, The Netherlands) at an operating voltage of 120KV. At all times low dose procedures were followed, using an electron dose of 8-10 electrons/Å² for all imaging. Images were recorded using a Megaview III CCD camera and AnalySIS camera control software (Olympus.) using magnifications in the range from 60, 000 to 110, 000.

7.3.4 DLS and ζ-potential.

The hydrodynamic diameter and zeta ζ-potential of the complex aggregates were measured on a Malvern Zetasizer Nano ZS instrument equipped with He-Ne laser with a wavelength of 633nm digital correlator. The temperature stability inside DLS sample holder was controlled at 25 °C, and the measurements were carried out at detection angle of 173°. Solutions of 0.5% (w/v) complex aggregates in water were used. The scattering intensity autocorrelation functions were analyzed by using the methods of CONTIN and Cumulant, which are based on an inverse-Laplace transformation of data. This gives access to a size distribution histogram for the analyzed complex solutions.

7.4 Results and discussion

7.4.1 Hydrogen bonding interactions

The possible interactions between ether oxygens (PEO) and the carboxylic acids (PAA) in the PAA/PS-*b*-PEO complexes is given in Figure 7.1

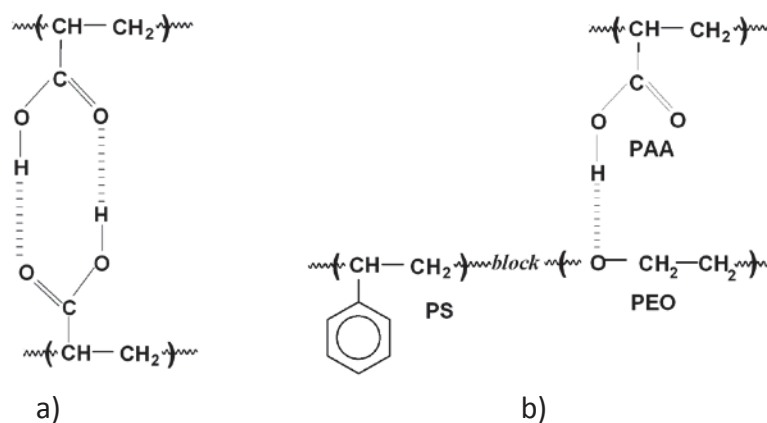


Figure 7.1 Schematic representation of possible bondings in PAA/PS-*b*-PEO complexes: a) Self-associated bonds of PAA; b) bond between PAA and PEO blocks of PS-*b*-PEO di-BCP.

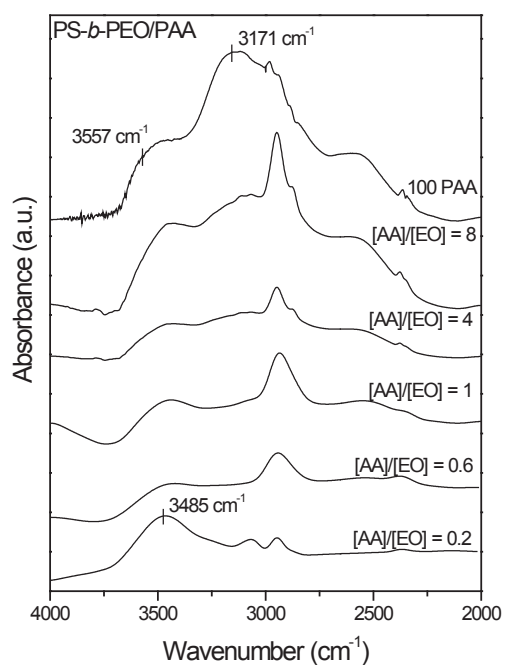


Figure 7.2 Infrared spectra of hydroxyl region of PAA/PS-*b*-PEO complexes

There exist two kinds of hydrogen bonds: (a) self-associated bonds between the hydroxyl (OH) groups of PAA homopolymer; (b) inter-macromolecular hydrogen bonds among the hydroxyl groups of PAA and ether oxygen of PEO blocks. Figure 7.2 shows the FTIR spectra of OH regions in PAA and the PAA/PS-*b*-PEO complexes. PAA homopolymer shows two bands in the OH region. It can be noticed that the hydroxyl region of PAA shows a broad band representing the overlapping species at 3556 and 3171 cm^{-1} . These absorptions are due to the non-associated free OH groups and self-associated hydroxyl groups, respectively.¹⁶ With increasing content of the PS-*b*-PEO BCP, the absorption related to the free OH groups declines in intensity, while the bonded peak shifts to low wave number area. The shift of the band corresponding to free hydroxyl group represents intermolecular interactions between PAA and PEO chains.

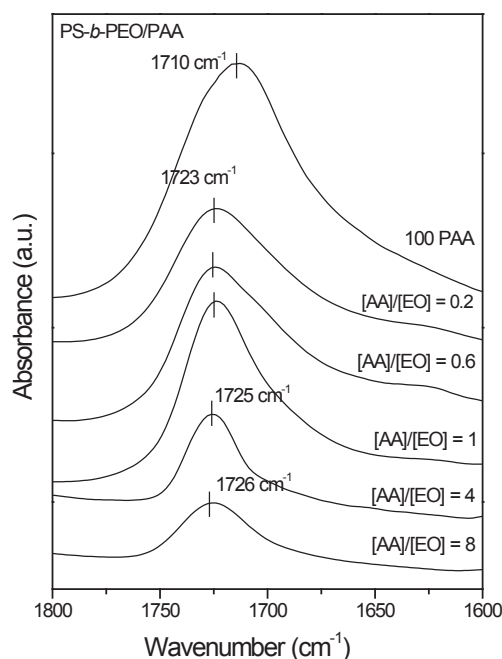


Figure 7.3 Infrared spectra of carbonyl region of PAA/PS-*b*-PEO complexes

The C=O region (1700–1750 cm^{-1}) of the complexes is shown in Figure 7.3. The band at 1710 cm^{-1} represents PAA homopolymer. Upon the addition of the BCP, this band shifts to high wave number area and a new sharp absorption forms at 1723 cm^{-1} . This is assumed to be the release of free C=O groups

during the formation of complexes.¹⁷ The hydrogen bonding between PAA and PEO can be confirmed from the results.

7.4.2 Morphological transitions in PAA/PS-*b*-PEO complexes

Aggregate structures are developed by solubilizing the BCP in a medium common for both polymers followed by the addition of a non-solvent, that is a precipitant for the core-forming block but good for the corona-forming block.¹⁸ It has been known that PAA and PEO can form polymer complexes.¹⁹ In the present study, the self-assembled complexes were prepared by the drop-wise addition of PAA/water solution into PS-*b*-PEO/THF solution. Because of the insolubility of PS in water, micellar aggregation can be induced by altering a solvent (i.e., THF) good for both blocks to a selective solvent (water). At a particular water concentration, the PS chains begin to aggregate and form micelles, that is, core-shell micelles with PS chains as the core and the PEO blocks as the corona. When a large excess of water is rapidly added to the micellar solution, the structure of the core-shell micelles can be kinetically frozen in water.²⁰ The morphology was finally fixed by dialysis against deionized water to remove THF. In such systems, the formation of aggregates in aqueous media can be examined by cryo-TEM as well as by DLS. Cryo-TEM is emerging as one of the finest methods for imaging aqueous assemblies of amphiphilic BCPs as a result of the rapid vitrification process. These experiments have the advantage to avoid any drying step of the aqueous part (artifacts) or staining with heavy metals, and the morphology and size are expected to be as similar as possible than they exist in the aqueous environment.²¹ It allows the examination and direct visualization of particular micelles and vesicles thereby avoids many of the artifacts associated with conventional TEM.²¹ The micelles and vesicles of some amphiphilic BCPs in aqueous solutions were visualized through cryo-TEM.²¹

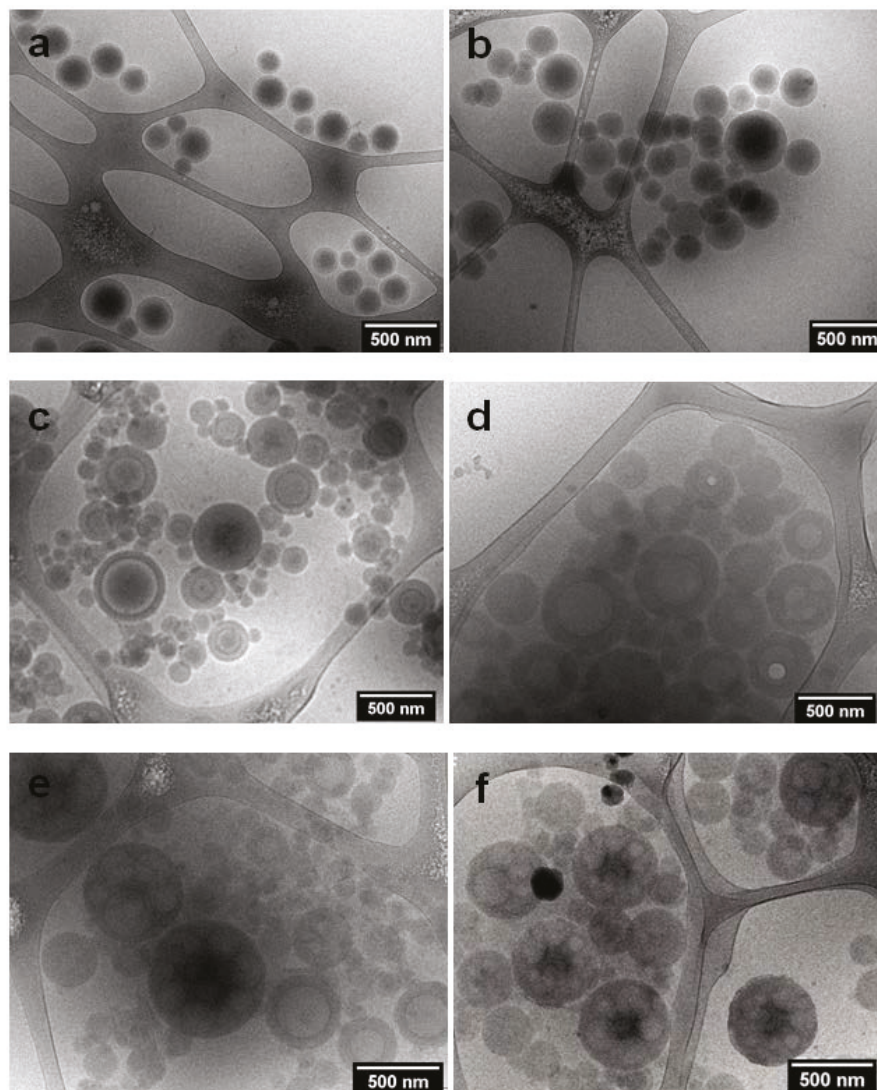


Figure 7.4 Cryo-TEM images of a) plain PS-*b*-PEO BCP and PS-*b*-PEO/PAA complexes in aqueous solutions with [AA]/[EO] ratios of b) 0.2, c) 0.6, d) 1, e) 4, and f) 8. Holey carbon films were used for embedding of the vitrified aqueous solution of the complexes.

Figure 7.4 shows cryo-TEM images of PS-*b*-PEO BCP and PS-*b*-PEO/PAA complexes formed at various molar ratios of [AA]/[EO]. The morphology of plain PS-*b*-PEO BCP in water is shown in Figure 7.4(a), which displays spherical micellar structure with an average size of about 90 nm. It can be observed that the micelles have a dark core and a relatively light corona. This suggests that the spherical micelles contain a PS core and PEO corona because PS has a higher electron density than PEO. We chose the low

molecular weight PAA because it can effectively diffuse and easily penetrate to corona of the PS-*b*-PEO micelles. Spherical micelles remain even after the addition of small amount of PAA as observed in the image of PS-*b*-PEO/PAA complex at $[AA]/[EO] = 0.2$ [Figure 7.4(b)]; however, the size of spheres is larger and polydispersity is apparent. When the $[AA]/[EO]$ ratio is 0.6, the size of the micelles become even more polydisperse and very large spherical microdomains start to form in solution [Figure 7.4(c)]. It can be seen that the complexes at this stage show a joint morphology containing both spherical micelles and vesicles. The aggregate morphology of the complexes again transforms as the concentration of PAA increases. At higher PAA content where $[AA]/[EO] = 1$, vesicles are the only morphology present [Figure 7.4(d)]. The hollow vesicles can be identified by a high level of transmission in the middle of the aggregate than at the periphery.^{5c} The ring-like structure of vesicles in Figure 7.4(c) and (d) is evident as reported by other authors.²² When the $[AA]/[EO]$ ratio increases further to 4 [Figure 7.4(e)], a compound vesicular morphology starts to appear. At very high concentration of PAA ($[AA]/[EO] = 8$), LCVs prevail as observed in Figure 7.4(f).

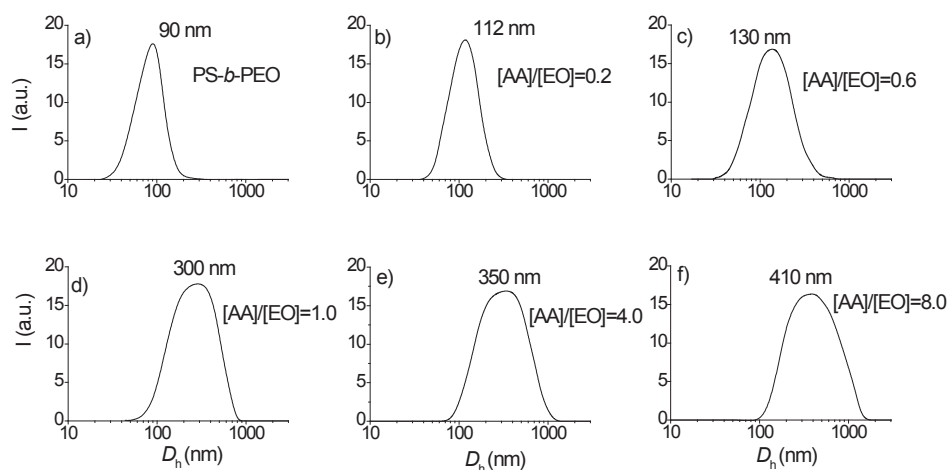


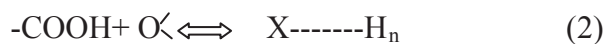
Figure 7.5 Hydrodynamic diameter (D_h) distributions of plain PS-*b*-PEO BCP and PS-*b*-PEO/PAA complexes measured by DLS in 0.5% (w/v) aqueous solution at $[AA]/[EO]$ ratios of a) PS-*b*-PEO, b) 0.2, c) 0.6, d) 1, e) 4, and f) 8.

Figure 7.5 shows the DLS results of the complexes at different molar ratios of $[AA]/[EO]$. The D_h distribution contains a single peak of different

widths, implying that the solution comprises aggregates of various sizes. The intensity reveals the relative population of the aggregates with different size, that is, D_h . The peak shifts toward higher D_h for the complexes with increasing PAA content, that is, $[AA]/[EO]$ ratio, indicative of an increase in size of the aggregates. The plain di-BCP gives the peak position at 90 nm, whereas the complex with the molar ratio $[AA]/[EO] = 0.2$ shows a broader peak at 112 nm, which reveals the polydisperse micelles at this concentration. The D_h distribution peak broadens with increasing molar ratio $[AA]/[EO]$. The PS-*b*-PEO/PAA complexes with $[AA]/[EO] = 0.6$ and above show an even broader peak at 130 nm, indicative of an increase in the polydispersity of aggregate size, agreeable with the coexistence of vesicles and the compound vesicles as observed by cryo-TEM [Figure 7.4(c)]. Figure 7.5(d-f), the D_h peak shifts from 300 to 410 nm as $[AA]/[EO]$ is increased from 1 to 8. This is in agreement with the TEM images in Figure 7.4(d-f) for vesicles and compound vesicles. The D_h peaks are quite broad, indicating that the vesicles and compound vesicles are rather polydisperse.

7.4.3 PAA-PEO complexation.

Variation of pH and degree of complexation of PAA with other polymers is well studied. Ikawa et al.²³ reported the relationship between turbidity and molar ratio of PAA/PEO aqueous solutions at various pH. They reported that complexes are not developed at high pH (i.e., $\text{pH} > 5$) because of the dissociation of $-\text{COOH}$ groups of PAA. At low pH, the undissociated carboxylic groups play a significant role in the complex formation through hydrogen bonding. Karayanni et al.^{23b} detailed the pH dependence of PAA with PVME in aqueous solution with increasing polyacid concentration. PAA is a weak polyanion, and its ionization degree is strongly pH-dependent, with a $\text{pK}_a \sim 5.6$. The hydrogen bonding between PAA/PEO occurs only at low pH values. With decreasing pH, the PAA/PEO segments contract and this association is improved due to the low degree of PAA-neutralization. At higher pH, the complexation-degree is actually less because of PAA ionization in water. The complexation among PEO and PAA can be described by the equation,



Where X---H is the complex and n is the number of carboxyl hydrogens related to the degree of PAA polymerization. But, the complexes formed, being a weak poly acid, is partially dissociated according to the equation,



Where $k \ll n$. At low PAA content, the complexes contains PEO in excess and the charge of the interpolymer complexes are due to the dissociation, which is represented in equation 2.

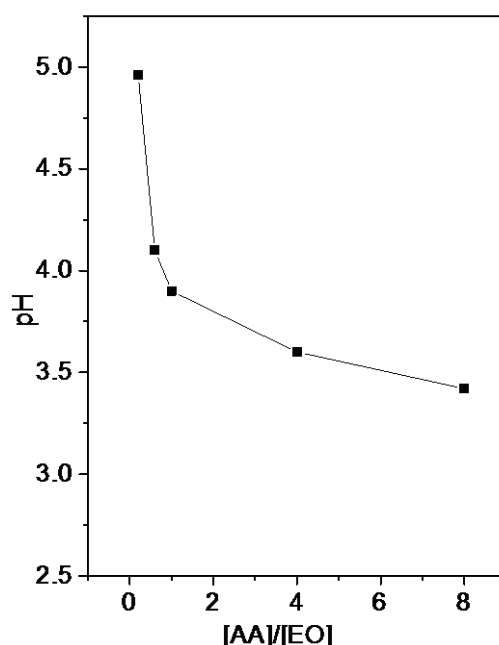


Figure 7.6 pH values as a function of different [AA]/[EO] ratios in 0.5% (w/v) aqueous solution.

The charge ratio among the -COOH of the PAA and the ether oxygen of the PEO block is an important parameter in the micelle/vesicle formation. The pH dependant association of PS-*b*-PEO/PAA complexes were measured in aqueous solution with increasing PAA content. From Figure 7.6, at low PAA, that is, [AA]/[EO] = 0.2, the pH of the complexes is equal to that of pure PAA

(pKa of pure PAA is ≈ 4.36).²³ When the concentration of PAA increases, a reduction in pH from 4.8 to 3.4 was observed. At all these pH values, the capability for protonation of the carboxyl group of PAA is enhanced, which leads to strong interactions between PAA and PEO. Maintaining the pH of the complexes below 4.8 at various [AA]/[EO] ratios, leads to the shifting of dissociation equilibrium towards left (Equation 4) that results in the reduction of H^+ content.²³ Such low pH micelles and vesicles can be used in areas such as biomimetic chemistry, molecular switching.²³

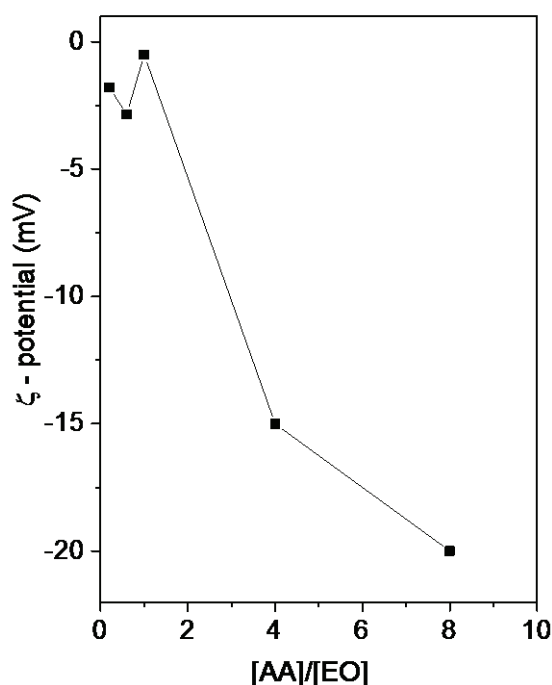
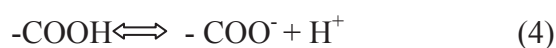


Figure 7.7 ζ -potential values as a function of different [AA]/[EO] ratios in 0.5% (w/v) aqueous solution.

To further confirm the binding of PAA to PS-b-PEO, we carried out ζ -potential measurements. The ζ -potential of the aggregates in aqueous solution is presented in Figure 7.7 as a function of molar ratio [AA]/[EO]. At the stoichiometric ratio [AA]/[EO] = 1, the ζ -potential value is -0.5, slightly lower than zero. This can be attributed to the weak acidic nature of PAA, the pKa of the PAA units is about 4.3.²³ Therefore the PAA will be slightly anionic in

water and the complexation between the PAA and the PEO block is not complete. The ζ -potential continues to decrease for molar ratio $[AA]/[EO] > 1$. The PAA can form hydrogen bonding interactions with the PEO ether oxygen binding sites. The negative value of the ζ -potential is due to the presence of an excessive PAA.

7.4.4 Mechanism of morphological transitions in complexes

The complex morphologies depend on a few factors such as the core stretching, the interfacial tension among the core and repulsion between the corona blocks due to reduction in configurational entropy.¹⁹ In PS-*b*-PEO/PAA complexes, the incorporation of a homopolymer can considerably affect the equilibrium state and also the charge density of the corona as PAA bears more charge. The corona radius increases slightly with the addition of PAA. In fact, there is an inherent balance between the number of bonded EO/AA sites and the remaining EO units of the PEO blocks which form hydrogen bonds with water, maintaining the solubility. Added to this phenomenon is the hydrogen bond formation resulting in interchain crosslinking whereby the aggregates change progressively from PEO to bonded PEO/PAA, then to the bonded PEO/PAA coexisting with excess of PAA. Both of these phenomena will change the packing behaviour of the hydrophilic domain composed of PAA and the PEO block. Therefore, the hydrophilic domain in the complex is enlarged while the amount of unbound EO units is decreased. Therefore it needs to increase the radius of curvature to fit in the required space.

When PAA forms strong hydrogen bonds with the corona chains of the PEO blocks, the effective size and radius of the corona chains increase dramatically. For minimizing the total energy, the micelle changes the morphology with less diameter and higher radius of curvature and thus formed the vesicles. The increase in the amount of interchain crosslinking, which originates from the outer surface of the spheres upon complementary hydrogen-bonding interactions, is responsible for the micelle-vesicle transformation.

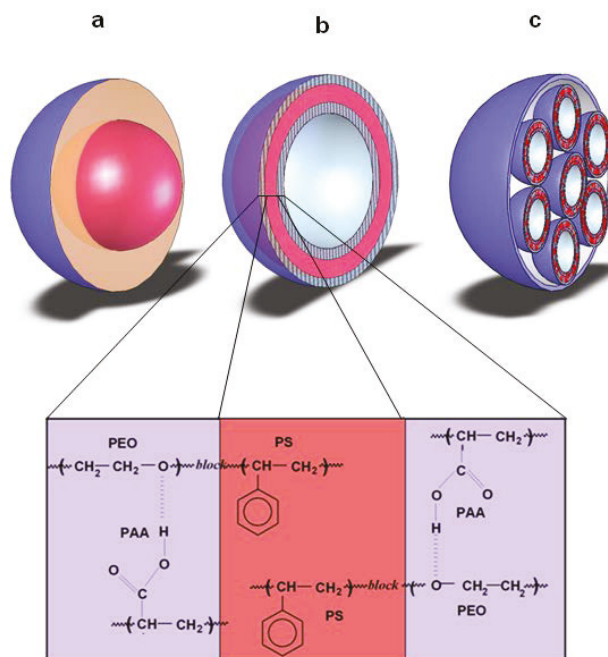


Figure 7.8 Schematic representation of morphological transitions in aggregates of PS-*b*-PEO/PAA complexes showing the hydrogen bonding interactions between the components: a) Spherical micelles formed at lower PAA contents, b) vesicles formed at higher PAA contents, and c) large compound vesicles (LCVs) formed at even higher PAA contents.

A scheme of morphology of the aggregates in the complexes is given in Figure 7.8. The morphology of micellar aggregates at lower PAA concentrations is represented in Figure 7.8(a). When the ratio $[\text{AA}]/[\text{EO}]$ is 0.2, the increase in the corona radius becomes more pronounced and the micelle size becomes more polydisperse [Figure 7.4(b)]. This implies that progressively more homopolymer PAA is adsorbed to the corona as the added homopolymer content is increased. The key factor responsible for maintaining the initial micelle morphology is believed to be the competition between complexation and micellization that occurred during the sample preparation.¹¹ Therefore, only part of the available PAA can form hydrogen bonds with the PEO blocks, which results in the spherical morphology.

When the molar ratio of $[\text{AA}]/[\text{EO}]$ reaches 0.6, an intermediate situation for the localization of PAA units leads to a coexistence of spheres and vesicles [Figure 7.4(c)]. This partial localization of the AA units gives an intermediate

situation where the hydrophilic domains are not uniform so that vesicles are formed along with spheres. Moreover, the strong intermolecular hydrogen bonding induces complex aggregation forming spherical micelles and vesicles. The micellar structure consists of a PS core and a hydrophilic domain of PAA and PEO containing corona. Note that when interactions between the PEO block and PAA take place, a more compact corona forms with neutral charge. This leads to less corona chain repulsion and hence change in the volume ratio of the hydrophilic domain to the hydrophobic PS core, favoring vesicles (lamellar structure) [Figure 7.8(b)]. In the same way, vesicles are formed at a particular PAA content ($[AA]/[EO] = 1$) in order to decrease the interfacial energy and also, to relieve the highly compacted corona domain. Also, in hydrogen bonding interactions, unlike other secondary interactions, the PAA blocks can penetrate into the shell of PS-*b*-PEO micelles and forms vesicles.²⁴ When the PAA content is very high ($[AA]/[EO] = 4$ and above), the complexes change the structure from vesicles to compound vesicles [Figure 7.8(c)]. This means that the addition of more PAA facilitates the vesicles to adhere together (in essence there is less repulsion between vesicles), and the individual vesicles overlap to form compound vesicles [Figure 7.4(f)]. The dissociation of the excessive PAA changes the charge balance to a significant net charge from the approximate neutrality. The PAA dissociates in water and maintains an extended chain configuration due to the charge repulsion, which increases the corona volume. The charge balance is such that the vesicles can undergo self-association which also helps to form compound vesicles. Similar kinds of large compound vesicles were observed by Yan and coworkers²⁵ in amphiphilic hyperbranched multi-arm copolymers. However, to our knowledge, compound vesicles have not been observed in BCP/homopolymer complexes in solution.

In BCP/homopolymer systems, the aggregate morphologies formed in solution depend on a few factors, such as block-length of BCP and homopolymer, composition, specific interactions, nature of solvent, etc. In PS-*b*-PEO/PAA complex mixtures, with increasing the amount of aqueous solvent, conditions are worse for PS blocks thereby the interfacial tension increases. Meanwhile, the corona repulsion may not change much since both THF and water are solvents for corona-forming PAA and the PEO block. In the PS-*b*-

PEO/PAA complexes with the addition of water, the core-stretching of PS blocks increases, which in turn increases the free energy. When the stretching is too high, the corona volume will considerably change. Thus complex aggregates have to adapt their geometry to relax the stretching and minimize the total free energy. The complex formation among PAA and the PEO segments is the reason for the variation in the shape of the corona, responsible for the morphological transitions from micelles to vesicles and then to compound vesicles. Increasing the molar ratios of [AA]/[EO] changes the number of the EO units available for hydrogen bonding and the charge density of the corona, which in turn causes the morphological transitions in the present system. In addition, there is an entropic increase during the mixing of two polymers. The increase in chain stretching is due to the change in entropy.

7.5 Conclusions

We have successfully prepared vesicles in mixtures of BCP with a homopolymer in aqueous media for the first time. Small vesicles and LCVs were formed and directly visualized using cryo-TEM. The multiple morphological transitions were observed from micelles of PS-*b*-PEO di-BCP to vesicular aggregates in PS-*b*-PEO/PAA complex mixtures and finally compound vesicles by addition of polyelectrolyte PAA. In these complexes, the intermolecular interactions among PAA and the PEO block induces the complexation and formation of multiple morphologies in water. These findings suggest that complexation of amphiphilic BCP and polyelectrolyte is an effective, simple approach to prepare polymer vesicles and LCVs in aqueous media.

7.6 References

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Conclusions and Future Works

8.1 General conclusions

This study provides a basic understanding of the formation of self-assembled nanostructures in block copolymer blends and complexes via hydrogen bonding interactions. The different combinations of block copolymer blends and complexes of AB/C, AB/CD, and ABC/D mixtures opens a convenient way to switch micellar morphologies with controlled size and shape. Self-assembled structures will be formed in block copolymer/homopolymer complexes if there exists at least one type of hydrogen bonding interaction. The general conclusions of this work include the following:

- Development of novel nanostructured blends and complexes via competitive hydrogen bonding interactions are performed with P2VP-*b*-PMMA/Phenoxy, PEO-*b*-PCL/PVPh and SVPEO/PVPh systems and the typical self-assembled nanostructures such as spherical, lamellae, hexagonal cylinder, and bicontinuous phases are formed based on the composition of block copolymer and homopolymer in the mixture.
- Selection of homopolymer is important in order to form different nanostructures via competitive hydrogen bonding interactions. Homopolymers such as PVPh, Phenoxy, PVAL, PAA etc., can be selected owing to their strong hydrogen bonding ability with other hydrogen accepting polymers.
- In selective hydrogen bonding interactions, the homopolymer can interact with only one block of the block copolymer and the non-interacting block gets phase separated. Block copolymer complexes like PS-*b*-PAA/PS-*b*-PEO and PS-*b*-PEO/PAA were studied in this category and the phase behaviour was correlated with the morphologies.

- By varying the compositions of the interacting polymers, their mixing ratio, and the solubility of the non interacting blocks in selective solvent, morphologies like multilamellar vesicles, thick walled vesicles, interconnected compound vesicles, entrapped vesicles and various micelles have been successfully developed via selective hydrogen bonding interactions in block copolymer mixtures.
- Block copolymer/homopolymer complexation involving selective hydrogen bonding interaction is a simple and viable method to minimize synthetic efforts and generate well defined stable morphologies in a nanometer scale for specific applications.

8.2 Future works

- Identify the stability of the self-assembled structures, establish a universal phase diagram and derive the association constants to investigate the self-assembly and morphological transitions in self-assembled complexes.
- Identify the morphology of different ordered/disordered nanostructures under different conditions and analyse these results with the fracture behaviour and mechanical properties of these systems.
- Development of different nanostructures can be employed in block copolymer/thermosetting polymers and establish the basic mechanism for the self-assembly via competitive hydrogen bonding.
- The morphological results obtained using TEM and AFM will be correlated with a temperature dependant SAXS to understand the detailed phase behaviour mechanism in the blends and complexes.
- Develop a better understanding of the morphology, physical properties and biological performance to guide future design and development of self-assembled complexes.
- Investigate the morphology, stability and biocompatibility of the block copolymer complexes in solution and also the analyses of their use in drug-carrying properties.