# CHAPTER II

# LITERATURE REVIEW

## 2.1 Polymer Morphology

Polymer morphology is normally referred to chain alignment in crystalline phase of semi-crystalline polymers. The chain alignment leads to various morphologies such as spherulite which grows outwardly out of the center (Figure 2.1(a)), and lamellar or in other words, the stacking organization of spherulites (Figure 2.1(b)), Fibrous polymer is a typical crystalline polymer which shish-kebab morphology represents its form of a narrow fiber (shish) followed by an overgrown lamellar shape (kebab) under the same orientational axis (Figure 2.1(b)).

The ordered structures are not only found in the crystalline polymers, but also in the amorphous ones. Block copolymer is a class of polymers which form the ordered phase, such as sphere, cylinder and lamellae through a self-assembly as will be discussed later.
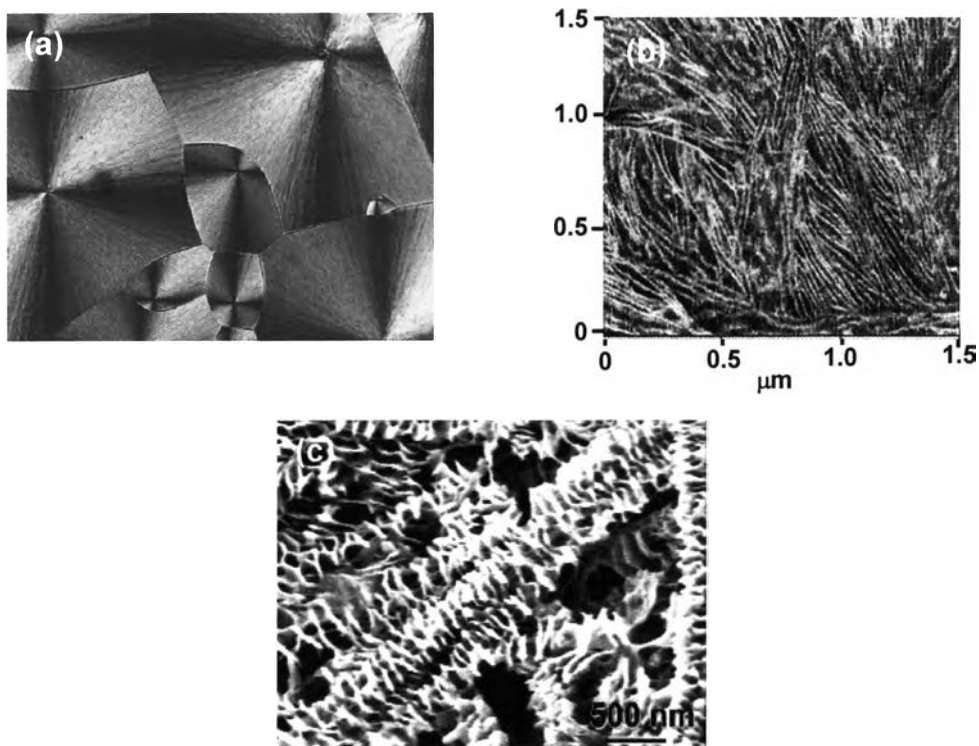
**Figure 2.1** (a) polarizing optical micrograph of spherulite of polyoxymethylene, (b) atomic force microscope (AFM) micrograph of crystalline-lamellar morphology of poly(ethylene terephthalate) (Reiter and Sommer. 2002), and (c) scanning electron microscope (SEM) micrograph of shish-kebab morphology of polyethylene (Somani et al. 2005).

## 2.2 Block Copolymer (Thermoplastic Elastomer)

Block copolymer is a macromolecule composing of two or more polymer chains orderly attached at their ends. The molecular architecture of the block copolymers can be designed and prepared in various fashions. For example, if two or more polymer chains connect together in linear sequence, they are classified as linear block copolymers (Figure 2.2(a) and (b)). While more than two polymer chains attach at a branch point, they are referred to star block copolymers (Figure 2.2(c) and (d)). A

development has been exponentially grown in the last three decades due to hybridization of material properties.

Thermoplastic elastomers (TPEs) are examples of block copolymers which contain hard segment (high-$T_g$ homopolymer: $T_g > T_r$) and soft segment (low-$T_g$ homopolymer: $T_g < T_r$). At ambient temperature, TPEs are classified as polymer alloys which behave like a rubber with glassy domains acting as physical crosslinks to enhance mechanical properties of the materials. Furthermore, it can be remolded at high temperature due to the non-covalent bond crosslinking. (Hamley 2004)
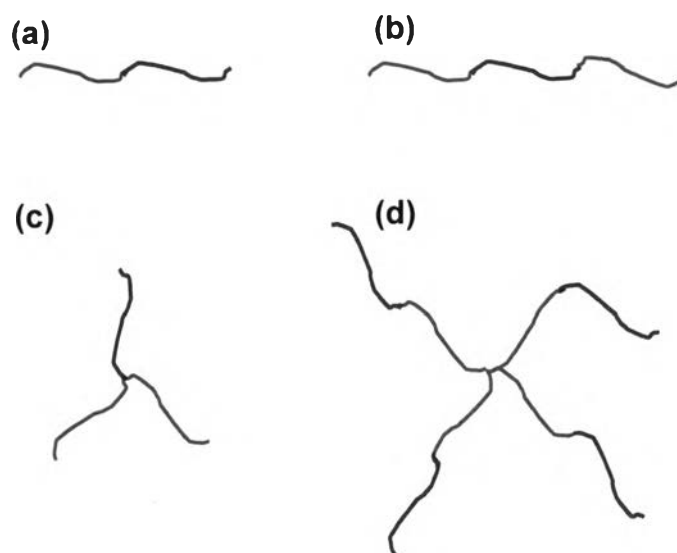


**Figure 2.2** Schematic of block copolymers represent in blue and red lines in various architectures: (a) linear AB di-block copolymer, (b) linear ABA tri-block copolymer, (c) Mixed-arm-star block copolymer, and (d) $(AB)_n$ star block copolymer.

## 2.3 Polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene triblock copolymer (SEBS)

Polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene triblock copolymer (SEBS) is one of the well-known TPEs for industrial and commercial uses. SEBS is obtained from hydrogenation of polystyrene-block-polybutadiene-block-

polystyrene triblock copolymer (SBS) which is commercially prepared by radical polymerization in solution or emulsion system. For polymerization of polybutylene in SBS, there are two possible isomers obtained from two possible addition types; 1, 4 and 1, 2 addition which yield polybutylene (PE) and polyethylene (PB), respectively, after hydrogenation as shown in Scheme 1. Thus, a middle segment of SEBS is a random copolymer of PE and PB which performs as a rubber matrix for glassy PS at ambient temperature. It leads to the excellent mechanical properties, such as toughness and impact strength based on cross-linked rubbers.

**Scheme 2.1** Possible addition reaction of PEB polymerization
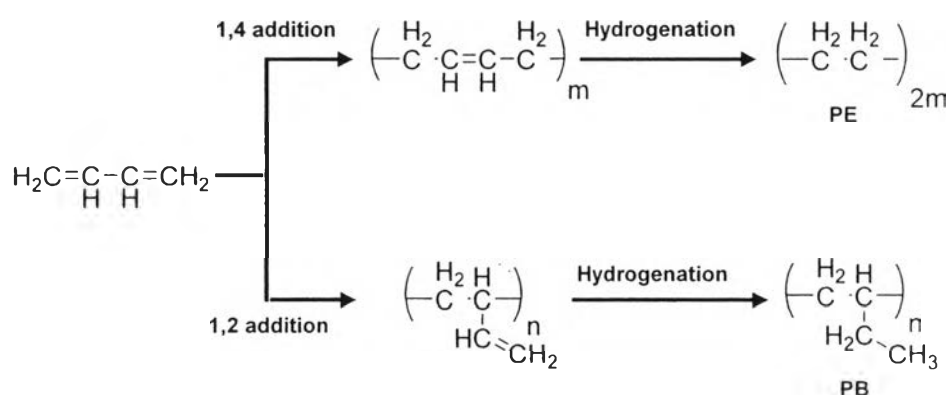


Furthermore, since only saturated bonds are presented in the structure, SEBS shows high oxidative resistance. Based on these specific structure and properties, it has been used in various applications, such as automotive parts, toys and stamping which its uses has continuously grown in the last decade.

## 2.4 Microphase Separation in Block Copolymer

Block copolymers, especially TPEs, have been extensively studied due to the advantages of their thermoplastic and elastomeric properties related to high strength and toughness. It should be noted that those advantages are from a physical cross-links of the high-$T_g$ homopolymer in the matrix of the low-$T_g$ homopolymer.

Due to the composing of different types of homopolymers in the material, a microphase separation is spontaneously formed. Basically, structure of microphase separation, microdomains, composes of three levels:

(i)    The local chemical structure of block segments.

(ii)   The individual microdomain.
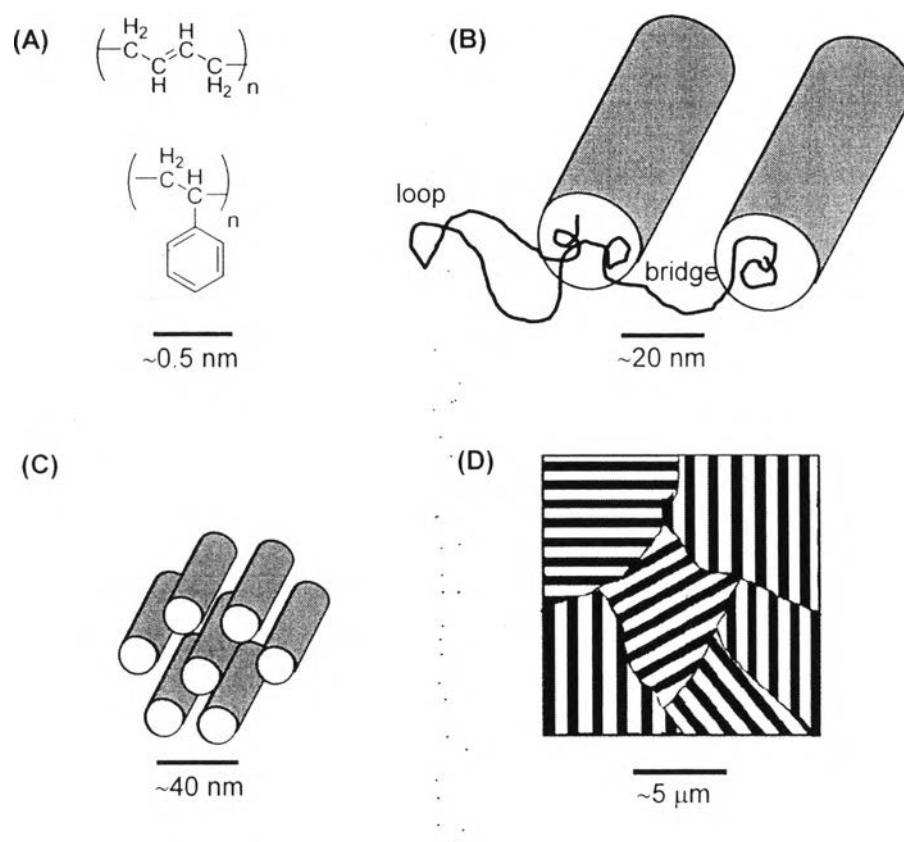
(iii)  The microdomain grains.



**Figure 2.3**  Hierarchy structure of microdomains composing of polybutadiene (PB) as majority and a minority of polystyrene (PS). (Honeker and Thomas 1996)

To clearly describe the formation of the microdomains in block copolymers, the hierarchy structure of SBS is shown as the example in Figure 2.3 the repeat unit length of PB and PS of SBS is around 0.5 nm. Due to the differences in solubility parameters of both polymers, the self-assembly between PB-rich and PS-rich

domains are formed. As in Figure 2.3, the minor PS forms into cylinder-shaped microdomains (Figure 2.3 (B)) with PB linkage; loop and bridge. Assemble of those PS microdomains grows into microdomain grain which its size is normally as high as 10 μm (Figure 2.3 (D)).

The morphology of microdomains has been reported in various ordered structures, such as spheres, cylinders, lamellae and gyroid. Conventionally, the microdomain morphology is characterized by transmission electron microscope (TEM) and small angle X-ray scattering (SAXS) as shown in Figure 2.4.
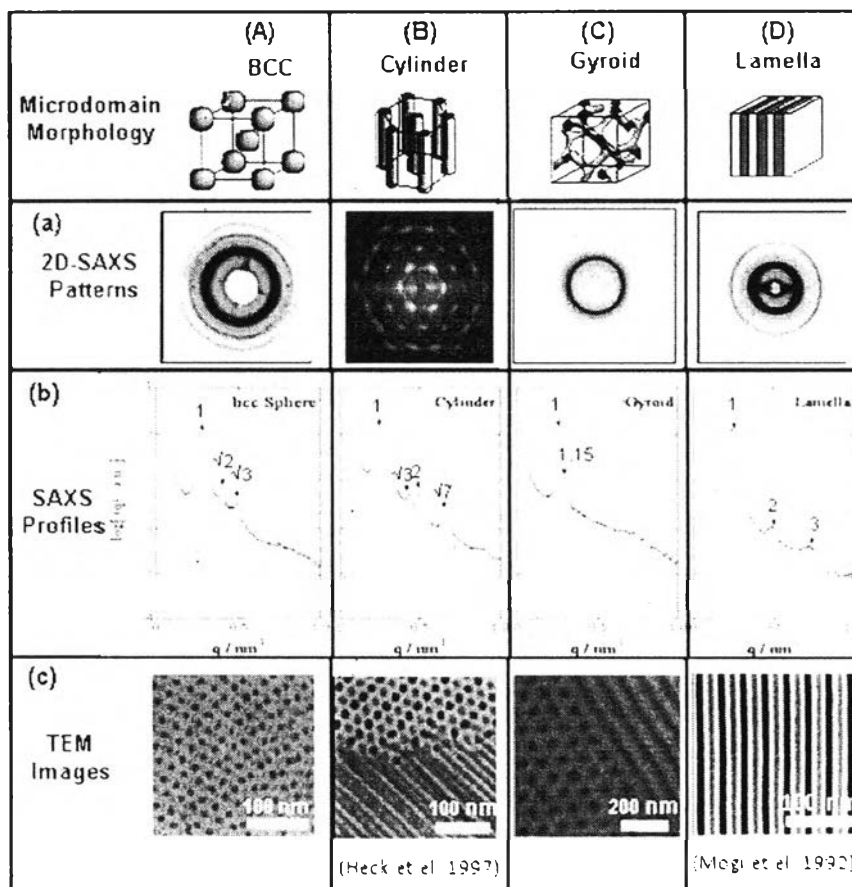


**Figure 2.4** Microdomain morphologies: (column A) BCC sphere, (column B) cylindere, (column C) gyroid and (column D) lamella with their (row a) 2D-SAXS patterns, (row b) SAXS profiles, and (row d) TEM micrographs. (Heck et al. 1997) and (Mogi et al. 1992)

The microdomain formation is governed by the interaction between A and B block as indicated by Flory-Huggin parameter ($\chi$), degree of polymerization (N) and volume fraction of A and B species in block copolymer chain. The relationship among those parameters and microdomain morphologies is shown as a phase diagram in Figure 2.5.
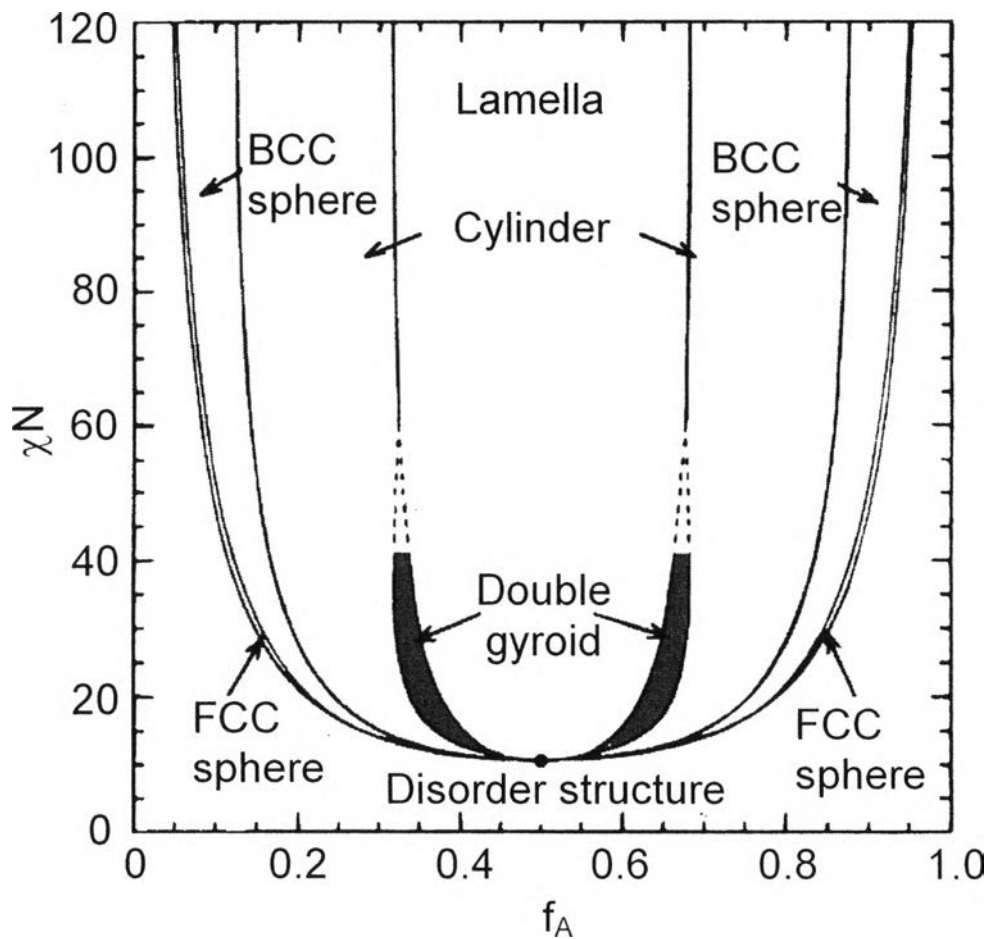


**Figure 2.5** Phase diagram of symmetrical di-block copolymer melt simulated from full mean-field theory. (Matsen and Bates 1996)

## 2.5 Electrospinning Technique for Nano-fiber Fabrication and Microphase Separation in Electrospun Fibers

The electrospinning is a versatile technique to fabricate ultra-fine fibers, possibly less than 100 nm. Two dominant forces, i.e. electrostatic and surface-tension force, play the role on control the shape and the stability of polymer jet which solidified to the fibers. At first, when a sufficient voltage is applied to the polymer solution, an electrostatic-repulsive force stretches the polymer droplet which is encountered by surface tension. At the critical point that the electrostatic force is dominant, the Taylor cone is formed before an eruption of the polymer jet as shown in Figure2.6. If a molecular cohesion is sufficient to maintain a continuous fluid jet, that fluid jet is solidified by solvent evaporation and stretched by whipping process resulting from electrostatic repulsion to yield the ultra-thin fibers.
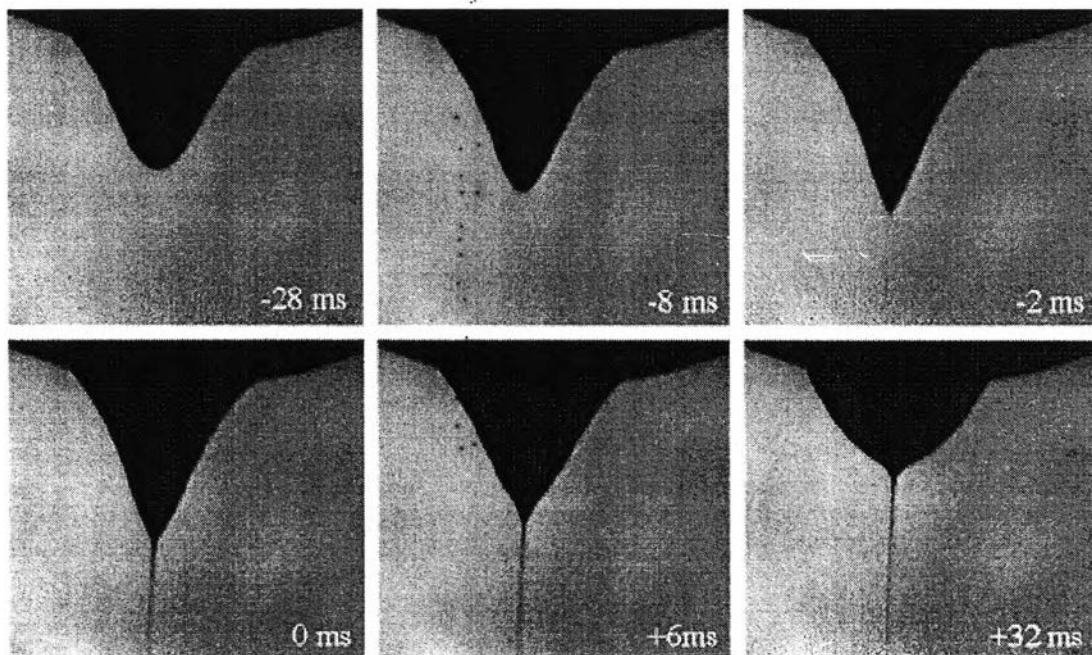


**Figure 2.6** Shape evolution of poly(ethylene oxide) solution in the electrospinning process which time zero is when the first eruption appears. (Reneker and Yarin 2008)

For the electrospun fibers of block copolymer, Fong and Reneker firstly reported a small and peculiar shape of phase-separated domain in the electrospun fibers of SBS. (Fong and Reneker 1999) Due to high evaporation rate of volatile solvents, the mobility of polymer chain was limited to end up with segregation in a thermodynamically unequilibrated microdomain structure. Kalra et al. showed the relevant results, small and disordered microdomains, which were termed as the non-equilibrium state of microphase separation, as evidenced from transmission electron microscope (TEM) images (Figure 2.7 (A)). (Kalra et al. 2006) However, the long-ranged ordered microdomains, such as lamellae (Figure 2.7 (C)) and spheres (Figure 2.7 (D)) as seen in film can be achieved by thermal annealing as reported by Ma et al. (Ma et al. 2006)
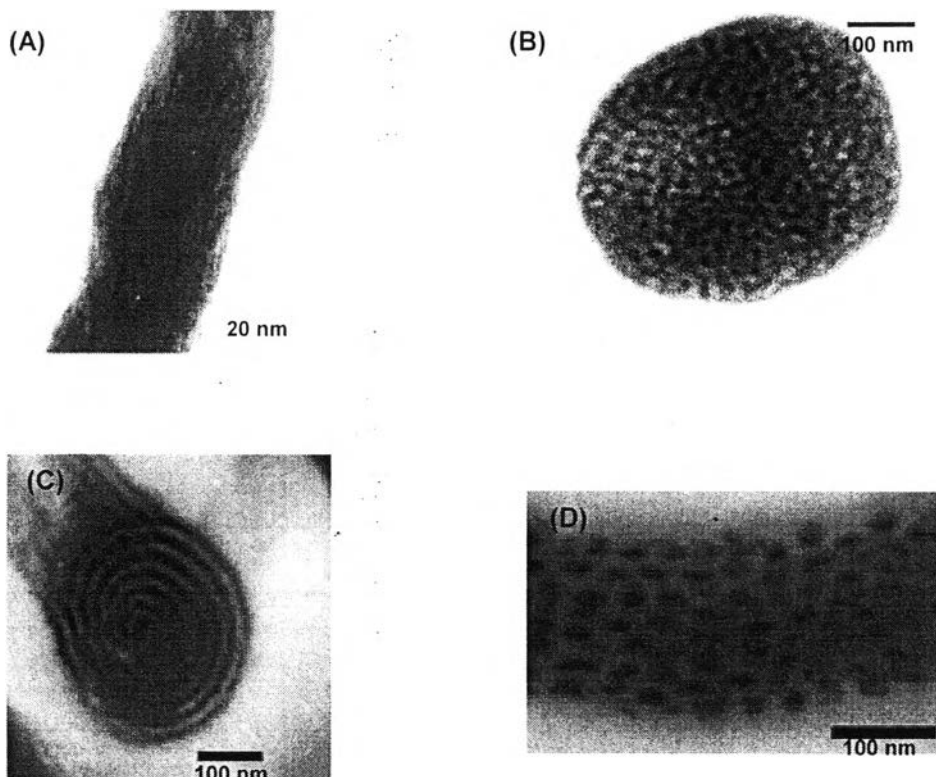


**Figure 2.7** TEM micrographs of: as-spun (A) SBS and (B) polystyrene-b-polyisoprene diblock copolymer (SI) fiber (Kalra et al. 2006); and annealed (C) SIS and (D) SI fiber (Ma et al. 2006).

## 2.6  Polybenzoxazine (polyBZ)

Polybenzoxazines (polyBZ) are recently developed phenolic-type thermosets which are obtained from thermal curing of BZ monomers. The BZ monomers can be easily synthesized from formaldehyde, amine and mono- or di-phenol through Manich reaction as schematically shown in Scheme 2.2. (Ning and Ishida 1994)

**Scheme 2.2**  Synthesis of di-phenol and mono-phenol based benzoxazine monomer
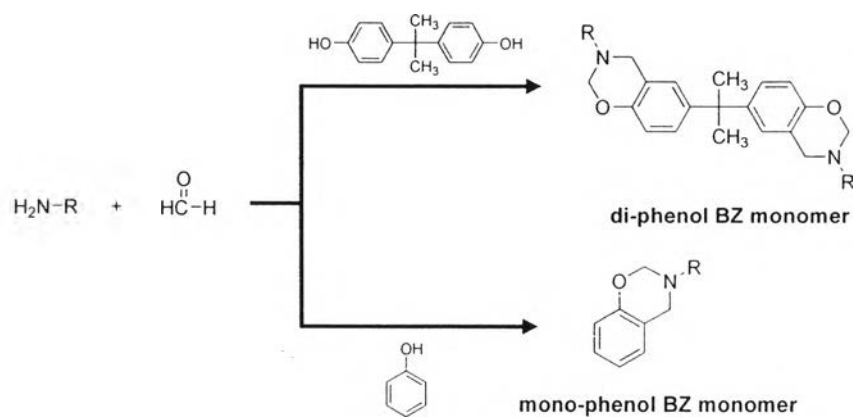


polyBZ does not show only the characteristic properties of conventional phenolic-type thermosets, performing high heat and flame resistance, but also provides the uniquely excellent properties, such as dimensional stability, low-water absorption and flexibility in molecular design. Furthermore, in curing process, any hardener or additives are not needed as the formation of polyBZ network is self initiated through oxazine-ring opening reaction (Scheme 2.3).

**Scheme 2.3** Chemical structure of di-phenol BZ monomer and its polyBZ



di-phenol BZ monomer                    polyBZ
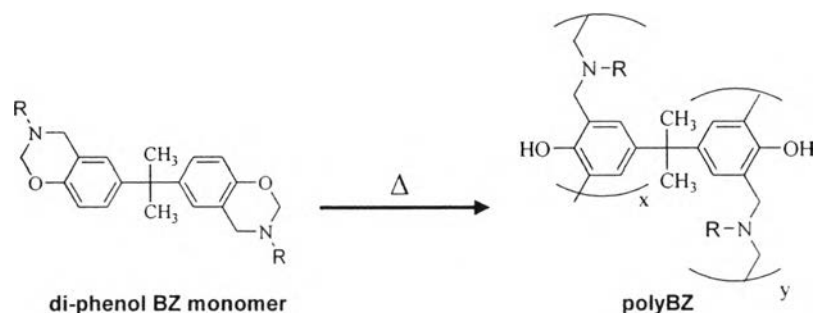
However, polyBZ has some shortcomings which are brittleness and high curing temperature (~200°C) as compared to other conventional thermosets. Furthermore, typically, polyBZ has low crosslink density has and it shows the $T_g$ around 160°C. Thus, the storage modulus dramatically drops at around that temperature. Therefore, further improvement in those properties has been continuously studied in various approaches, such as molecular modification and incorporating with inorganic materials.

## 2.7 Molecular Self-Assembly

Molecular self-assembly is a versatile tool to construct higher order structures under specific noncovalent interaction i.e., hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, and/or electrostatic effects (Figure 2.8) (Lehn 1988). Based on those specific interactions, various self-assembly structures have been continuously developed, such as deoxycholic acid (Sada et al. 2001), calixarenes (Corbellini et al. 2005) and rotaxanes (Bissell et al. 1994). Apart from those small molecules, self-assembly in polymeric materials has been reported. Mostly, amphiphilic structure is dealt with spontaneous self-assembly in polymer. Amphiphilic structure consists of hydrophilic (water-loving) parts and lipophilic (oil-loving) parts which separately organized into an

ordered structure to minimize interaction energy with two different environments (Rotello and Thayumanavan 2008). Amphiphilic polymers, such as block copolymer, graft polymer, as well as dendrimer are known to form self-assembly structure in micelle structure in solution with selective solvents or micro- or nano-phase separation in solid state.

Numerous applications from biological therapies to novel materials and electronic devices based on self-assembly concept have been reported. Gene therapy is one of the good and high performance examples which the self-assembly approach for binding the mutant gene in individual strand to form a double-helical structure through hydrogen bonding is effective.



(A)

(Sessler et al. 2003)

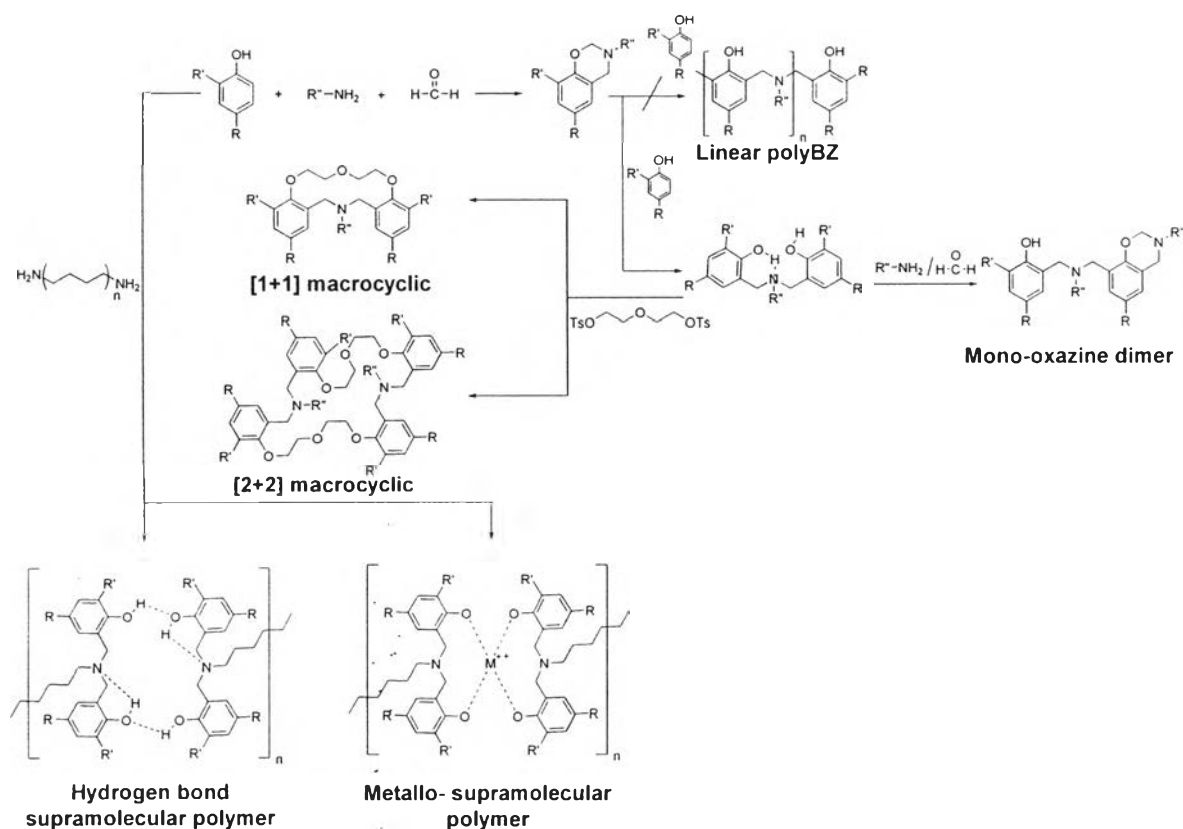(B)

(Zhao et al. 2003)

(C)

(D)
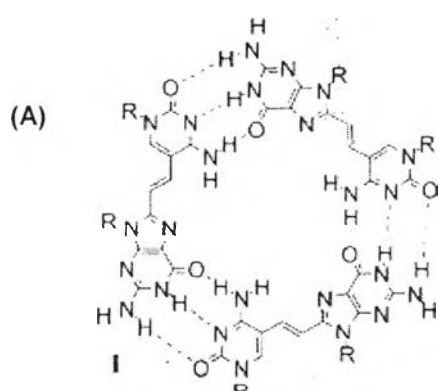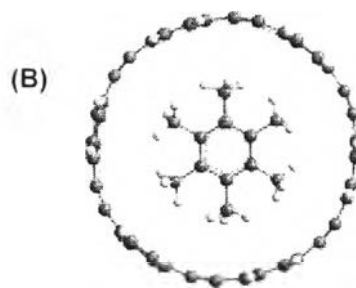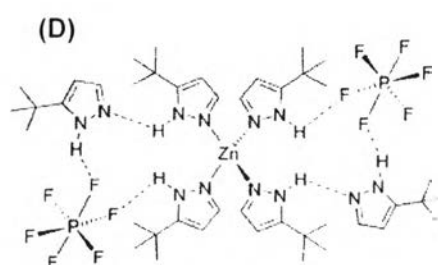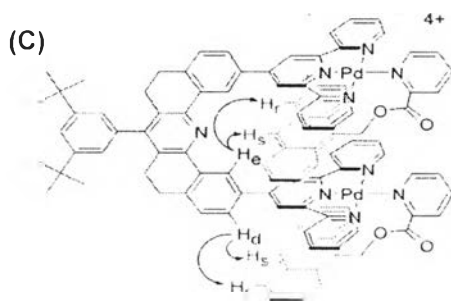
(Renard et al. 2006)

**Figure 2.8** Typical examples of supramolecular structure via: (A) hydrogen bonding (B) van der Waals forces, (C) π-π interactions and (D) metal coordination.

## 2.8 Development of Supramolecular Chemistry Based on BZ Dimers ( N,N-bis(2-hydroxybenzyl)alkylamine Derivatives (HBA))

For the past few decades, Ishida et al. has successfully developed a polybenzoxazine (pBZ), a novel class of phenolic-type thermoset resin, from bisphenol-type monomers. Considering a mono-phenol-type BZ monomer, a linear pBZ from the oxazine-opening reaction is expected. However, our group found that the reaction terminates itself to yield only the dimer (N,N-bis(2-hydroxybenzyl)alkylamine derivatives or HBAs) due to the role of inter- and intra-hydrogen bonding of aza-di-phenol structure. We originally proposed the supramolecular chemistry of HBAs with several alkaline ions which can be confirmed by spectrophotometry and single-crystal analysis. Furthermore, we also succeeded in preparing a series of aza-crown-ether derivatives from HBA and di-tosyl compounds via a simple approach, without any complicated purification resulting in a high-yield (up to 80%) product with specificity under a single species ([1+1] or [2+2]) of macrocycle. The cyclic ether performs an inclusion property with several metal ions which the cavity size enhances the guest selectivity. Recently, we have extended our work to polymer-like structure, so-called supra-polymer, via either hydrogen or metal-coordinated bonding of di-functional HBAs which show unique properties with controllable morphology.

**Scheme 2.4** Development of supramolecular chemistry of HBA in Suwabun research group



**Linear polyBZ**

**[1+1] macrocyclic**

**[2+2] macrocyclic**

**Mono-oxazine dimer**

**Hydrogen bond supramolecular polymer**

**Metallo- supramolecular polymer**

## 2.9 Polydiacetylenes (PDAs)

PDAs are known as a conductive polymer which can be polymerized in solid state, topochemically polymerized, such as in form of mono-layer film or crystal via UV- or γ- irradiation. (Wegner 1969) It results in a highly ordered orientation of ene-yne conjugated back bone of obtained PDAs. However, a preorganization of diacetylene monomer in closed-packing structure under a repeat distance ~5 Å and an orientation angle ~45°is required. (Lauher et al. 2008) Thus, alternatively, polymerization by thermal treatment in solid (Chance et al. 1978) or melt (Fomina et al. 1995) state has been reported. Due to the conjugated back bone of

PDAs, it shows unique electrical and optical properties which are promising in various applications, especially, for sensor materials.
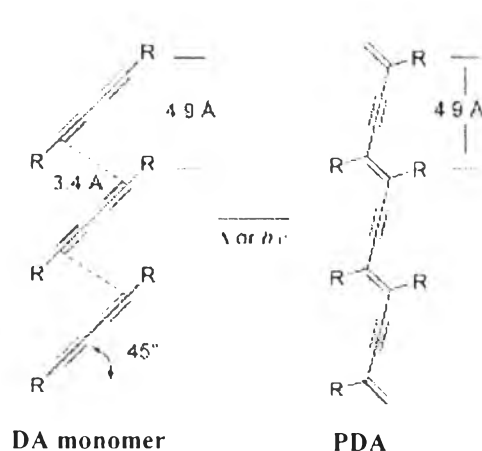


DA monomer      PDA

**Figure 2.9**    Typical preorganization of DA monomer for topochemical polymerization. (Lauher et al. 2008)

## 2.10 Points of the Research

As mentioned in 2.3, only peculiar and irregular segregated domains have been reported in the as-spun of TPEs. In Chapter III, we focus on clarification an existence of microdomains in as-spun TPEs fibers through a case study of SEBS by 2D-SAXS technique. Furthermore, an electrospinning setup equipped with high-speed rotational disk collector was used to induce the orientation of those microdomains in preferential direction. The fact that the microdomains play the role on the properties, such as strength and toughness of materials as an internal-supporting structure, the control of their alignment and orientation are important point to further develop the unique products. In Chapter IV, we focus on directing the microdomains to the SD direction via self-assembly approach. BZ monomer which is clarified to form π-π interaction with PS segments in SEBS chain shows its unique role to induce the vitrification of the PS glassy domains. This leads to an effective response to the applied external stress, i.e. drawing from high-speed disk collector, which results in the orientation of both microdomains and their grains almost parallel

to the SD. Here, the π-π interaction between BZ and PS segments not only plays the role on microdomain orientation of SEBS, but also controls the morphology of polyBZ after curing. In Chapter V, the work is extended to show that the BZ cluster is formed in the molecular pocket-like structure of PS segments via the π-π interaction, and this leads to the formation of polyBZ nano-sphere in the SEBS matrix. The results show the nano-sphere qualitatively and quantitatively formed in various BZ:SEBS ratios (from 10:90 to 90:10). This can be well explained based on the comparative studies between the specific system of BZ and SEBS and the conventional blending ones.

For five decades, topochemical polymerization in solid state of PDAs has been extensively studied due to their conjugated backbone with high ordered-packing structure. For that reasons, PDAs have been considerably received much attention for several applications, such as non-linear optical devices, molecular sensors and molecular or ion channel in other advance applications. Cyclic supramolecules, such as crown ether and calixarene, have been well known as supramolecular compounds with specific cavity which can form the molecular channel via self-assembly. By combining these two concepts, we expect to see the molecular channel with high-ordered arrangement. In the past, several PDAs based on those cyclic compounds have been reported (Shimada et al. 2000) (Lim et al. 2008), however, the preparations of those DA monomers always deal with the complicated steps and low production yield (less than 30% for crown ether preparation). In Chapter VI, we demonstrate the preparation of DA monomer containing aza-crown ether in a simple and effective approach with relatively high yield, more than 40% and 60% for crown ether and diacetylene dimer preparation steps, respectively, via the chemistry of HBAs and their cyclization. As there is no complicated purification in all synthesis steps needed, this work shows a promising preparation for DA monomer containing crown ether.