

CHAPTER I

INTRODUCTION

Polymer morphology is generally defined as the arrangement of polymeric chain to the order structures which normally refers to the crystalline structure. However, in the case of amorphous polymer, other specific morphologies, such as sphere, rod or cylinder are also reported. Self-assembly through non-covalent bonding i.e., hydrogen bonding, hydrophobic forces, van der Waals bonding, π - π interactions, and/or electrostatic effects is the key concept for polymeric morphological manipulation.

Block copolymers are also known as self-assembly materials due to an immiscibility of chemically different components. This leads to a phase separation which assembles to order-characteristic structures, microdomains, such as cylinder, lamellae, sphere and gyroid, in nano-scale range. The microdomains form the superstructure of the grains which sometimes extends to ten micrometers. It acts as an internal-reinforcing structure which affects directly to macroscopic properties of the materials. Therefore, the perfect single grain of microdomains like a single-crystal structure of small organic molecules or inorganic compounds is ideally preferred. Various techniques, such as annealing, applying stressing force, and leaving in electrical field, have been used to improve or control the microdomain perfection; i.e., microdomain orientation, unification of microdomain grains, shape of microdomains and others.

Thermoplastic elastomers (TPEs) is one type of block copolymers composing of hard segment ($T_g > T_r$) and soft segment ($T_g < T_r$). At ambient temperature, TPEs 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. Due to its specific properties, the development of TPEs including synthesis, functionalization and internal-structure architecture has grown exponentially in the last decades.

Polystyrene-block-poly(ethylene-co-1-butene)-block-polystyrene triblock copolymer (SEBS) obtained from hydrogenation of polystyrene-block-polybutylene-

block-polystyrene triblock copolymer (SBS) is one of the well-known TPEs. Due to a saturated chemical structure of SEBS chain, it yields a high oxidative resistance which has been used in various applications, such as toy, medical instruments and automotive parts. Although the morphology of microdomains has been extensively studied, the confined structure and/or the ultimate stress conditions to control the microdomain are yet to be studied.

Electrospinning is known as a versatile technique to fabricate ultrafine fibers, in nanometer scale to a few micrometers. Electrical force is used to draw the fluid jet from the needle in the time of milli-second scale. In other words, the fluid jet is pulled down to the collector with extreme stress, and solidified into nano or micro fibers. For this reason, the electrospinning is an excellent technique to control the microdomain orientation and arrangement since it is not only applying the extreme stress to the block copolymeric fluid jet, but also restraining the microdomain formation in the confined geometry, i.e. nano or micro fibers.

Fong and Reneker (1999) are the first who reported the microphase separation of the SBS in the electrospun fibers. However, they found a small and peculiar shape of microdomain in the SBS as-spun electrospinning fibers due to the high evaporation rate of volatile solvents, which limit the polymer chain mobility to segregate into a thermodynamically equilibrated microdomain structure. Since then, the performance of microdomain in block copolymer as evidenced in SBS has received much attention and several reports also showed the relevant results.

As detailed above, there is no report on an ordered-microdomain structure of TPEs in the as-spun fibers. Although much effort has been put in the direct observations by transmission electron microscope (TEM), the complicated morphologies, such as transient and fragmented structures, obstruct the clear images to clarify the morphologies. Based on this viewpoint, the present work, thus, for the first time, proposes a study case which we can easily develop microdomain by using SEBS as a material and electrospinning technique as an approach to prepare the confined structure of microfibers. The present work shows how we can apply two-dimensional small-angle X-ray scattering (2D-SAXS) to declare the short-range ordered microdomains in the as-spun SEBS fibers (Chapter III). The work also

demonstrates the way to apply an external force through a high-speed disk collector to develop the preferential orientation of those microdomains in the fibers.

Benzoxazine (BZ) thermoset is a new class of phenolic-type thermoset resin which conventional BZ monomer is synthesized from phenol derivative, primary amine and formaldehyde in either solution or melted state to form the oxazine ring through the Mannich reaction. Conventionally, BZ monomers are polymerized to polyBZ by thermal curing at high temperature at 170°C to 190°C without any curing agents or catalysts (Ning and Ishida 1994). Because of the advantages of polyBZ over traditional phenolic resin, such as no release volatiles during curing process, good mechanical properties, high thermal stability and flexibility in molecular design development in both academic research and industrial production is still received much attention and the many unique polyBZ have been reported.

For the past several years, Chirachanchai et al. have proposed the new area of benzoxazine, i.e., supramolecular chemistry. They focused on N,N-bis(2-hydroxybenzyl) alkylamine derivatives, so-called benzoxazine dimers, and showed the macrocyclization (Laobuthee et al. 2001) of these derivatives in high yield, above 80%, via a simple ring-opening reaction of para-substituted BZ monomer. The evidences that the macrocycles show host-guest inclusion based on molecular assembly with several metal ions through the studies by single crystal analysis not only confirm the supramolecular chemistry of benzoxazine dimers, but also related to the role of specific hydrogen bond network (Phongtamrug et al. 2004).

Here, it comes to our question whether the microdomains can be directed according to the stretching direction (SD) or not. The present work shows a successful case to direct the microdomain orientation by simply fixing the network of SEBS via molecular interaction using bisphenol-type benzoxazine (BZ) monomer. Chapter IV covers the studies of the molecular assembly structure of bisphenol-type benzoxazine (BZ) monomer in PS segments of SEBS chain via π - π interaction. The work extends to the clarification of microdomain orientation related to the vitrification of PS glassy domains.

The present work shows another unique phenomenon based on the π - π interaction between BZ monomer and SEBS. The work clarifies how the π - π

interaction not only enhances a microdomain orientation of SEBS, but also provides nano-specific channel for monomer entrapment. This leads us to propose a simple and direct thermoset nano-sphere preparation which the regular size can be controlled (Chapter V).

The ring-opening BZ dimers and their macrocyclic derivatives are also the points to be considered. It is a challenge to us to propose other unique benzoxazine based supramolecules including the potential properties related to the supramolecular structure. In Chapter VI, aza-crown ethers containing propargyl moiety was synthesized through oxazine-ring opening and ditosylated coupling reaction. The aza-crown ethers containing diacetylene dimers derived from oxidative coupling reaction are expected to perform topochemical polymerization by γ -ray irradiation in the crystal form. The success of the work should bring us to another novel type of highly oriented and well-aligned diacetylene polymer.