Morphological reorientation by extensional flow deformation of a triblock copolymer styrene–isoprene–styrene

Won-Ki Lee [a], Han Do Kim [b], Eun Young Kim [b],*

[a] *Division of Chemical Engineering, Pukyong National University, Pusan 608-739, Republic of Korea*
[b] *Division of Chemical Engineering, Pusan National University, Pusan 609-735, Republic of Korea*

Abstract

An oriented morphology has been generated by shear aligning a triblock copolymer SIS below its order–disorder transition (ODT) temperature. Elongational flow deformation was conducted on a polystyrene-block–polyisoprene-block–polystyrene (SIS) triblock copolymer having soft spherical microdomains composed of polyisoprene block chains in a hard matrix of polystyrene block chains with extensional rheometer (RME). The triblock copolymer has an equilibrium microphase-separated morphology of spheres (body centered cubic, BCC) of polystyrene in a polyisoprene matrix. The evolving structure was investigated with rheology, transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). The structure related to various condition of elongational flow deformation has been determined from SAXS patterns by considering separately changes in the single particle scattering, which influence the scattering patterns. The TEM and SAXS data of the film samples show that the spherical PS-domain was deformed and reoriented along the direction of elongation. It was found that the spheres microdomains are transformed into cylinder microstructures with short-range order.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Polystyrene-based triblock copolymers are widely used as thermoplastic elastomers (TPE). TPE's are composite materials having a soft, rubbery matrix in intimate contact with a hard, glassy domain. The rubbery phase accounts for the elastomeric properties while the glassy domains are the reinforcing phase that increases the modulus and yield strength of the block copolymer system. Also, TPE's have the elastomeric properties of a crosslinked rubber but can easily be processed by conventional means. Polystyrene–polyisoprene triblock copolymers (SIS), with a continuous phase of rubbery polyisoprene, have been a commercially manufactured thermoplastic elastomer for many years.

The ability of block copolymer systems to phase separate into distinct mesophase structures has been extensively studied and characterized. The phase behavior of the block copolymer systems has been found to be a function of three parameters: the volume fraction of the components, f_a; the degree of polymerization of the polymers, N; and the Flory–Huggins interaction parameter between the two polymers, χ, which is inversely proportional to temperature [1,2]. An understanding of these interactions allows us to predict the equilibrium mesophase structures of the block copolymer systems. The four equilibrium mesophase structures are spheres, cylinders, gyroids and lamella. The type of

---

* Corresponding author.
 E-mail address: ekim@pusan.ac.kr (E.Y. Kim).

structure formed, and which polymer is the continuous phase, is a function of the volume fraction of the polymers. The tendency for blocks to segregate on lowering the temperature leads to a process termed microphase separation, where separation of the components occurs into nanoscale domains. Phase separation on a macroscopic level is prevented by connectivity of the polymer chains that defines block copolymers. The transition from a homogeneous melt of ordered microphase-separated domains is called the order–disorder transition (T_{ODT}). Thermoplastic elastomers based on linear A–B–A triblock copolymers of styrene and isoprene or butadiene have been widely investigated because their simple structure makes them model copolymers, which can serve as a bases for understanding more complicated systems such as segmented multiblock copolymers. They also constitute good model systems for testing theories of polymer physics [3].

Most research has focused on the use of shear flows to orient block copolymer domains, extensional flows might be expected to be more expect. The pioneering work of Keller and co-workers [4–7] in the 1970's showed that the microdomains in block copolymers could be oriented by flow during melt processing. A large body of later works showed that orientation of block copolymers during flow is quite common: most experiments have employed either oscillatory shear [8–10] or steady shear [11,12] in parallel-plate or cone-and-plate geometries, either in specially-constructed devices or in research rheometers. In the original work of Folks et al. [6], it was noted that strong orientation occurs only in the centers of the extruded plugs: along the centerline, the flow is purely extensional, while closer to the capillary walls the flow is predominantly shear.

Uniaxial elongational rheology plays an important role in the understanding of viscoelastic properties in polymer processing such as blow molding, film molding and melt spinning. Elongational viscosity at constant strain rate increases as a function of time in two steps. The first step is a gradual increase in viscosity in the so-called linear region. This is followed by a rapid increase in viscosity in the non-linear region. The extent of the rapid increase in viscosity is defined as the non-linearity. The effects of molecular parameters, such as molecular weight, molecular weight distribution (MWD) and long chain branching, on the non-linearity have been studied [13,14].

We have studied a polystyrene–polyisoprene triblock copolymer which exhibits the sphere morphology. To investigate the effect of the block copolymer to the deformation behavior, we conducted RME measurements using a triblock copolymer. And we observed of the results of the RME study on the elongation flow behavior of the triblock copolymer melt of SIS between the glass transition of PS domain ($T_{g(PS)}$), ~110 °C and T_{ODT}, ~180 °C. The oriented sample produced by RME is submitted to a uniaxial extensional deformation experiment and the evolution of the microdomain structure during deformation is observed.

2. Experimental

2.1. Material

The sample studied here is a polystyrene-block–polyisoprene-block–polystyrene (SIS), Kraton D1107 of Shell Development Company. This commercial SIS is widely used in pressure-sensitive adhesive formulations contains 15% styrene by weight. Size exclusion chromatography (SEC) indicates that the as-supplied SIS contains approximately 20 wt.% uncoupled diblock. It has a number-average molecular weight M_n = 175.000 g/mol and polydispersity index M_w/M_n = 1.49, where M_w is weight-average molecular weight.

2.2. Rheology

Three times the linear viscoelastic transient viscosity, $3\eta_0(t)$, was measured in a Rheometric Mechanical Spectrometer RMS 800 at a shear rate of $\dot{\gamma} = 0.001 \ s^{-1}$ at 170 °C on a cone and plate type rheometer. The Rheometric Scientific RME is a commercial version of the extensional rheometer. Samples were prepared from pellets, which were melted at 150 °C and compression molded to make plate like samples with dimensions of $\approx 8 \times 1.5 \times 60$ mm. The sample is placed between the belts of the RME and allowed to melt. A flow of inert gas through the air table suspends the sample between the belts. And then the sample was extended with a various strain rates (0.03–1 s^{-1}) and temperatures (110–180 °C).

2.3. Small angle X-ray scattering

Small angle X-ray scattering (SAXS) was performed using a Rigaku rotating anode X-ray generator producing CuKα radiation (λ = 1.542 Å). Samples consisted of films between 1.0 and 2.0 mm in thickness. Sample-to-detector distance ranged from 1 to 2.30 m. The resulting two-dimensional images were averaged azimuthally to obtain trace of intensity versus the scattering were vector $q[q = (4\pi/\lambda)\sin(\theta/2)$, θ: the scattering angle].

2.4. TEM

A Reichert Ultracut microtome was used to obtain ultrathin sections 60 nm for transmission electron microscopy (TEM). The ultrathin sectioning of the quenched specimens was performed by cryo-ultramicrotomy at −120 °C, below the glass transition temperature (T_g = −68 °C) of polyisoprene (PI), to attain the