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The effect of casting temperature on morphology of poly(styrene-ethylene/butylene-styrene) triblock copolymer

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Abstract

The morphology of poly(styrene-ethylene/butylene-styrene) (SEBS) triblock copolymer films cast from the solution in xylene at different temperatures was investigated by transmission electron microscope. The SEBS solution was first heated to a certain temperature, which ranges from 20 to 140°C and then cast onto the surface of phosphoric acid at the same temperature to prepare specimen films. Three different kinds of morphologies including coexistence of a large number of branched cylinders and a small number of spheres, coexistence of cylinder region and near homogenous region, and coexistence of non-branched cylinders and spheres were observed corresponding to 20, 80–110, and 130–140°C temperature zones, respectively. Moreover, it was found that the diameter of cylinders increases with the casting temperature. All these show an obvious casting temperature dependence of the microphase separation phenomenon. © 2001 Published by Elsevier Science Ltd.

Keywords: Casting temperature; Poly(styrene-ethylene/butylene-styrene); Morphology

1. Introduction

Morphology of block copolymers has attracted widespread attention for the past three decades because it is responsible for the valuable mechanical properties of these systems [1]. It is fundamental that its particular microphase separation structure is due to the incompatibility between the connected different block chains. For a given block copolymer, it has been known that techniques such as using different cast solvents [2], adding its homopolymer [3], annealing [4] and shearing [5] can change its morphology. One aspect that needs additional investigation is the temperature dependence of the microphase separation [6]. In the earlier works by Shibayama et al. [7] and Hashimato et al. [8] performed by small-angle X-ray scattering (SAXS) technique, it was found that the interdomain distance D decreases with an increase in temperature, which may be interpreted as a consequence of decreasing segregation power of different block chains. Later, Gohil [6] reported the temperature dependence of the phase separation morphology using transmission electron microscopic (TEM) technique. It was shown that with increasing temperature, there is an intermixing tendency of the two-phase components of the block copolymer that may result in phase inversion.

In this study, we report a relatively easier method of preparing the block copolymer thin films (<100 nm) at a wide range of temperature for the TEM observation, whose potential use for studying the temperature dependence of phase separation seems bright. By using the technique, the phenomenon of casting temperature dependence of morphology is found, which to our knowledge has few reports so far.

2. Experimental

The SEBS triblock copolymer Kraton G-1650 is a commercial product of Shell. The molecular weight M_n, polydispersity and styrene content are 7.5×10^4, 1.36 and 27%, respectively [9].

In order that a wide range of casting temperature could be investigated, a neutral solvent, xylene whose boiling point is around 141°C and a liquid cast substrate, phosphoric acid whose boiling point is much higher than 141°C are chosen. Moreover, since phosphoric acid is a mutual solvent of

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Table 1
The film forming time at different casting temperatures

Temperature (°C)	20	80	100	110	130	140
Time (s)	<1000	<14	<10	<8	<4	<2

water, it can be easily removed from the surface of the cast films with water.

The specimens for TEM observation were prepared as follows: to begin with, the SEBS powders were dissolved into xylene to make 0.5 wt% solution. The 0.5% SEBS solution and phosphoric acid were heated to the same temperature, respectively. The solution was dripped onto the surface of phosphoric acid at the same temperature. After dripping, the container of the cast solution was covered quickly with a watch glass to somewhat slow down the solvent evaporation rate and the time was recorded simultaneously till the specimen films were formed completely (see Table 1); next, as soon as the film was formed, these thin films cast at different temperatures were quickly transferred from the phosphoric acid surface to distilled water surface at room temperature (a quenching process for the specimen films cast at high temperature) and rinsed with distilled water to get rid of residual phosphoric acid; finally they were transferred further to copper grids and stained by RuO_4 vapor.

The TEM equipment for observation was mode H-800 from Hitachi using an accelerating voltage of 100 kV. According to the obtained TEM micrographs of the films cast at different temperatures, the corresponding diameters of polystyrene (PS) cylinders were measured by scale microscope. The measurements were performed at least five times at different spots for one image to have the mean value.

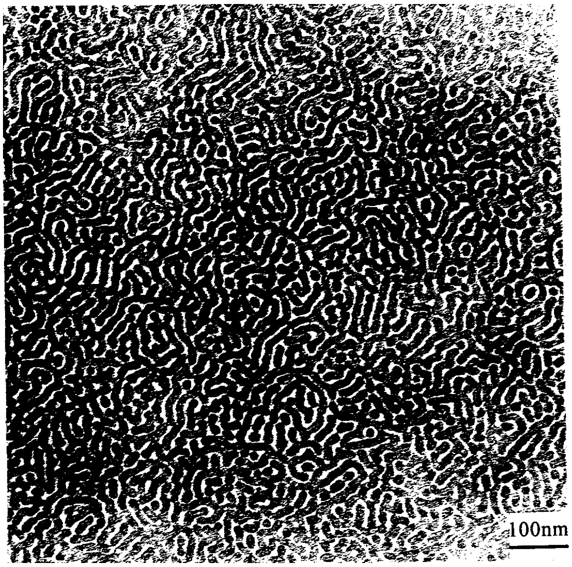

Fig. 1. Electron micrograph of the specimen cast at 20°C (rt).

3. Results and discussion

Solution-cast technique to prepare block copolymer films involves two competitive processes between phase-separation kinetics and vitrification due to the evaporation of the solvent. Because vitrification prevents the phase separation from developing fully, the morphology of the solution-cast film is usually in non-equilibrium state [10], especially when the film forming process is very quick at a high casting temperature as in our case (see Table 1). Although the non-equilibrium morphological pattern makes theoretical approach difficult, the temperature dependence of microphase separation phenomenon shown in our experiment is beyond doubt.

Fig. 1 shows an electron micrograph of the SEBS film cast at 20°C (room temperature). The dark regions [11] correspond to the PS microdomains selectively stained with RuO_4 vapor, and the bright region corresponds to the rubber phase. The coexistence of a large number of PS cylinders, mostly with branches and a small number of PS spheres in the rubber matrix can be seen.

Figs. 2–4 are electron micrographs of the SEBS films cast at 80, 100 and 110°C, respectively. It can be seen that the images obtained at the three temperatures are much alike and quite different from the one cast at room temperature (Fig. 1). In the above-mentioned three cases, all the TEM images exhibit two representative regions denoted as A and B. Region A exhibits a relatively well-developed microphase separation morphology, and long PS cylinders arraying in a near order state is the characteristic of this region. Region B dose not show any clear structure, which means that in this region vitrification takes place before the microphase separation process so that a near homogenous structure is preserved. Considering that the polymer pair can phase separate by spinodal decomposition (SD) or nucleation and growth (NU) mechanism depending upon composition and temperature, and that the pattern development in NU is much slower than in SD [12], we deduce that the phase separation mechanism for the film cast at the

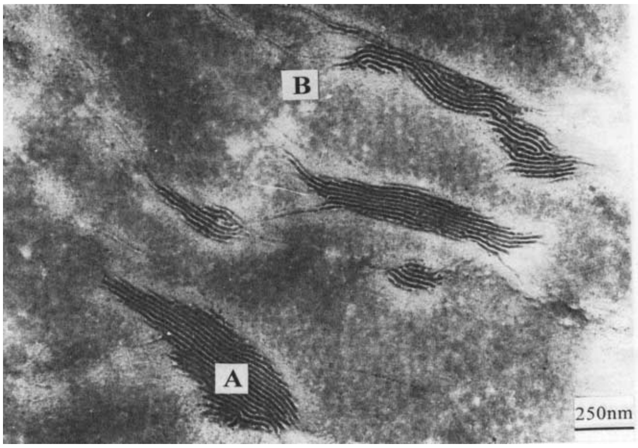

Fig. 2. Electron micrograph of the specimen cast at 80°C.

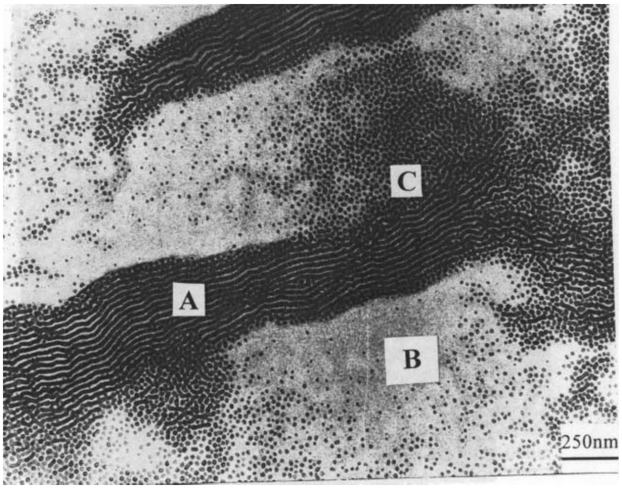

Fig. 3. Electron micrograph of the specimen cast at 100°C.

above three temperatures is the NU mechanism based on the phenomena of the coexistence of region A and region B. The fast vitrification process pins down the slowly developed NU process at some middle stage resulting in the structure seen in the solid films. Moreover, in Figs. 3 and 4, a clear transitional boundary denoted as region C consisting of the PS spheres and the very short PS cylinders between region A and B is observed. It seems that region A enlarges itself through first forming region C, and then gradual incorporated region C into itself. This provides further evidence for the NU mechanism.

Figs. 5 and 6 show electron micrographs of the SEBS films cast at 130 and 140°C, respectively. At a glance, the two images seem to be somewhat different because the discrete PS domains in Fig. 5 are denser than those in Fig. 6. However, by comparing the two images closely, we find that they are the same because both the micrographs show a similar coexistence of the irregular short PS cylinders and the spheres. The reason for the seemingly density difference of the PS domains between the two images is that the TEM images are projections through the specimens [13] and a dense and overlapped image (see Fig. 5) can be given when the specimen contains multiple layers of microdomains. Thus, the density difference is result of the thickness difference of the specimens rather than their structure difference.

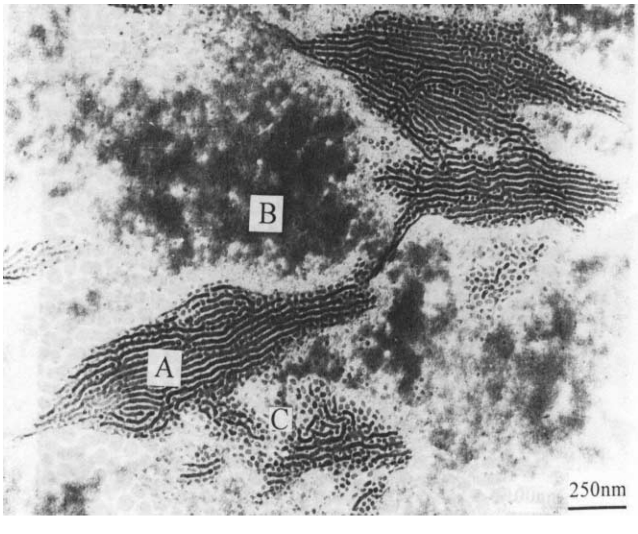

Fig. 4. Electron micrograph of the specimen cast at 110°C.

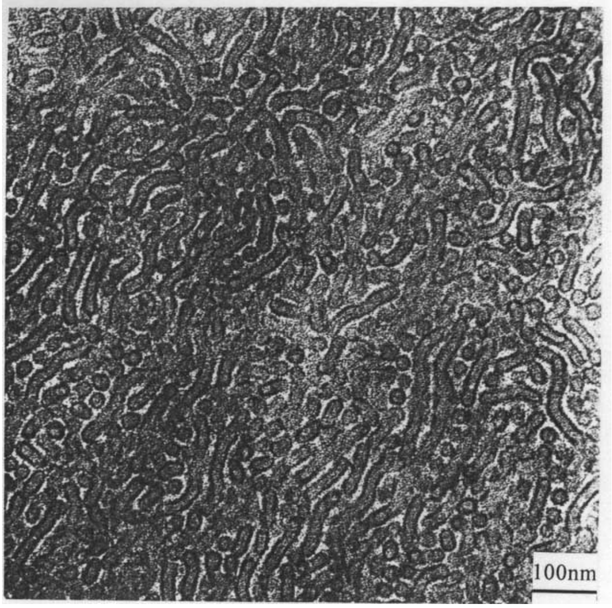

Fig. 5. Electron micrograph of the specimen cast at 130°C.

In addition, it is found that the diameter of the PS cylinders increases with the casting temperature (see Fig. 7). The result is basically in agreement with the report of Gohil [6] in a similar study, but not following the SAXS research

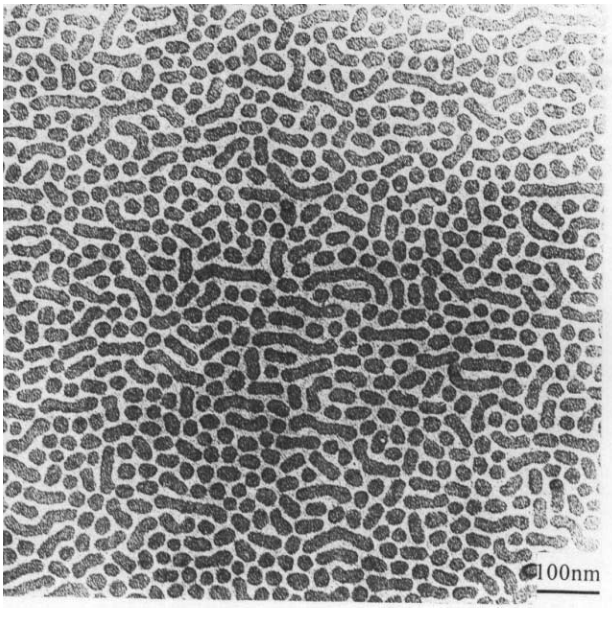

Fig. 6. Electron micrograph of the specimen cast at 140°C.

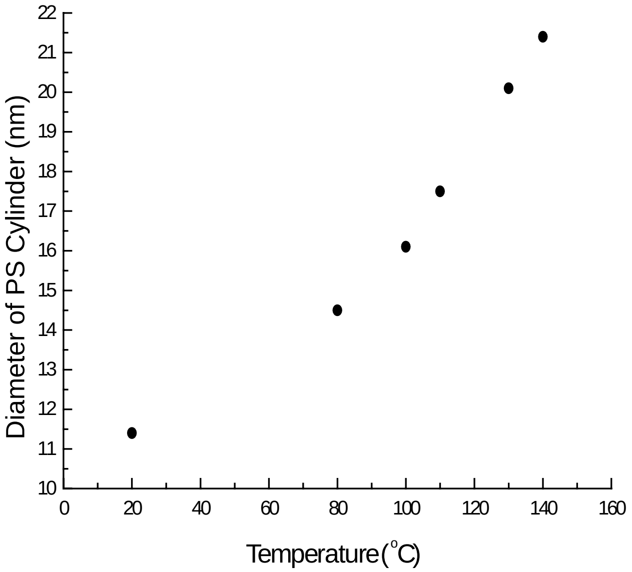

Fig. 7. Casting temperature dependence of the diameter of PS cylinders.

results [7,8]. It should be noted that the results of inter-domain distance *D* decrease with increasing temperature obtained by SAXS is at a constant concentration in equilibrium state. So, it may be true for the initial cast stage in our system. However, during the film forming process, the concentration increases resulting in an increase in the *D* value due to an increase in the segregation power between different block chains in a neutral solvent system [8,14]. In other words, it is possible that at higher temperatures, the flexibility of polymer chain increases, so vitrification tends to pin down the morphology at higher concentrations, which favors a larger domain size. Further evaporation of the solvent process causes a shrinkage of the domain size due to a non-equilibrium effect [14,15]. The higher the pinning down concentration, the smaller the shringkage, which also favors a larger domain size. So, herewith we assume that the effect of high pinning down concentration, which leads to an increase in the domain size, outweighs the effect of high temperature, which leads to a decrease in the domain size. Another possible reason for the increase in the domain size at higher temperature is that with increasing temperature the interfacial area grows larger (intermixing effect) due to a decrease in the segregation power [8], so stains of not pure PS domain may lead to increasing diameter phenomenon [6]. A more conclusive explanation needs further investigation.

In conclusion, with an increase in the casting temperature, both the domain pattern and the domain size changes that show an obviously temperature dependence of the microphase separation phenomenon.

Acknowledgements

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