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A new control method of segregation power between block chains in block copolymers and their order-disorder transition

Shigeru OKAMOTO*[1], Yasuyoshi Fujii[1], Shinichi SAKURAI[2], Junichi OKU[1]
[1]Nagoya Institute of Technology, Gokiso, Nagoya 466-8555, Japan
[2]Kyoto Institute of Technology, Goshokaido, Sakyo-ku, Kyoto 606-8585, Japan

Introduction

Thermally induced morphological transition and phase-separation transition of block copolymers have been studied by many researchers. However, the transition mechanism near transition temperature is not well understood. In the studies of the transitions of block copolymers, fraction of each block and temperature are chiefly used as the variables. As to each block itself, those employed in most of studies consist of a single component and only its molecular weight has been used as a variable. Here we want to survey the effects of the monomer sequence of a block chain such as azeotrope copolymer on the phase structures and its transition mechanism.

Previously, we found that styrene (St) and benzyldimethylvinylsilane (BDMVS) undergo azeotrope copolymerization anionically in some condition [1,2], which yields a " random " copolymer (i.e. , NOT a tapered one). Since the anionic polymerization of BDMVS and the copolymerization of these monomers are quasi-living, various block copolymers each block chain of which has any composition of constituent components can be prepared.

Such versatility in the block copolymerization enables us to vary the miscibility between the blocks continuously and widely. In order to reveal phase transition mechanism of these copolymers, time-resolved Small-Angle X-ray Scattering (SAXS) experiments upon temperature sweep (T-sweep) was performed. Two types of copolymers (H-H and H-R, where H and R denote homopolymer and random copolymer, respectively) was employed.

Experimental

Materials

A polystyrene (PS)-*block*-polybenzyldimethylvinylsilane (PBDMVS) diblock copolymer (hereafter denoted as SB), and the diblock copolymers consisting with PS and random copolymers of PS-*co*-PBDMVS (R), i.e., PS-*block*-R diblock copolymers (hereafter denoted as SR), were synthesized. Here the total mole fraction of St units in the PS block chains of these diblock copolymers was set constant, 50 mol%, while the mole fraction (ϕ) of St units in the random copolymers was varied from 5 to 30 mol%. The total molecular weights of these block copolymers were kept constant ca. 35000 g/cm^3. These materials were first desolved in the benzene solution with the concentration about 5 wt. %. Gradually the solvent was evaporated and the film specimen was obtained after the complete drying.

Methods

T-sweep SAXS experiments were carried out to investigate a transition temperature between ordered phase and disordered phase with increasing temperature. The scattering intensity was measured with a one-dimensional detector, Position-Sensitive Proportional Counter (PSPC).

Results

The specimen with ϕ=30 mol% had only one T_g, which implies PS and R phases were molecularly mixtured to form disordered one phase. Contrarily, the specimens with ϕ < 30 had T_g's around 60°C and 25°C, which correspond to T_g'S of PS and R, respectively. This means that these two components phase-separated to form micro-phase separated domains. For these specimens, T-sweep SAXS was performed to show they exhibit the order-disorder transition and the transition temperatures.

The inverse SAXS intensity, I^{-1}, against the inverse Temperature, T^{-1} successfully showed the ϕ-dependence of the miscibility between the PS and R block chanis. According to the theory by Leibler, and that by Fredrickson and Helfand, the order-disorder transition of the specimen with ϕ = 5 mol% was observed arround 129°C (T_{ODT}), while the deviation from the linear relationship between I^{-1} and T^{-1} was observed about 135°C (T_{MF}). This result means that the concentration fluctuation of the system was well-described by the mean-field theory above T_{MF}, while the deviation can be attributed to the fluctuation effect. The discontinuity at T_{ODT} means that the structural formation and extinction took place at this temperature. As we had expected, the T_{MF} and T_{ODT} decreased with increasing ϕ. This can be explained by the decrease of the segregation power between the two constituent block chains.

References

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* okamoto@mse.nitech.ac.jp