

Features of Microphase-Separated Structures in Asymmetric Triblock Copolymers A₁-B-A₂

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Introduction

Equilibrium behavior of ABA triblock copolymer with different lengths of end-block A chains was examined using self-consistent field theory (SCFT) by Matsen.[1] It was found that at small asymmetries, the A block bidispersity reduces the stretching energy of the A domains. This effect causes a slight increase in the domain spacing and shifts the order-order transitions (OOTs) toward higher A volume fractions. At large asymmetries, a significant number of the short A blocks pull free of their domains allowing their B blocks to relax. This effect produces a much greater increase in domain spacing and shifts the OOTs toward lower A volume fractions. We experimentally examined that a feature of microphase-separated structure of poly(methyl acrylate) (PMA)-*b*-polystyrene(PS)-*b*-PMA asymmetric triblock copolymer. Small-angle X-ray scattering reveals the microphase-separated structures. Molecular mobility of middle PS blocks and short A chains is directly detected by DSC and ESR, respectively. These measurements give evidence of the solubilization of short A chains to the B domains.

Experimental

Samples. Asymmetric ABA (PMA-*b*-PS-*b*-PMA) triblock copolymers were synthesized by ATRP. Prepared triblock copolymers were listed in Table 1. Short PMA chain was partially spin-labeled with 4-amino-TEMPO to detect its molecular motion.

Measurement. SAXS measurement was performed at beamline BL-9C and 15A in Photon Factory (PF) of the High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. A modulated-temperature differential scanning calorimetry (MDSC, MDSC 2920) manufactured by TA Instruments was used. Modulation amplitude of 1.5 K and a period of 60 s were used at a heating rate of 2 K/min. The calorimeter was calibrated with an indium standard. ESR spectra were observed at low microwave power level to avoid power saturation and with 100 kHz fielded modulation using JES-RE1XG spectrometers (X-band). The signal of 1,1-diphenyl-2-picrylhydrazyl was used as a *g* tensor standard. The magnetic field was calibrated with the well-known splitting constants of Mn²⁺.

Table 1. Characteristics of Asymmetric Triblock Copolymers

code	M_{nMA}^a	M_{nPS}^a	M_{nMA}	PDI ^b	ϕ_{PS}^c	Mor ^d
MS ^e	10500	17500	-	1.12	64	L
MSM1.5	10500	17500	1500	1.17	61	C
MSM2.0	10500	17500	2000	1.14	59	L
MSM3.6	10500	17500	3600	1.15	56	L
MSM4.5	10500	17500	4500	1.16	55	L

^a number average molecular weight of PMA and PS, obtained by SEC, calibrated polystyrene standards ^b M_w/M_n , ^c volume fraction of PS obtained by ¹H NMR, ^d Morphology confirmed by SAXS, ^e diblock copolymer (precursor)

Result and Discussion

Morphology. Diblock copolymer MS (precursor of ABA) showed a lamellar morphology as predicted its volume fraction 64%. In the case of the triblock copolymer MSM, volume fraction of PS increases toward 50 % with adding short PMA chain as shown Table 1. Therefore, a lamellar phase is expected to be kept for MSM samples. MSM2.0, MSM3.6, and MSM4.5 indicated the lamellar morphology, in contrast; MSM1.5 did not show a lamellar but a cylindrical morphology. This can be explained by the assuming that the short PMA chain was pull into the PS domain and apparent volume fraction of PS phase (PS rich phase) resulted in increasing. This feature is really consistent with the prediction by Matsen [1]. We here tried to

observe a change in molecular mobility of the polymer chains in order to elucidate the solubilization of short PMA chain to PS domain. Taking advantage of a large difference of the glass transition temperature of PS and PMA, we will discuss the phase behavior from the viewpoint of molecular dynamics. If the short PMA chains is pulled into PS domain, the glass transition temperature T_g of PS rich phase should decrease as compared with the PS pure domain (e.g. PS phase in diblock copolymer MS and PS homopolymer). Additionally, the molecular mobility of the short PMA chain solubilized in PS hard domain should decrease in comparison with PMA pure domain. At large asymmetry (MSM1.5), a significant decrease of glass transition of PS phase was observed, which reasonably indicating the mixing the short PMA chain with PS blocks. The T_g of the PS phase is assumed to obey the Fox relation that is often used for a miscible polymer blend, it is suggested that almost all short PMA chains should be solubilized into PS phase, which was consistent with the result from the SAXS profile. Separately, molecular mobility of short PMA chains was investigated by ESR spin-label method. Calculated correlation time τ was obtained from the temperature dependent ESR spectra. As decreasing M_n of short PMA chain, the τ decreases. At large asymmetry (MSM), the τ drastically changed and increased, indicating that the molecular mobility was slowing down. This reduction of the mobility was concluded to be caused by the solubility of short PMA chains to PS phase.

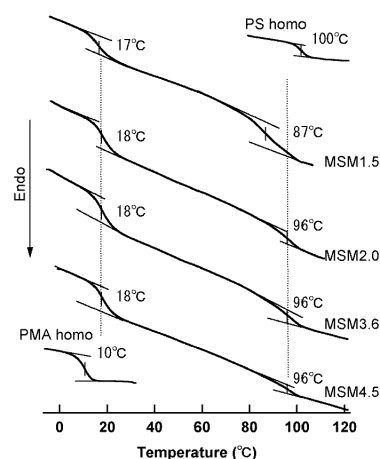


Figure 1. DSC thermogram of PS, PMA, and MSM samples.

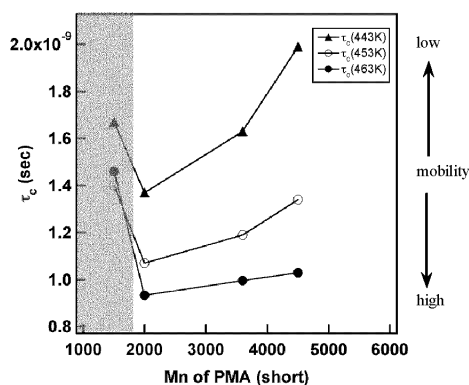


Figure 2. ESR correlation time of MSM samples.

Conclusions

We elucidated features of asymmetric ABA triblock copolymer using SAXS, DSC, and ESR measurements. ESR selective spin-labeling revealed the miscibility of PS and short PMA. Our experimental results strongly support the equilibrium behavior reported by Matsen.

References

[1] Matsen, M. W. *J.Chem.Phys.* **1999**, *113*, 5539.