새로운 Closed-Loop 상거동을 가지는 블록공중합체

류두열 [a], 정운용 [a], 김진곤* [a], **Thomas P. Russell** [b]

[a] 포항공과대학교 화학공학과

[b] University of Massachusetts, Amherst, MA01003

Closed-Loop Phase Behavior in Block Copolymers

Du Yeol Ryu [a], Unyong Jeong [a], Jin Kon Kim* [a] and Thomas P. Russell [b]

[a] Department of Chemical Engineering and Polymer Research Institute
Pohang University of Science and Technology, Kyungbuk, 790-784, Korea

[b] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA01003

Introduction

Block copolymers have widely used in industry and science as their self-assembled materials.[1~5] The ability to separate between each block unit gives these materials ingenious structures in nano-scale lamella, cylinder, sphere etc. This microphase separation of a block copolymer can be driven by the enthalpy of repulsive interactions or the entropy of negative volume change on mixing between block units. Here we introduce the novel diblock copolymer with closed-loop phase behavior which is composed of lower critical ordering transition (LCOT) and then upper critical ordering transition (UCOT) on heating process. The control of these two transition zones in a block copolymer let it be able to utilize as a smart material.

Experimental

Diblock copolymers composed of polystyrene and poly(n-pentyl methacrylate) were anionically polymerized on symmetric composition with narrow polydispersity.

The characteristics of copolymers are given Table 1. BCL-Ⅱ,Ⅲ are prepared by solution mixing of BCL-Ⅰ,Ⅴ to induce proper transition zones. These two samples are not affected negligibly by the dependence of each owing to little molecular weight difference between BCL-Ⅰ and Ⅴ, as given polydispersity data.

Small angle x-ray scattering experiments were done as synchrotron source at 4C1 beam line, Pohang Light Source using the wavelength, 0.1608 nm equipped a monochromatic device.

Table 1 Characteraction of block copolymers

sample code	Mn	Mw / Mn	f_{PS} (weight %)
BCL-Ⅰ	46470	1.01	50.1
BCL-Ⅱ	48720	1.01	50.1
BCL-Ⅲ	48860	1.01	50.1
BCL-Ⅳ	49900	1.01	50.1
BCL-Ⅴ	51250	1.01	50.1

Rheological measurements are powerful methods to detect thermal transitions between an ordered and disordered state of block copolymers as viscoelastic materials. These measurements with parallel plates of 40mm diameter were performed as a dynamic temperature and a dynamic frequency sweep within linear viscoelastic range.

Result & Discussion

Figure 1a gives the linear scale scattering intensity of BCL-Ⅳ as a function of the scattering vector $q = (4\pi/\lambda)\sin\theta$, where λ is wavelength q the scattering angle, shifted by 2.5℃ with increasing temperature. These profiles were acquired as circular average value of q with 2d-ccd detector. At temperatures below 139℃, typical weak and broad peaks are observed indicating a disordered block copolymer melt. As, however, passed at this temperature, the first-order Bragg peak becomes intense and sharp. This observation indicates that on heating process BCL-Ⅳ gives a disorder-to-order transition driven by entropic contribution which corresponds to LCOT. Initial ordered peak maximum is $q = 0.272\ nm^{-1}$

corresponding to Bragg spacing of 23.1 and 23.4 at increased temperature of 210℃. On further heating, these strong peak are weak and broad at 220℃ which means a typical order-to-disorder transition block copolymer melts by the reduction of unfavorable enthalpic interaction which means UCOT.

The competition between enthalpic and entropic contribution of this diblock copolymer melt endows it two distinct transitions namely LCOT and UCOT specially resulting in a connected closed-loop phase diagram

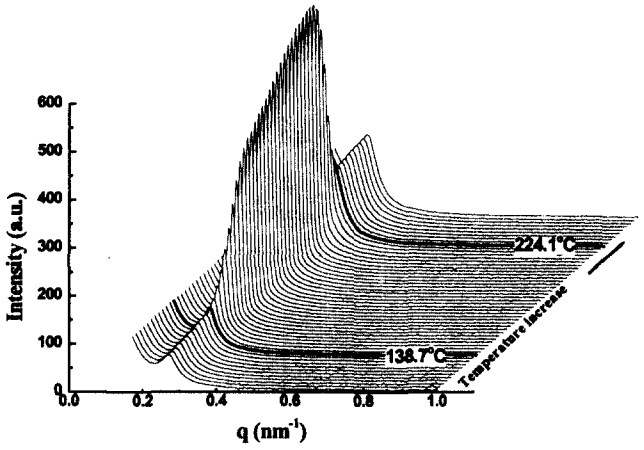

Figure 1. Small angle x-ray scattering for B-IV P(S-b-nPMA) as a function of the scattering vector at various temperatures with a 2.5 °C increment. For clarity, two SAXS profiles with the corresponding temperatures are shown in bold

When the specific interaction does not exist between two block segments, the thermal expansion stemmed from negative volume change on mixing drives disorder-to-order transition named as at increased temperature unusually.

Russell et al. reported LCOT for the first time in a diblock copolymer of polystyrene-b-poly(n-butyl methacrylate).[6~8] These diblock copolymers have order-to-disorder transition at

lower temperature and disorder-to-order transition at higher temperature, respectively. When the molecular weight is low, the phase behaviors give two separated UCOT and LCOT diagram. Hourglass type phase diagram was described in case of higher molecular weight. Here our study show that competing between the enthalpic and entropic contribution in a diblock copolymer melt give two transitions named LCOT and UCOT both resulting in closed-loop phase behavior which does not appear in the most block copolymers so far.

References

1. Paul, D. R. & Newman, S. in *Polymer Blends* (Academic Press ,1978).
2. Sanchez, I. C. in *Polymer Compatibility and Incompatibility*, Solc K. (ed.) (MMI press, 1980).
3. Koningsveld, R., Stockmayer, W. H. & Nies, E. in *Polymer Phase Diagram* (Oxford Univ. Press, 2001).
4. Bates, F. S. & Fredrickson, G. H. Block copolymers thermodynamics: theory and experiment. *Annu. Rev. Phys. Chem.* 41, 525-557 (1990).
5. Hashimoto, T. in *Thermoplastic Elastomers*, Legge, N. R., Holden, G. & Schroeder, H. E. (ed.) (Hanser, New York, 1987).
6. Russell, T. P., Karis, T. E., Gallot, Y. & Mayes, A. M. A lower critical ordering transition in a diblock copolymer melt, *Nature* 368, 729-731 (1994).
7. Pollard, M., Russell, T. P., Ruzette, A. V. G., Mayes, A. M. & Gallot, Y. The effect of hydrostatic pressure on the lower critical crdering transition in diblock copolymers. *Macromolecules* 31, 6493-6498 (1998).
8. Ruzette, A.V. G., Banerjee, P., Mayes, A. M., Pollard, M., Russell, T. P., Jerome, R., Slawecki, T., Hjelm, R. & Thiyagarajan, P. Phase behavior of diblock copolymers between styrene and n-alkyl methacrylates. *Macromolecules* 31, 8509-8516 (1998).