

Supporting Information

Tuning the Phase Behavior of polystyrene-*block*-poly(*n*-alkyl methacrylate) Copolymers by Introducing Random Copolymer for Methacrylate Block

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1. Randomness of the Pn(O-*r*-M)MA block

We synthesized Pn(O-*r*-M)MAs at various polymerization times, and each aliquot was extracted and characterized. Figure S1a indicates SEC traces for all the extracted samples. With increasing time, the total molecular weight of the random copolymer increased steadily up to 70 min and then saturated. The change of the molecular weight and the composition with reaction time is summarized in Table S1. The molecular weight was determined from the calibration curve based on PS standards. Since the composition changes very little with reaction time, we consider that the synthesized Pn(O-*r*-M)MA is regarded as a random copolymer, not tapered (or block) type copolymer.

Figure S1b shows DSC thermograms of three polymers of PMMA, PnOMA, and Pn(O-*r*-M)MA. Pn(O-*r*-M)MA showed a single glass transition temperature (T_g) of $\sim 17^\circ\text{C}$, which is between that of PnOMA ($\sim -20^\circ\text{C}$) and PMMA ($\sim 132^\circ\text{C}$). When the Fox equation was used ($1/T_{g,\text{Pn(O-}r\text{-M)MA}} = w_{\text{PnOMA}}/T_{g,\text{PnOMA}} + (1 - w_{\text{PnOMA}})/T_{g,\text{PMMA}}$, in which w_{PnOMA} is the weight fraction of the PnOMA in the random copolymer), w_{PnOMA} was calculated at 0.66, which is similar to that from NMR analysis. This result also supports that synthesized Pn(O-*r*-M)MA is a random copolymer.

However, one might raise the question that even though the synthesized Pn(O-*r*-M)MA is tapered (or block) copolymer, a single T_g could be observed when the molecular weight of Pn(O-*r*-M)MA is small and becomes disordered state. To exclude this possibility, we

carried out turbidity experiment of 70/30 (wt/wt) PnOMA/PMMA mixture. The molecular weight and polydispersity are 3200 and 1.05 for PnOMA, and 1500 and 1.07 for PMMA. The blending ratio was selected to be similar to that in the synthesized Pn(O-*r*-M)MA (PnOMA/PMMA ~ 70/30(wt/wt)).

Figure S1c is an optical microscopy image of this mixture at 220 °C, from which the macrophase-separated morphology was observed even at 220 °C, which suggests poor miscibility between PMMA and PnOMA. If the synthesized Pn(O-*r*-M)MA with a molecular weight of 138,000 and a weight fraction of PnOMA having 0.65 (thus, the molecular weight of PnOMA and PMMA in the Pn(O-*r*-M)MA is ~28 times larger than that of PnOMA and PMMA used in turbidity experiment) had been tapered (or block copolymer), it should have exhibited the microphase separated morphology, resulting in two T_g s for PnOMA and PMMA. Since a single T_g was observed for the synthesized Pn(O-*r*-M)MA with a molecular weight of 138,000, as shown in Figure S1(b), the turbidity experiment confirms again that the synthesized Pn(O-*r*-M)MA is not a block or tapered copolymer but a random copolymer.

Table S1. Molecular characteristics of extracted Pn(M-*r*-O)MAAs at different polymerization times

Polymerization Time	M_n	PDI	Composition wt% (POMA/PMMA)
1min	10000	1.09	61/39
3min	16000	1.06	62/38
6 min	24000	1.06	63/37
12 min	40000	1.05	62/38
22 min	61000	1.05	62/38
31 min	76000	1.05	63/37
70 min	136000	1.05	64/36
2 h	138000	1.05	65/35
5 h	138000	1.05	65/35

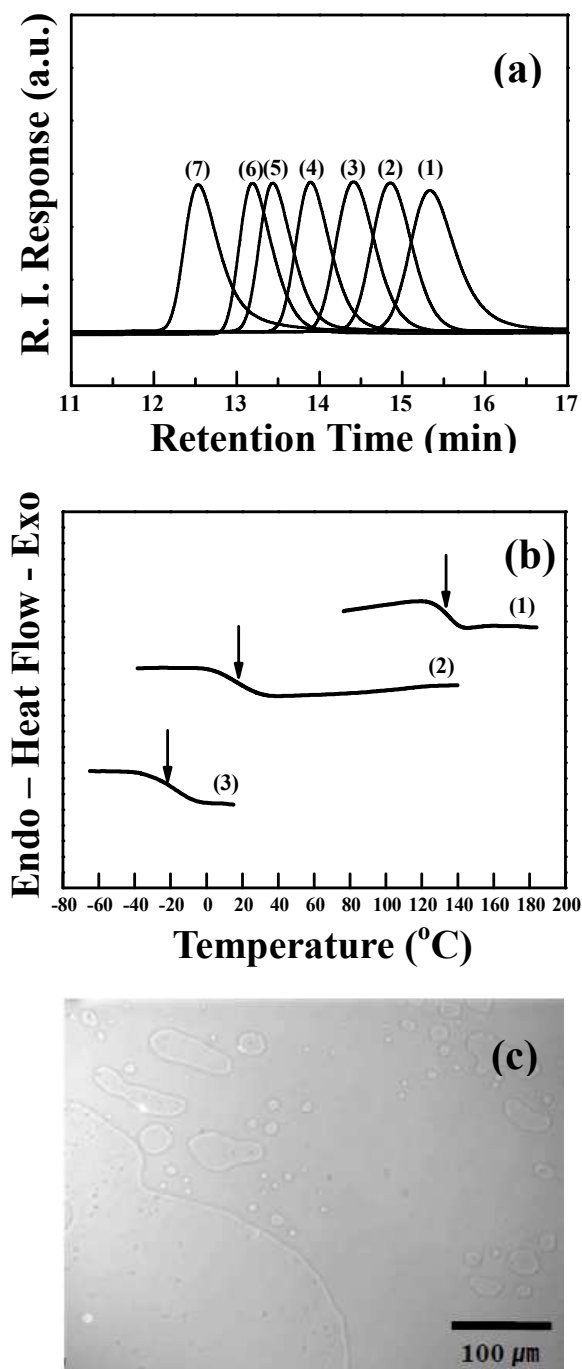


Figure S1. (a) SEC traces of Pn(O-*r*-M)MA aliquots at various polymerization times (min): (1) 1 , (2) 3, (3) 6, (4) 12, (5) 22, (6) 31, and (7) 70. The SEC traces at reaction times of 2 h and 5 h are essentially the same as those at 70 min. (b) DSC thermograms of (1) PMMA, (2) Pn(O-*r*-M)MA, and (3) PnOMA. (c) OM image of the mixture of 70/30 (wt/wt) PnOMA/PMMA at 220°C.

2. Birefringence result for PS-*b*-Pn(O-*r*-M)MA-B2.

To confirm again that the SAXS peak corresponds to the microdomain lattice, not a correlation hole effect, we performed the birefringence experiment. When a block copolymer having lamellar or cylindrical microdomains becomes an ordered state, it gives a non-zero birefringence. Figure S2 gives temperature dependence of birefringence for PS-*b*-Pn(O-*r*-M)MA-B2, from which a distinct birefringence was observed between 190 to 250 °C. Thus, the LDOT and UODT of PS-*b*-Pn(O-*r*-M)MA-B2 are 190 and 250 °C, respectively, which is consistent with the results given in Figures 1b and 2b. Therefore, the SAXS peak in Figure 2a corresponds to the microdomains, not to the correlation hole effect.

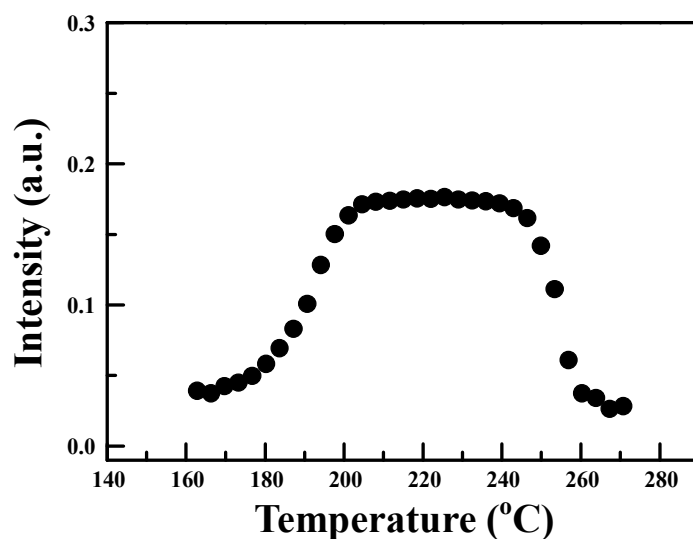


Figure S2. Temperature dependence of birefringence for PS-*b*-Pn(O-*r*-M)MA-B2

3. Detailed explanations of employed theory and calculation of transition temperature for PS-*b*-Pn(O-*r*-M)MA

To predict the closed-loop phase behavior observed for PS-*b*-Pn(O-*r*-M)MA, the effective Flory interaction parameter χ_F was considered. It is in general divided into two terms, χ_{app} and χ_{comp} . χ_{app} is the dimensionless exchange energy density, and expressed by $\chi_{app} \propto \Delta\epsilon/T$, where $\Delta\epsilon$ is the typical exchange energy between like (ϵ_{ii}) and dislike monomers (ϵ_{ij}). If a directional interaction (DI) exists between two monomers, ϵ_{ij} is modified to be $\epsilon_{ij} + \delta\epsilon$ due to the pair-wise energy increment. χ_{comp} arises from the finite compressibility, which is given by $\chi_{comp} \propto [\partial P/\partial\phi]^2/B_T$, where $\partial P/\partial\phi$ is the derivative of pressure with respect to composition (ϕ) and B_T is the bulk modulus of the copolymer.¹

If $\delta\epsilon$ is significant as for PS-*b*-PnAMA with $n = 2$ to $n = 5$, $\Delta\epsilon$ becomes negative at lower temperatures. However, the entropic penalty to make DI increases greatly at higher temperatures, which causes nondirectional interactions to become more important; thus $\Delta\epsilon$ becomes positive. χ_{app} starts to decrease beyond a certain temperature due to thermal energy, around which it becomes the maximum. χ_{comp} is substantial if $\partial P/\partial\phi \neq 0$. Also, with the increase of temperature the diminished B_T gradually increases χ_{comp} . Therefore, χ_F still possesses a maximum. Such a temperature dependence of χ_F corresponds to the closed-loop type phase behavior.

If $\delta\epsilon$ is insignificant as for either PS-*b*-PMMA or PS-*b*-PnAMA ($n \geq 6$) including PnOMA, $\Delta\epsilon$ is insensitive to temperature. In this case, χ_{app} (and also χ_F) decreases with increasing temperature, which is the ODT type phase behavior.

To explain the closed-loop phase behavior for the PS-*b*-Pn(O-*r*-M)MA copolymer, we employ a Hartree (fluctuation correction) analysis based on a compressible random-phase approximation (RPA) approach. Equation-of-state (EOS) properties for polymers are incorporated into the theory by using an off-lattice EOS model by Cho and Sanchez,^{2,3} which requires ij -interaction ϵ_{ij}/k , theoretical monomer diameter σ_i , and a composite parameter $(N\pi\sigma^3/6M)_i$ representing N/M ratio. Here, the symbols k , N , and M denote the Boltzmann constant, chain size, and molecular weight, respectively. We consider the random

copolymer block as an internal mixture and the subsequent diblock copolymer as an external mixture. There is a need for some mixing rules for the description of mixtures. σ for the mixture adopts the Lorentz mixing rule ($\sigma = (\sigma_A + \sigma_B)/2$), which is the simplest and does not give an additional contribution to the composition derivatives of thermodynamic functions. The cross interaction parameter ϵ_{ij} is taken around Berthelot's rule ($(\epsilon_{ii} \epsilon_{jj})^{1/2}$). It has been given for PS and PMMA that $\epsilon_{PS}/k = 410.7$ and $\epsilon_{PMMA}/k = 438.8$ K with fixed $\sigma_i = 4.04$ Å.⁴ As $\partial P/\partial \phi \sim [\epsilon_{AA} - \epsilon_{BB}]$ for the symmetric copolymer,¹ the similar values of ϵ_{PS} and ϵ_{PMMA} give PS-*b*-PMMA having a small pressure dependence of their ordering temperatures (8 – 20 °C/1000 bar) due to small χ_{comp} .^{4,5} For PnOMA, if the volume data of neat PnOMA⁶ and a fixed σ_{PnOMA} of 4.32 Å are used to obtain ϵ and N/M , ϵ_{PnOMA}/k is 326.3 K. As $\epsilon_{PnOMA} \ll \epsilon_{PS}$ (or ϵ_{PMMA}), PnOMA homopolymer is much more compressible than PS (or PMMA). This would make PS-*b*-PnOMA to exhibit large baroplasticity. However, the experimentally measured pressure coefficient of PS-*b*-PnOMA was very small ($dT_{ODT}/dP = -5$ °C/kbar).⁵ Such a small value might be due to the change of the conformation of n-octyl chains of PnOMA. Namely, n-octyl chains in the PS-*b*-PnOMA would have more collapsed conformation compared with those in neat PnOMA because of the large disparity in the self interaction between PS and PnOMA. In this situation, the pressure response on the free volume would decrease significantly because the collapsed PnOMA chains would become less penetrable upon pressurization. It would be an interesting work to check by molecular simulation (or dynamics) whether this argument is valid.

Thus, in this study, we used the enlarged spherical monomers of PnOMA to have $\sigma_{PnOMA} = 4.9$ Å, which gives us the refitted ϵ^*_{PnOMA}/k of 378.3 K. The reduced $|\epsilon_{PS} - \epsilon^*_{PnOMA}|$ decreases $\partial P/\partial \phi$ for PS-*b*-PnOMA to yield small baroplasticity. This simple argument on PS-*b*-PnOMA is tentative, because in our model polymer chains are assumed as perturbed hard sphere chains. A better study on this particular block copolymer might require the description of specific monomer conformation as in the lattice cluster theory by Freed et al.⁷⁻¹⁰

As discussed qualitatively in the main text, Pn(O-*r*-M)MA is treated as a pseudo-homopolymer having averaged molecular parameters. We assume that the averaged self interaction parameter for Pn(O-*r*-M)MA with f_j being the volume fraction of either PMMA or PnOMA is given by

$$\epsilon_{\text{Pn(O-}r\text{-M)MA}} = \epsilon_{\text{PnOMA}} f_{\text{PnOMA}}^2 + \epsilon_{\text{PMMA}} f_{\text{PMMA}}^2 + 2 (\epsilon_{\text{PnOMA}} \epsilon_{\text{PMMA}})^{1/2} f_{\text{PnOMA}} f_{\text{PMMA}} \quad (1)$$

Strict Berthelot's rule ($\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2}$) leads to eq (1), where the desired amounts of MMA and nOMA are mixed to make Pn(O-*r*-M)MA. For $N\pi\sigma^3/6M$ of the random copolymer, the arithmetic mean value is used, which is the adaptation of the simplest Lorentz rule. When f_{PnOMA} is fixed to 0.65, the parameter set for Pn(O-*r*-M)MA is given as $\epsilon_{\text{Pn(O-}r\text{-M)MA}}/k = 363.8$ K, $\sigma_{\text{Pn(O-}r\text{-M)MA}} = 4.18$ Å, and $(N\pi\sigma^3/6M)_{\text{Pn(O-}r\text{-M)MA}} = 0.41458$ cm³/g, which are close to those of PnPMA as 368.1 K, 4.04 Å, and 0.43073 cm³/g, respectively. σ and $(N\pi\sigma^3/6M)$ for the final diblock copolymer adopt the Lorentz-type rule again. At this point, ϵ_{12} and $\delta\epsilon$ are still required. If we assume that the average force field generated by Pn(O-*r*-M)MA is similar to that by PnPMA, the corresponding parameters for PS-*b*-PnPMA would fit here as $\epsilon_{12}/(\epsilon_{\text{PS}} \times \epsilon_{\text{Pn(O-}r\text{-M)MA}})^{1/2} = 0.983$ and $\delta\epsilon/\epsilon_{\text{PS}} = 0.185$.^{11,12}

References

- (1) Cho, J. *Polymer* **2007**, *48*, 429.
- (2) Cho, J.; Sanchez, I. C. *Macromolecules* **1998**, *31*, 6650.
- (3) Cho, J. *Macromolecules* **2000**, *33*, 2228.
- (4) Ryu, D. Y.; Shin, C.; Cho, J.; Lee, D. H.; Kim, J. K.; Lavery, K. A.; Russell, T. P. *Macromolecules* **2007**, *40*, 7644.
- (5) Ruzette, A. V. G.; Mayes, A. M.; Pollard, M.; Russell, T. P.; Hammouda, B. *Macromolecules* **2003**, *36*, 3351.
- (6) Song, K. H.; Kwon, K. W.; Cho, J. *Macromol. Res.*, accepted (2009).
- (7) Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5076.

- (8) Dudowicz, J.; Freed, K. F. *Macromolecules* **1993**, *26*, 213.
- (9) Dudowicz, J.; Freed, K. F. *Macromolecules* **2000**, *33*, 5292.
- (10) Freed, K. F.; Dudowicz, J. *Adv. Polym. Sci.* **2005**, *183*, 63.
- (11) Cho, J. *Macromolecules* **2004**, *37*, 10101.
- (12) Moon, H. C.; Han, S. H.; Kim, J. K.; Li, G. H.; Cho, J. *Macromolecules* **2008**, *41*, 6793.