Control of Block Copolymer Microdomain: In-Situ and Real-Time SANS Studies of Polymerization-Induced Self-assembly of Block Copolymer Microdomain Structure

Satoshi Koizumi[1,a], *Kazuhiro Yamauchi*[2], *Hirokazu Hasegawa*[2], *Hirokazu Tanaka*[1,2], *Ryuhei Motokawa*[1], *and Takeji Hashimoto*[1,2,a,b]

[1]Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki-ken 319-1195, Japan, and [2]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Introduction

In this study, we shall investigate "reaction-induced self-assembling process" of an AB diblock copolymer during living anionic polymerization process as a general problem in the interface between Chemistry (reaction at specific sites) and Physics (reaction-induced self-assembly at specific sites). Up to now, living-anionically synthesized block copolymers (bcp's), which are reaction-terminated and hence "dead" in a sense, have been used to study their self-assembling behaviors. In this case, the total degree of polymerization (DP) N and composition f ($= N_A/N$, N_A being DP of A block sequence) values are fixed during the course of the experiment. However, what would happen if we use a "living" polymer system for our study, instead of the reaction-terminated polymer? We can change χ, N, and f with the progress of the polymerization reaction. Here χ is net repulsive interactions between two block chains in the reaction medium. Controls of reactions in the living polymer system may allow finer controls of the domain structure than the conventional methods.

Polymerization-induced microphase transition is quite interesting in terms of morphology control. For instance, when the microphase separation occurs during the polymerization, the living ends of bcps are confined in one side of the microphases (A or B microdomains in the case of AB di-bcp). A further polymerization after the microphase separation occurs in the specific sites of so-called confined nano-space (microdomain structure). As a example, let us consider the case where polymerization of AB di-bcp has completed, and the living ends still exist in the cylindrical microphase rich in B of AB di-bcp. If a further polymerization of C monomer occurs in the B cylindrical microdomains by adding C monomer (in this case, ABC triblock terpolymer is produced), new C microdomains embedded in B cylinders may appear in the A matrix phase. The morphology created here may be generally considered as non-equilibrium, metastable one and hence may not be necessarily the same as that expected for the corresponding synthesized (and reaction-terminated) ABC triblock terpolymer formed from disordered state. Thus, there is a large possibility to create a new microdomain structure by utilizing polymerization-induced microphase transition. Moreover, if we can directly observe this self-assembling process, we will be able to stop polymerization at the stage when a desired morphology is attained. Thus direct observation of self-assembling process may bring a breakthrough for manipulation of morphology.

In this paper, we would like to report the preliminary results of our time-resolved SANS study of the living anionic polymerization process of polyisoprene-*block*-poly(styrene-d_8) (PI-*block*-dPS) in benzene-d_6 as a solvent. Since SANS contrast depends on the scattering length density of substances, only non-deuterated isoprene units (I) are highlighted in this system because hydrogen atoms have negative scattering length, while deuterium atoms have positive scattering length. In a non-polar solvent such as benzene, it is well known that the anionic reactivity of isoprene (I) is much larger than that of styrene (S). Therefore, we can observe not only the growth of non-deuterated I, but also the reaction of deuterated S after consumption of I by means of SANS. This is the first report of our studies on the *in-situ* observation of self-assembling process induced by a living anionic polymerization.

[a] Corresponding author. Tel.: +81-29-284-3833; Fax: +81-29-282-5939;
E-mail address: hashimoto.takeji@jaea.go.jp (T. Hashimoto) & koizumi.satoshi@jaea.go.jp (S. Koizumi)
[b] Present address; Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki-ken 319-1195, Japan

Experiments

The living anionic polymerization was carried out under dry argon atmosphere in a baked glass tube as a reaction vessel equipped with a three-way stopcock and a magnetic stirring bar. All reagents were transferred into the vessel via dried syringes through the three-way stopcock against a dry argon stream. The synthesis procedure in this study was as follows: A mixture of I, S-d_8, and benzene-d_6 in the ratio of 1:1:2 by weight was introduced into the vessel under dry argon atmosphere at room temperature. A measured amount of cyclohexane solution of *sec*-butyllithium was added to the mixture via the syringe technique, which gave a light yellow color of isoprenyl anion. In a non-polar solvent, it is well known that the anionic reactivity of I is much larger than that of S, resulting in the formation of PI-*block*-dPS bcp even when the two monomers coexist.

As soon as *sec*-butyllithium was added to the mixture, a part of the mixture solution was extracted and introduced into a quartz cell for SANS measurement under dry argon atmosphere. Immediately, time-resolved SANS measurement was started with the SANS-J instrument installed at 20 MW JRR-3 research reactor at JAEA, Tokai, Japan. Cold neutrons were monochromatized with a velocity selector to have the mean wavelength λ of 0.70 nm and $\Delta\lambda / \lambda = 0.12$. The solution under living anionic reaction in the quartz cell was kept at 30°C without stirring during time-resolved SANS measurements. Characteristics data of PI-*block*-dPS synthesized in this study was shown in Table I. The results suggest that a well controlled polymerization was attained with our method.

Table 1. Characteristics of PS-*block*-PI diblock copolymer

	$M_n \times 10^{-5}$	M_w/M_n	Composition[a]
PS-*block*-PI	1.41	1.03	1:1

[a] The weight ratio of PS:PI.

Results

Figure 1 shows the change in the SANS profiles with reaction time during the living anionic polymerization of I/S-d_8 mixture in benzene-d_6. Scattering intensity is plotted in logarithmic scale against magnitude of scattering vector q ($q = (4\pi/\lambda)\sin(\theta/2)$ where λ and θ are the wavelength of neutrons and the scattering angle, respectively). The scattering profiles in Figure 1 were obtained at $t = 6333$, 19602, 29851, 31375, 32107, 32716, 41512, and 50034 s after injection of the initiator; the initiation of polymerization was set at $t = 0$ s. Figure 1 includes the scattering profile before polymerization ($t = 0$) also. These changes in the scattering profiles shown in Figure 1 suggest that the primary structure of the polymer chains and their higher-order structure dramatically changed during the polymerization process.

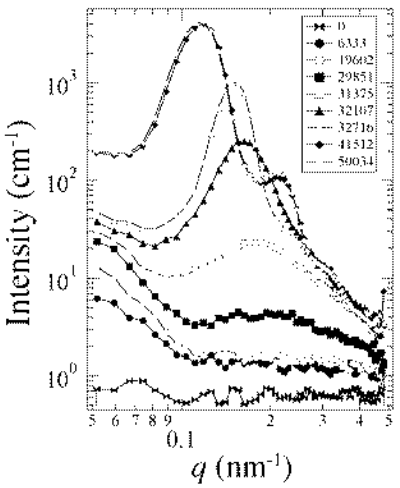

Figure 1 Time dependence of the SANS profiles during the living anionic polymerization of isoprene/styrene-d_8 mixture in benzene-d_6. The intensity is shown in logarithmic scale. The numbers attached to the markers denote the reaction time in seconds.

Figure 2 shows the time evolution of scattering maximum $I(q_m)$ and the q value at the maximum intensity q_m from the beginning to the end of polymerization. From the viewpoint of time dependence of the scattering shown in Figures 1 and 2, the polymerization process

can be divided into three regions as follows: In Region 1, from $t \sim 0$ to 2.25×10^4 s, the upturn in the scattering intensity was observed at low $q < 0.1$ nm^{-1}, and its scattering intensity increased with time. However, the scattering intensity at $q = q_m \cong 0.2$ where the scattering maximum appears at later times only slightly increase with time. In Region 2, from $t \sim 2.25 \times 10^4$ to 3.09×10^4 s, a peak appeared at $q = q_m \cong 0.2$ nm^{-1}. $I(q_m)$ gradually increased with time, while q_m remained almost constant. In Region 3, from $t \sim 3.09 \times 10^4$ to the end of polymerization, q_m rapidly shifted toward smaller q, and $I(q_m)$ also rapidly increased, and then, higher-order scattering maxima appeared. The details of Region 1 to Region 3 are discussed below.

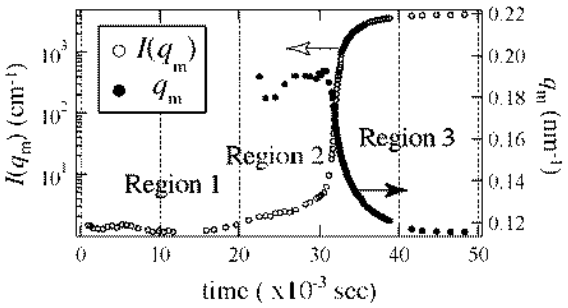

Figure 2 The time evolution of the q_m and the intensity $I(q_m)$ of scattering maximum at $q = q_m = 0.2$nm^{-1} from $t = 300$ s to $t = 50034$ s. ($I(q_m)$: unfilled circles, q_m: filled circles) This polymerization process viewed from SANS was divided into three regions (Region 1-3).

Discussion

A. Region 1: The polymer solution had a light yellow color throughout Region 1. This color suggests the presence of polyisoprenyllithium (PILi) but not polystyryllithium (PSLi), i.e., the difference in the reactivity of the two monomers in benzene allowed the dominance of PILi in spite of the coexistence of I and S in the solution. Therefore, Region 1 is the period where PILi selectively propagates to increase its chain length. This is consistent with the established law on copolymerization kinetics in non-polar solvents[1]:

$$k_{SI} > k_{SS} > k_{II} > k_{IS} \qquad (1)$$

where k_{JL} is the reaction rate constant for Jth living end to Lth monomer, J and L being either I or S.

Since the scattering contrast for SANS exists between PI and the others in the solution (I, S-d_8 and benzene-d_6), it is possible to observe only PILi under propagation by means of SANS. The SANS profiles in Region 1 reveal the intensity upturn at low q region (see Figure 1). This upturn was not observed before polymerization without initiator (as shown by the profile at $t = 0$ in Figure 1). Moreover the upturn disappeared when the living polymerization was terminated by methanol. These results suggest that PILi did not exist as single chains isolated in the benzene solution but rather aggregated together at the living chain ends to form a fundamental structure unit of star-like structure (multiple-ion pairs) which are further aggregated into the larger aggregates[2-5].

B. Region 2: In Region 2, the scattering peak appeared, indicating formation of the bcp due to addition of styrene-d_8 to the living ends of PILi. The scattering maximum originates from the correlation hole effect[6,7] due to the bcp formation. Actually, the color of the living polymer solution gradually changed in this region from light yellow to red, implying a gradual change in the living chain end from PILi in the end of Region 1 to PSLi in the end of Region 2. Interestingly enough, the color of the polymer solution did not completely change into red inherent to polystyryllithium until the end of Region 2. The chain length of the newly formed block is expected not to increase significantly in Region 2, judging from almost constant value of q_m with time.

It is crucial for us to recognize that there are two regions (Region 2 and 3) which have distinctly different behaviors in the time-evolution of microscopic parameters such as M_n and q_m as well as macroscopic parameter regarding the solution color, which reflects back the microscopic state of the living chain end, as highlighted and summarized in Table 2. Strikingly enough our results elucidate that k_{ss} in region 2, $(k_{ss})_{\text{region 2}}$, is much smaller than k_{ss} in the region 3, $(k_{ss})_{\text{region 3}}$.

$$(k_{ss})_{\text{region 2}} = (k_{ss})_{\text{region 3}} \qquad (2)$$

We postulate that this is a consequence of PILi-association-induced slowing down of k_{ss} in Region 2.

Table 2. Characteristics of Region 2 and Region 3

Region Properties	Region 2	Region 3
Solution color	Extremely slow change from light yellow to red	red
M_n	Nearly constant with time	Rapid increase
q_m	Nearly constant with time	Rapid decrease

C. Region 3: In Region 3, $I(q_m)$ and q_m rapidly increased and decreased with time, respectively. After all PILi had changed into PI-S-Li in the end of Region 2, PI-S-Li rapidly reacted with S, resulting in producing PI-*block*-dPS. At $t = 32107$ s, a discontinuous change in the width of the peak at q_m was observed as shown in Figure 1, and appearance of the higher-order peaks at $\sqrt{3}$ and $\sqrt{7}$ positions of q_m was observed, indicating that order-disorder transition (ODT) occurred and the hexagonally-packed cylindrical microdomains of dPS are formed in the matrix of PI.

After $t \geq 41500$ s, the higher-order peaks at the integer-multiple positions (2 and 3) of q_m was observed in Figure 1, indicating that the polymerization-induced order-order transition (OOT) occurred from the hexagonally-packed cylinders to the lamellar microdomains. After $t = 46000$ to 66000 s the profile showed almost no change with time as also revealed in Figure 2.

Conclusion

We found that the time-resolved SANS measurements during the bcp polymerization is quite useful for exploring the polymerization process and polymerization-induced self-assembly of the reaction products. This technique may be applied to many different systems for exploring relationships between chemical reactions and structural changes in the systems and for manipulating self-assembled structures of systems.

References

[1] Worsfold, D. J. *J.Polym.Sci., Part A* **1967**, *5*, 2783.

[2] Fetters, L. J.; Balsara, N. P.; Huang, J. S.; Jeon, H. S.; Almdal, K.; Lin, M. Y. *Macromolecules*, **1995**, *28*, 4996.

[3] Stellbrink, J.; Willner, L.; Jucknischke, O.; Richter, D.; Lindner, P.; Fetters, L. J.; Huang, J. S. *Macromolecules*, **1998**, *31*, 4189.

[4] Stellbrink, J.; Allgaier, J.; Willner, L.; Richter, D.; Slawecki, T.; Fetters, L. J. *Polymer*, **2002**, *43*, 7101.

[5]Niu A. Z.; Stellbrink, J. Willner, L.; Radulescu, A.; Richter, D.; Koening B.W.; May, R.P.; Fetters,bL.J.J. *J. Chem. Phys.* **2005**, 122, 134906.

[6] de Gennes, P. G. *Scaling Concepts in Polymer Physics; Cornell Univ. Press: Ithaca, NY*, **1979**.

[7] Leibler, L. *Macromolecules*, **1980**, *13*, 1602.