Macromolecules **2005,** *38,* 8811−8815

Three-Phase Hierarchical Structures from AB/CD Diblock Copolymer Blends with Complemental Hydrogen Bonding Interaction

Takeshi Asari,† Shigeo Matsuo, Atsushi Takano,‡ and Yushu Matsushita*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

Received June 3, 2005; Revised Manuscript Received July 12, 2005

ABSTRACT: Complex phase structures of AB/CD diblock copolymer blends were investigated. Two pairs of poly(isoprene-*block*-2-vinylpyridine) (IP) and poly(styrene-*block*-4-hydroxystyrene) (SH) diblock copolymers with different molar ratios, 5:5 and 9:1, were used; they were coded IP-55, IP-91, SH-55, and SH-91, respectively. Two polymer species, that is, poly(2-vinylpyridine) and poly(4-hydroxystyrene), out of four components are miscible with each other via hydrogen bonding interactions in bulk as well as in solution. From morphological observation using TEM and SAXS, it was confirmed that IP/SH blends were self-assembled to form the complex three-phase microphase-separated structures. Namely, two kinds of hierarchical structures were observed, that is, one is a unique lamellar structure from a IP-55/SH-55 = 50/50 blend, where mixed one phases from P and H form alternating lamellae, whereas I and S phases are arranged alternatingly in every second lamellar phase. The other one from IP-91/SH-91 = 50/50 consists of another peculiar lamellar structure, where the P/H mixed phase forms isolated cylinders between lamellar S and I layers.

Introduction

Block copolymers composed of incompatible components are known to be self-assembled to form various microphase-separated structures in bulk,[1−4] so many researchers have paid more attention to them as attractive soft materials that can create nanoscale materials with various functions.[5] The morphological features of several types of block copolymers, such as AB,[6−9] ABA,[10] ABC linear,[11−13] and ABC star-shaped[14−15] molecules have been investigated extensively so far. Recently, a very characteristic centrosymmetric four-phase six-layer lamellar structure has been observed from a linear ABCD tetrablock quaterpolymer, even if A and D are compatible with each other,[16] whereas an ABCA tetrablock terpolymer partially forms a noncentrosymmetric three-phase lamellar structure[17]

In recent years, several approaches have been carried out to form complex structures by utilizing the intermolecular interactions between block chains and low molecular weight compounds. Especially, the most attention has been paid to hydrogen bonding interactions to form several hierarchical structures.[18−22] Among them, ten Brinke et al. reported on the formation of a hierarchical structure with two different length scales, utilizing interaction between poly(4-vinylpyridine) and pentadecylphenol (PDP).[20−22]

Concerning polymer blend systems with attractive interactions between component polymers, Jiang et al. reported on the microphase-separated structures from AB/C-type polymer blends by TEM,[23,24] whereas Tucker et al. examined the phase structures of the same AB/C systems, where the boundary between microphase separation and macrophase separation was estimated theoretically.[25] Abetz et al. observed several unique structures from blends of an ABC triblock terpolymer and an AD diblock copolymer, where hydrogen bonding interaction can be formed between components C and D so that these two component polymers can be mixed into one phase.[26−31] The work by Abetz et al. shows that the macrophase separation can hardly be observed; however, the nonstoichiometry of two attractive components gives less-ordered microdomain structures. One resolution to overcome this problem is to match the number of these functional groups.

If an AB/CD diblock/diblock copolymer blend is prepared, where components B and D are miscible by the aid of hydrogen bonding interaction, then we may have a three-phase structure from this blend. A similar approach was made using electrostatic interactions for an AB/CD system in solution.[32] Here we anticipate a different structure from that of the ABC linear triblock copolymer as compared in Figure 1 assuming lamellar structures. Namely, the AB/CD system considered here will form a three-phase structure, however, components A and C cannot be separated completely by the mixed phase because B/D combined chains can play the role of a “loop-type” chain as well as a “bridge-type” one as shown in Figure 1a; the resulting structure must be a complex one. However, an ABC linear molecule has to possess a bridge-type conformation in bulk as in Figure 1b. Thus, it must be very interesting to study the morphology of the AB/CD copolymer blend in comparison to that of the simple ABC triblock copolymer system; therefore, we focus on this issue in this report.

First, we report on the AB/CD blend system having two symmetric diblock copolymers. There are no reports concerning microphase-separated structures of blends of AB/CD diblock copolymers in bulk where B and D are miscible through hydrogen bonding interaction. Second, the same polymer system but composed of two asymmetric block copolymers, with B and D being small volume fractions, will be studied, where the attractive interaction between B and D component polymers works as a molecular adhesive. This morphology control method must be useful for constructing unknown highly ordered complex nanostructures.

---

* Corresponding author. E-mail: yushu@apchem.nagoya-u.ac.jp. Tel: +81-52-789-4604. Fax: +81-52-789-3210.

† E-mail: h031201d@mbox.nagoya-u.ac.jp.

‡ E-mail: atakano@apchem.nagoya-u.ac.jp.

10.1021/ma051156s CCC: $30.25

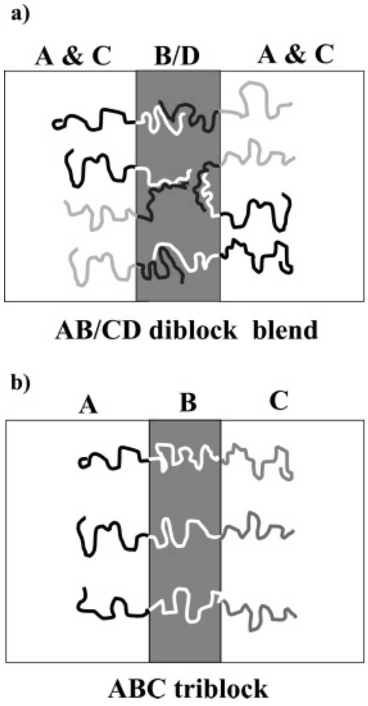

Figure 1. Schematic views of microphase-separated structures formed by (a) an AB/CD diblock copolymer blend and (b) an ABC triblock copolymer.

Table 1. Molecular Characteristics of IP and SH Diblock Copolymers

			mol fraction[c]			
polymers	$M_w \times 10^{-4}$ [a]	M_w/M_n [b]	Φ_I	Φ_P	Φ_S	Φ_H
IP-55	8.4	1.06	0.54	0.46		
SH-55	7.4	1.02			0.49	0.51
IP-91	8.0	1.06	0.91	0.09		
SH-91	8.6	1.03			0.86	0.14

[a] Determined by MALLS. [b] Estimated by GPC. Eluents are 2 wt % TMEDA in THF for IP and THF for SH and polystyrene standards. [c] Calculated from ^{1}H NMR spectra.

Experimental Section

The polymer samples used are two poly(isoprene-*block*-2-vinylpyridine) (IP) and poly(styrene-*block*-4-hydroxystyrene) (SH) and their blends. The molecular characteristics of the parent block copolymers are summarized in Table 1. Two pairs of IP/SH copolymers were blended at the weight ratio of 50/50. The details of polymer synthesis and preparation of the blend films were reported in the preceding paper. Blend sample films obtained by solvent casting and annealing were cut into ultrathin sections with thickness of ca. 50 nm by an ultramicrotome, Ultracut UCT of LEICA. The sections were stained with OsO_4 for 8 h and occasionally further stained with I_2 for 30 min, and their microphase-separated structures were observed by a transmission electron microscope (TEM), H-800, of Hitachi under an acceleration voltage of 100 kV. In the TEM image, it is known from our experience for several simple cases that I, P, H, and S show deep, intermediate, light, and very light contrasts, respectively, by OsO_4 staining, whereas the P domain is selectively stained with I_2. Small-angle X-ray scattering (SAXS) was performed by using two SAXS apparatuses. One is the Rigaku NanoViewer used for SH-55, IP-55, and their blends. The wavelength of the monochromated X-ray was 0.154 nm, a point-collimated beam with size of 0.2 × 0.2 mm^2 was irradiated on the cut and stacked film specimens from the directions perpendicular (through view) and parallel (edge view) to the film surface. The other instrument used is the one installed at the synchrotron radiation facility in beamline 15A at the Photon Factory in Tsukuba, Japan. The measurements for SH-91, IP-91, and their blends were carried out using the latter apparatus. The wavelength of the monochromated beam was 0.150 nm, a point-collimated beam with size of 0.4 × 0.7 mm^2 was irradiated on the film specimens under the same geometry as for the former instrument.

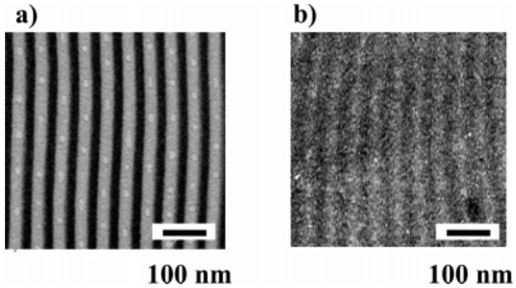

Figure 2. TEM images of (a) IP-55 and (b) SH-55 symmetric diblock copolymers. Ultrathin sections were stained with OsO_4.

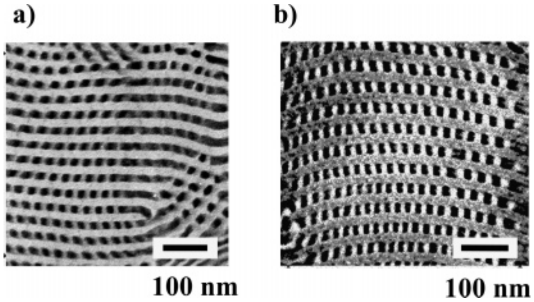

Figure 3. TEM images of the IP-55/SH-55 blend, whose weight ratio is 50/50. Sample specimens were stained with (a) OsO_4 and (b) OsO_4 and I_2.

Results and Discussion

Microphase-Separated Structure from the Blend of Symmetric Block Copolymers. Figure 2a and b compares the bright-field TEM images of IP-55 and SH-55 diblock copolymers. It is evident that both samples form alternating lamellar structures as expected. A typical TEM image for IP-55/SH-55 = 50/50 stained with OsO_4 is shown in Figure 3a. This structure shows a lamellar structure stacked in the vertical direction combined with a cylindrical structure in which hexagonally packed cylinders are embedded in every second lamellae, although only two contrasts can be recognized. Therefore, additional staining was made with I_2, and the observed result is compared in Figure 3b. It is clear that the contrast of every second lamellae is enhanced compared to the image in Figure 3a, indicating that P blocks are included in this phase so that three phases can be distinguished clearly in Figure 3b.

More detailed analyses were carried out using both TEM and SAXS results concerning this blend. Figure 4a shows an enlarged TEM image of this blend sample, where the inset figure is a fast Fourier transform (FFT) from the 2D image. In addition to periodic dots in the vertical direction at the center of the reflecting lamellar arrangement, a hexagonal pattern is observed in the reciprocal lattice space; therefore, we consider the packing manner of the cylinders embedded in every second lamellae to be hexagonal, although hexagons in the FFT image are somewhat compressed in the vertical direction. Figure 5 compares SAXS diffraction patterns from this blend. The top curve is the circular-averaged intensities from the 2D through view data. Integer ordered peaks representing a lamellar structure are observed on this curve at 0.136, 0.273, 0.410, 0.543, and

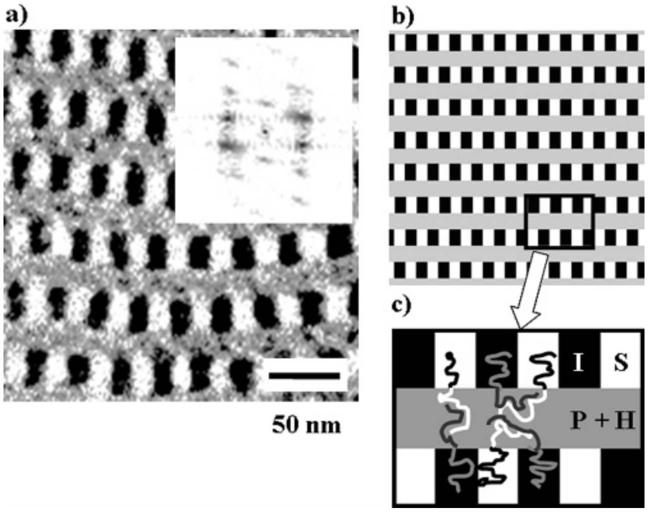

Figure 4. (a) Enlarged TEM image of the IP-55/SH-55 = 50/50 blend. The inset is the FFT pattern for all areas in this TEM image. (b) Schematic drawing of the microdomain arrangement for the corresponding blend observed in Figure 4a. (c) The enlarged domain assembly and possible molecular arrangement in this structure.

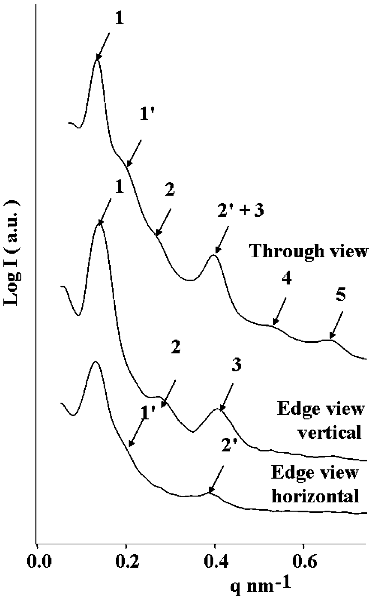

Figure 5. SAXS profiles of IP-55/SH-55 = 50/50. The curves are shifted in the vertical direction to make the difference clear.

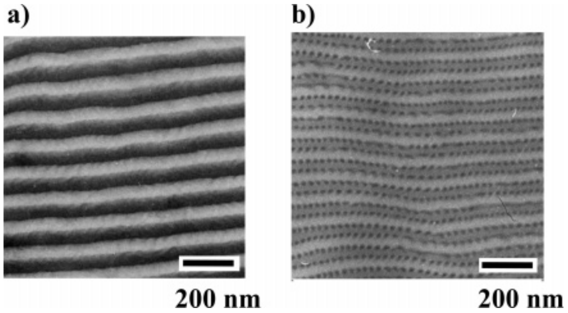

Figure 6. TEM images of the IP-91/SH-91 = 50/50 blend. Sample specimens were stained with (a) OsO_4 and (b) I_2.

0.670 nm^{-1}, whereas one additional peak can be seen at 0.197 nm^{-1} between the 1st peak and the 2nd one for the lamellar structure. The middle and bottom curves are for the sector-averaged intensities at around the vertical axis and the horizontal axis, respectively. There are no intermediate peaks in the middle curve, whereas they are clearly included in the bottom one at 0.195 and 0.39 nm^{-1}, where the ratio of the magnitudes of scattering vector for two peaks is about two. This fact means that these peaks originate from the periodic microdomain arrangement along the horizontal direction, so we are convinced that these are expressing the periodic distance for a pair of isolated cylinders aligned in this direction. From the location of the peaks, the repeating distance of alternating cylinders in the horizontal direction can be estimated as 32 nm; the value is about two-thirds of that of the lamellar distance, 46 nm, along the vertical direction. These results are consistent with the microdomain sizes shown in Figure 4a and the corresponding data in the inset figure in a reciprocal lattice space. The microdomain arrangement was drawn schematically in Figure 4b, and the partition of every component of the polymer chains is also displayed in Figure 4c. From these auxiliary figures, one can recognize easily that P and H chains can be mixed into one phase by hydrogen bonding interactions, whereas I chains and S chains are both self-assembled individually and two phases are aligned alternatingly in the vertical direction within the lamellar layers. It is quite natural that I and S microdomains are mutually alternative in lamellae, considering that the selective interactions between P and H chains as can be recognized easily from Figure 4c. This kind of morphology has been the first observed one to the best of our knowledge. Thus, a hierarchical structure with two different repeating periods has been observed from the present blend system, where P and H can be mixed to form one phase.

Microphase-Separated Structure from the Blend of Asymmetric Block Copolymers. Figure 6a and b compares the bright-field TEM images of IP-91/SH-91 diblock copolymer blends. A typical TEM image for IP-91/SH-91 = 50/50 stained with OsO_4 is shown in Figure 6a, where only two contrasts can be conceived, and this structure looks like a simple alternating lamellar one with a periodic length of ca. 100 nm. On the contrary, Figure 6b shows the TEM image from the same sample but stained with I_2. It is clear that small cylinders have emerged between the lamellar layers, indicating that P blocks are included in this phase in contrast to the simple lamellar-like structure in Figure 6a. The same kind of three-phase structure was observed for a cross-linked poly(styrene-*block*-butadiene-*block*-methylmethacryrate) triblock terpolymer.[33]

Figure 7a shows an enlarged TEM image, where the inset figure expresses the FFT for the whole TEM image. Periodicity exists because of the lamellar structure in the vertical direction, and furthermore another distinct periodicity is observed in the horizontal direction. Figure 8 compares the SAXS diffraction patterns from this blend. The top curve is the circular-averaged intensities from the 2D data. Integer-ordered peaks representing lamellar structure are observed on this curve, and one additional peak designed as 1′ can be seen at 0.15 nm^{-1} between the 2nd peak and the 3rd one from the lamellar structure. The middle and the bottom curves are for the sector-averaged intensities at around the vertical axis and the horizontal one, respectively. There are no intermediate peaks in the middle curve, whereas they are shown in the bottom one at 0.15 and 0.30 nm^{-1}. Again these peaks can originate from the aligned cylindrical microdomains along the hori-

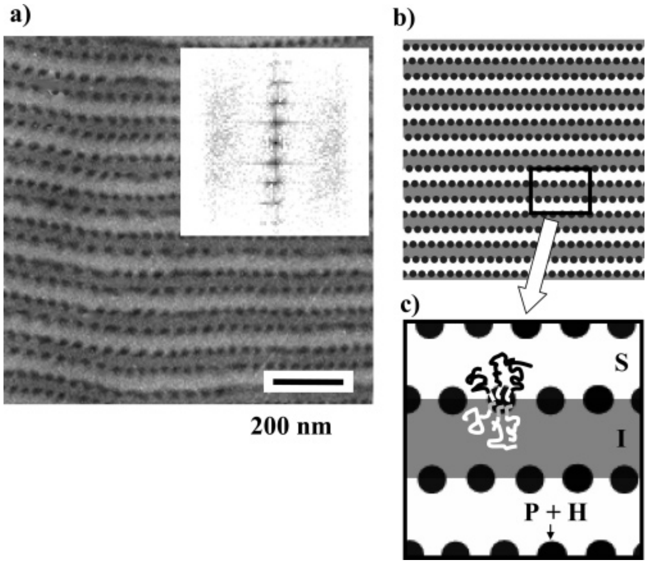

Figure 7. (a) Enlarged TEM image of the IP-91/SH-91 = 50/50 blend. The inset is the FFT pattern for all areas in this TEM image. (b) Schematic drawing of a microdomain assembly for the corresponding blend observed in Figure 7a. (c) The enlarged domain assembly and possible molecular arrangement in the complex structure.

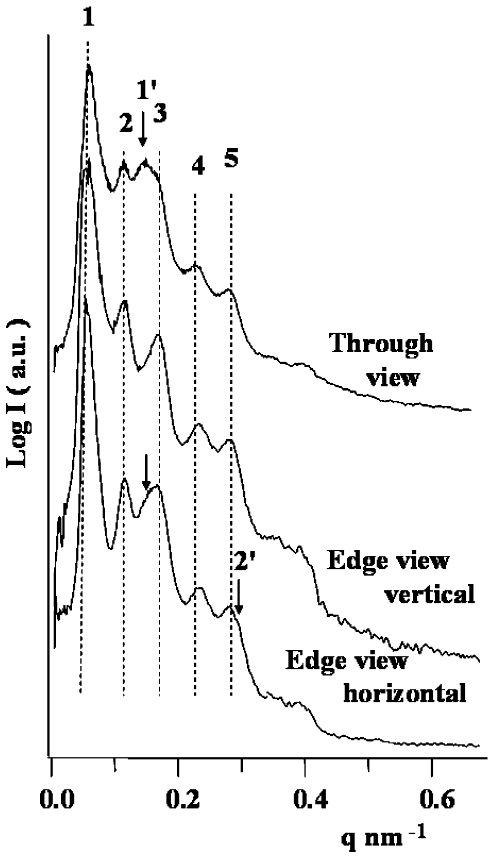

Figure 8. SAXS profiles of IP-91/SH-91 = 50/50. The curves are shifted in the vertical direction to make the difference clear.

zontal direction. From the location of the peaks, the repeating distance of cylinders can be estimated as 40 nm; the value is about two-fifths of that of the lamellar distance along the vertical direction, 107 nm, indicating this structure also has a hierarchical nature, the results being consistent with those in Figure 7a and the corresponding reciprocal lattice data in the inset figure.

The microdomain arrangement was drawn schematically in Figure 7b, and the partition of every component of the polymer chains is also displayed in Figure 8c. Similar to the IP-55/SH-55 system, one can recognize easily that P and H chains can be mixed into one phase by hydrogen bonding interactions, whereas I chains and S chains are both self-assembled individually to form independent lamellae. In this complex structure, the mixed P/H Phase is formed periodically; however, the environment of this mixed phase is totally different from that of the IP-55/SH-55 blend, where the mixed phase is a two-dimensionally continuous lamellar one. It should be noted that these interactive chain components form a simple miscible phase, even if the content of interactive chain is merely about 10% in mole fraction.

The lamellar domain spacing, D, of the IP-91/SH-91 blend, 107 nm, is fairly large considering the molecular weights of both diblock copolymers. As a matter of fact, D of poly(styrene-*block*-isoprene) was studied well and the scaling law, $D = 0.024\ M^{2/3}$ (nm), is known in the strong segregation regime.[34] If the sum of the total molecular weights of the two block copolymers, 166 k, is introduced into this relationship, then we have 73 nm. The observed value is evidently larger than the estimated one, although the P/H mixed phase was inserted into the intermediate region of I and S phases. This fact suggests that the longer I and S chains are much more elongated toward the normal to the lamellar interface than regular block copolymers. Regarding the short P and H chains that are forming a mixed phase so that it plays the role of a giant junction point of I and S block chains, we notice that the real junction points are condensed in the small microdomain. In this structure, the average distance between junction points must be very short; it leads to the increase of segmental density of I and S components near the P + H microdomain surface. As a result, the chains tend to elongate along the direction normal to the interface, so the microdomain expands much more than the regular block copolymer system. The situation of the present case resembles that of two-component star-shaped block copolymers,[35] where domain expansion was also observed.

Conclusions

The bulk morphology of symmetric and asymmetric AB/CD type block copolymer blends was studied and compared. From the morphological observation for these blends, P chains and H chains can be mixed into one phase in bulk even if they are fairly short. In a symmetric block copolymer blend, that is, IP-55/SH-55 blend at 50/50, a simple mixed phase from P and H forms single lamellae, whereas I and S chains are phase separated alternatingly and combined into single lamellae that are sandwiched between the mixed layers. Alternatingly, an asymmetric block copolymer blend, that is, IP-91/SH-91 = 50/50 blend, also basically forms a lamellar structure, where the P/H mixed phase forms isolated cylinders between continuous I and S lamellae.

The blending of block copolymers with complemental hydrogen bonding chains is a novel method to give a mixed phase and results in highly complex structures. These hierarchical structures are difficult to determine from the simple block copolymer systems. Thus, here we propose a system to construct the higher-ordered complex but regular nanostructures by combining simple block copolymers with the aid of selective polymer–polymer interactions.

Acknowledgment. T.A. is thankful for a JSPS Research Fellowship (no. 50451) for Young Scientists. This work was also done under the support of the 21st center of excellence (COE) program entitled "The Creation of Nature-Guided Materials Processing" in the School of Engineering, Nagoya University, which has been assigned as one of the 21st century COE programs and one that Y.M. is grateful for support.

References and Notes

(1) Matsuo, M.; Ueno, T.; Horino, H.; Chujyo, S.; Asai, H. *Polymer* **1968**, *9*, 425.

(2) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.

(3) Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204*, 265.

(4) Ruzette, A. V.; Leibler, L. *Nat. Mater.* **2005**, *4*, 19.

(5) Forster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688.

(6) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(7) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

(8) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *J. Polym. Sci., Part A: Polym. Chem.* **1969**, *7*, 1283.

(9) Matsushita, Y.; Mori, K.; Mogi, Y.; Saguchi, R.; Noda, I.; Nagasawa, M.; Chang, T.; Glinka, C. J.; Han, C. C. *Macromolecules* **1990**, *23*, 4317.

(10) Matsushita, Y.; Nomura, M.; Watanabe, J.; Mogi, Y.; Noda, I.; Imai, M. *Macromolecules* **1995**, *28*, 6007.

(11) Mogi, Y.; Kotsuji, H.; Kaneko, Y.; Mori, K.; Matsushita, Y.; Noda, I. *Macromolecules* **1992**, *25*, 5408.

(12) Suzuki, J.; Seki, M.; Matsushita, Y. *J. Chem. Phys.* **2000**, *112*, 4862.

(13) Stadler, R.; Auschra, C.; Beckmann, J.; Krappe, U.; Volgtmartin, I.; Leibler, L. *Macromolecules* **1995**, *28*, 3080.

(14) Takano, A.; Wada, S.; Sato, S.; Araki, T.; Kazama, T.; Kawahara, S.; Isono, Y.; Ohno, A.; Tanaka, N.; Matsushita, Y. *Macromolecules* **2004**, *37*, 9941.

(15) Yamauchi, K.; Takahanshi, K.; Hasegawa, H.; Iatrou, H.; Hadjichristidis, N.; Kaneko, T.; Nishikawa, Y.; Jinnai, H.; Matsui, T.; Nishioka, H.; Shimizu, M.; Furukawa, H. *Macromolecules* **2003**, *36*, 6962.

(16) Takano, A.; Soga, K.; Asari, T.; Suzuki, J.; Arai, S.; Saka, H.; Matsushita, Y. *Macromolecules* **2003**, *36*, 8216.

(17) Takano, A.; Soga, K.; Suzuki, J.; Matsushita, Y. *Macromolecules* **2003**, *36*, 9288.

(18) Pollino, J. M.; Weck, M. *Chem. Soc. Rev.* **2005**, *34*, 193; and references therein.

(19) Ikkala, O.; ten Brinke, G. *Chem. Commun.* **2004**, *19*, 2131.

(20) Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Komanschek, B. E.; ten Brinke, G.; Ikkala, O. *Macromolecules* **1997**, *30*, 2002.

(21) Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Komanschek, B. E.; Ikkala, O.; ten Brinke, G. *Phys. Rev. E* **1996**, *54*, 6646.

(22) Ruokolainen, J.; Makinen, R.; Torkkeli, M.; Makela, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557.

(23) Jiang, M.; Huang, T.; Xie, J. *Macromol. Chem. Phys.* **1995**, *196*, 787.

(24) Jiang, M.; Huang, T.; Xie, J. *Macromol. Chem. Phys.* **1995**, *196*, 803.

(25) Tucker, P. S.; Paul, D. R. *Macromolecules* **1988**, *21*, 2801.

(26) Jiang, S. M.; Göpfert, A.; Abetz, V. *Macromolecules* **2003**, *36*, 6171.

(27) Markgraf, K.; Abetz, V. *e-Polymers* (online) **2001**, no. 15.

(28) Abets, V.; Markgraf, K.; Rebizant, V. *Macromol. Symp.* **2002**, *177*, 139.

(29) Abetz, V.; Goldacker, T. *Macromol. Rapid Commun.* **2000**, *21*, 16.

(30) Abetz, V.; Jiang, S.; Göpfert, A. *e-Polymers* (online) **2004**, no. 40.

(31) Jiang, S.; Abetz, V. *e-Polymers* (online) **2004**, no. 54.

(32) Schrage, S.; Sigel, R.; Schlaad, H. *Macromolecules* **2003**, *36*, 1417.

(33) Liu, Y.; Abetz, V.; Müller, A. H. E. *Macromolecules* **2003**, *36*, 7894.

(34) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.

(35) Grayer, V.; Dormidontova, E. E.; Hadziioannou, G.; Tsitsilianis, C. *Macromolecules* **2000**, *33*, 6330.

MA051156S