1152 *Macromolecules* **2004,** *37,* 1152−1155

Notes

Self-Organization and Phase Behavior of Hydrogen-Bonded Mixtures of End-Functional Polymer with Surfactant

I. Akiba,*,† H. Masunaga,‡ K. Sasaki,‡ Y. Jeong,†
K. Sakurai,† S. Hara,§ and K. Yamamoto§

Faculty of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0135, Japan; Kitakyushu Foundation for the Advancement of Industry, Science and Technology; and Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

Received October 31, 2003
Revised Manuscript Received December 3, 2003

Introduction

Blends and composites of polymers with different components, such as polymer, oligomer, and liquid crystalline molecules, are expected to be novel polymeric materials.[1−7] Because self-organized structures in these systems indicate characteristic properties, such as anisotropic and stimuli responsive properties,[1−5] they have attracted attention. Hence, the self-organized structures and phase behavior in these systems must be controlled to develop functional materials.

In blends of polymer with polymer or oligomer that tend to separate into two phases, it has been well-known that attractive interactions between the components strongly affect miscibility and aggregated structures.[1,8−12] Therefore, it is considered that the intermolecular interactions are effective in controlling the organized structures in these blends. However, when the intermolecular associations randomly occur along the polymer chains, they should form random aggregation or merely miscible situation.[8,9,11−13] To prepare the nanoorganized structures in the polymer−polymer or polymer−oligomer blends, architectures of molecular structures of the components should be required.[1,10,14−17] When the components are connected to each other at specific sites of the molecules, the systems should form the nanoorganized structures reflecting the molecular structures and intermolecular associations.[1−4,14−24]

In this study, we focus on the nanoorganization and phase behavior in the polymer−oligomer mixtures in which the components are connected to each other between the chain ends by hydrogen bond. For this purpose, we employ mixtures of tertiary amino-terminated poly(methyl methacrylate) (AT-PMMA) and dodecylbenzenesulfonic acid (DBSA) as a model compounds of end-functional oligomer.

Experimental Section

Materials. Dodecylbenzenesulfonic acid (DBSA), methyl methacrylate (MMA), dubsyl chloride (DC), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) were purchased from Tokyo Chemical Industry Co., Ltd. CuBr was purchased from Kanto Chemical Co., Ltd. MMA was purified with activated alumina before using. The other reagents were used without further purification.

Synthesis of AT-PMMA. AT-PMMA was synthesized following Scheme 1 with atom transfer radical polymerization technique.[25] PMDETA as a ligand, MMA, and DC as an initiator were added to dry flask with CuBr. Here, the molar ratio of [MMA]/[DC]/[PMDETA]/[CuBr] was set at 80/1/1/1. The solution was degassed with the freeze−pump−thaw method for three times. The flask was sealed under vacuum and placed in an oil bath held at 90 °C. After 1 h, the polymerization was stopped by cooling the flask into ice water. The resulting AT-PMMA was coarsely purified by several times of reprecipitations from toluene solution to a large amount of methanol. After the reprecipitaions, the AT-PMMA was dissolved in toluene. Activated alumina was added to the solution to remove residual copper. Finally, the activated alumina was filtered off, and the solution was reprecipitated into methanol. The resulting AT-PMMA showed an orange color due to (*N*,*N*-dimethylamino)azobenzene unit of end group. Gel permeation chromatography (GPC) measurements calibrated with standard polystyrenes were carried out to estimate molecular weight of AT-PMMA. The GPC measurements were performed using a column packed with styrene−divinylbenzene gel and tetrahydrofuran as an eluent. Estimated number- and weight-averaged molecular weights of the AT-PMMA were 6.3×10^3 g mol^{-1} and 7.5×10^3 g mol^{-1}, respectively. The GPC measurements were performed

Preparation of Blend. The AT-PMMA and DBSA were separately dissolved in $CHCl_3$ at a concentration of 10 g L^{-1}. The DBSA solution was added into the AT-PMMA solution until desired weight ratio of the AT-PMMA to DBSA. The orange color of the AT-PMMA solution turned to a deeply red color due to interaction between the DBSA and AT-PMMA. The solution was cast on glass plate. The resulting red samples were further dried in reduced pressure for 24 h. The mixtures of AT-PMMA and DBSA were represented as AT-PMMA−DBSA(φ), where φ denotes weight fraction of DBSA.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out using a Perkin-Elmer Pyris 1 DSC set in Instrumentation Center of The University of Kitakyushu. The DSC measurements were performed under dry N_2 atmosphere at a heating rate of 10 deg min^{-1}.

Small-Angle X-ray Scattering (SAXS). SAXS measurements were carried out at the BL-40B2 station of SPring-8 in Japan and the BL-9C station of Photon Factory in Japan. Two-dimensional SAXS patterns were obtained by a Rigaku R-AXIS IV++ imaging plate at the BL-40B2 station. The one-dimensional SAXS profiles ($I(q)$ vs q, where I and q denote the scattering intensity and the magnitude of the scattering vector) were converted from the two-dimensional SAXS patterns by circular averaging. At the BL-9C station, one-dimensional SAXS profiles were obtained by a PSPC.

Results and Discussion

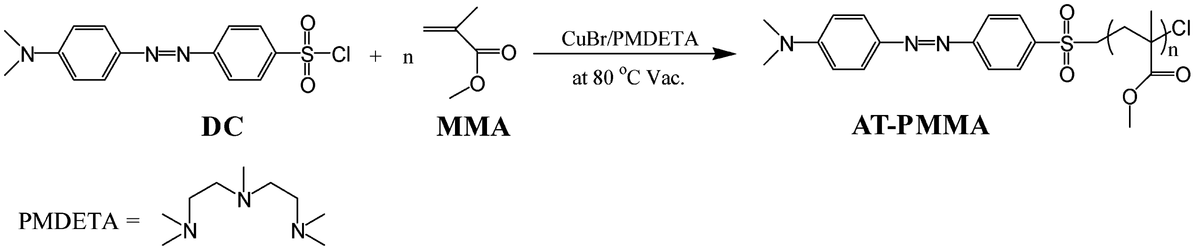
For analyses of the intermolecular interactions in polymer−surfactant mixtures, Fourier transform infrared spectroscopy is a powerful tool.[8,21,26] However, in this case, the concentration of the amino group of the AT-PMMA is extremely low due to only one amino group

---

† The University of Kitakyushu.
‡ Kitakyushu Foundation for the Advancement of Industry.
§ Nagoya Institute of Technology.
* Corresponding author: e-mail akiba@env.kitakyu-u.ac.jp.

10.1021/ma0356414 CCC: $27.50

Scheme 1. Synthesis of AT-PMMA



in one AT-PMMA. Therefore, interactions between terminal groups of the AT-PMMA and DBSA were not clearly revealed by infrared spectroscopy. On the other hand, change of color tone should be sufficiently sensitive to observe interaction and complexation of extremely dilute (dimethylamino)azobenzene unit due to the high molar absorptivity of the (dimethylamino)azobenzene unit.[27] In general, the (dimethylamino)azobenzene unit shows a orange color in the case that the dimethylamino group is not associated or protonated.[27−29] When the dimethylamino group is associated with acidic proton, the color tone of the (dimethylamino)azobenzene unit changes to red.[27−29] Since the AT-PMMA−DBSA solutions shows red color by mixing the orange AT-PMMA solution and colorless DBSA solution, hydrogen bonds between $-SO_3H$ and dimethylamino groups as shown in Figure 1 are formed in the solution. The red colors of the solutions are maintained in the cast film of the AT-PMMA−DBSA mixtures. Therefore, the hydrogen bonds between the $-SO_3H$ and dimethylamino groups are also formed in the AT-PMMA−DBSA mixtures.

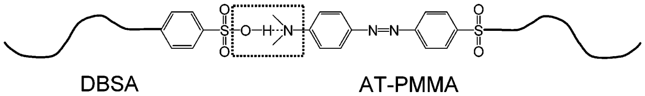


Figure 1. Hydrogen bond between DBSA and end group of AT-PMMA.

Figure 2 shows one-dimensional SAXS profiles of the AT-PMMA−DBSA($0.7 \geq \varphi \geq 0.3$), AT-PMMA, and DBSA at ambient temperature. The SAXS profiles are obtained by conversion from the two-dimensional SAXS patterns. The SAXS profiles indicate that the AT-PMMA and DBSA take disordered states. On the other hand, the SAXS profiles of the AT-PMMA−DBSA mixtures clearly show up to third-order diffraction peaks. Since the q position of the first-order peak is 2.04 nm^{-1} and the q positions are relatively assigned to 1:2:3, the AT-PMMA−DBSA mixtures take lamellar structure with 3.08 nm of the periodic length despite variation of the compositions. These results are observed for the AT-PMMA−DBSA($0.75 \geq \varphi \geq 0.25$) mixtures. On the other hand, we have confirmed that the AT-PMMA−DBSA($\varphi \geq 0.8$ and $\varphi \leq 0.2$) mixtures form disordered (miscible) phase.[30] Therefore, it is considered that the mesomorphic lamellar structures of the AT-PMMA−DBSA($0.75 \geq \varphi \geq 0.25$) mixtures consist of the AT-PMMA−DBSA($\varphi \sim 0.75$) and AT-PMMA−DBSA($\varphi \sim 0.2$) phases at ambient temperature. However, the periodic length of the lamellar structure in the AT-PMMA−DBSA mixtures must be changed with variation of the composition because the volume fraction of each phase constructing the lamellar structure depends on the composition, except for the case that the excess AT-PMMA and DBSA are macroscopically separated from the lamellar phase. The macroscopic phase separations in the AT-PMMA−DBSA mixtures are not observed in the overall composition range. On the other hand, the broadness of the first-order diffraction peaks of the AT-PMMA−DBSA mixtures is changed with the composition. Because the broadness of the diffraction peak corresponds to the distribution of the periodic length of ordered structure, they should provide information on the irregularity of the structure. Figure 3 shows plots of the half-width of the half-maximum (hwhm) of the first-order diffraction peak of the AT-PMMA−DBSA mixtures as a function of the composition of the DBSA. When $\varphi < 0.5$, the hwhm increases with increasing composition of the AT-PMMA, and the AT-PMMA−DBSA(0.5) mixture provides the minimum value of the hwhm. In addition, the hwhm is simply increasing with increasing composition of the DBSA when $\varphi > 0.5$. Therefore, it is considered that the AT-PMMA−DBSA(0.5) mixture forms the lamellar structure with the highest order and excess AT-PMMA or DBSA should cause disturbance on the regularity of the lamellar structure. Anyway, the hydrogen-bonded AT-PMMA−DBSA mixtures form the ordered phase-separated structures in nanospace like a block copolymer. Therefore, it is expected that they show order−disorder phase transition like a block copolymer and/or macroscopic phase separation like a polymer blends with changing temperature.

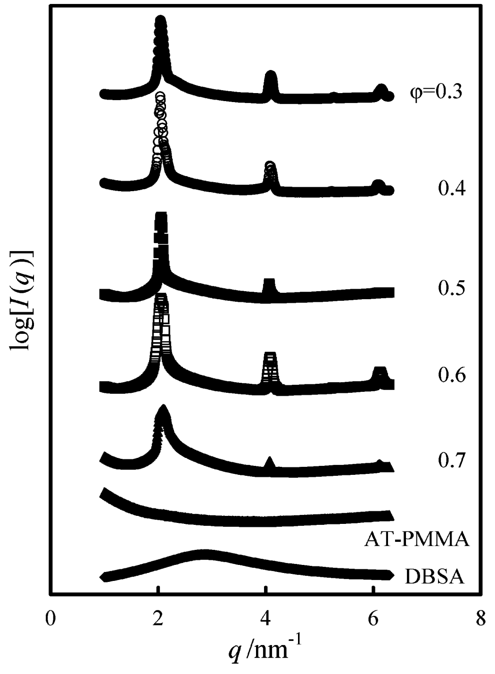


Figure 2. SAXS profiles of AT-PMMA−DBSA mixtures at ambient temperature.

Parts a and b of Figure 4 show variation of the one-dimensional SAXS pattern with elevating temperature and plot of the square of the half-width of the half-maximum (hwhm^{2}) of the first-order diffraction peak of

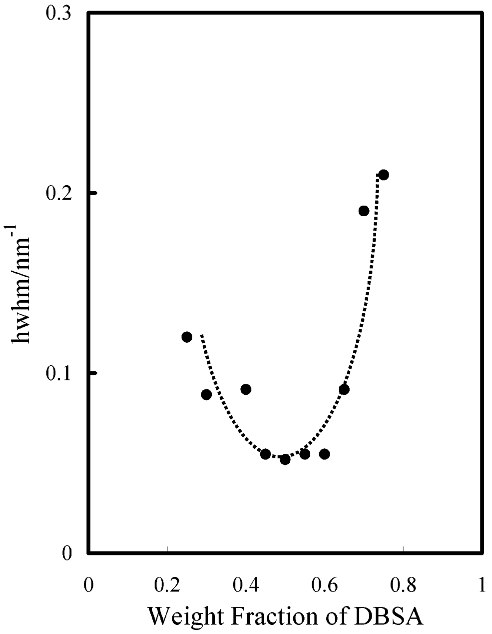


Figure 3. Plots of hwhm of the first-order diffraction peaks of the AT-PMMA–DBSA mixtures as a function of the weight fraction of the DBSA.

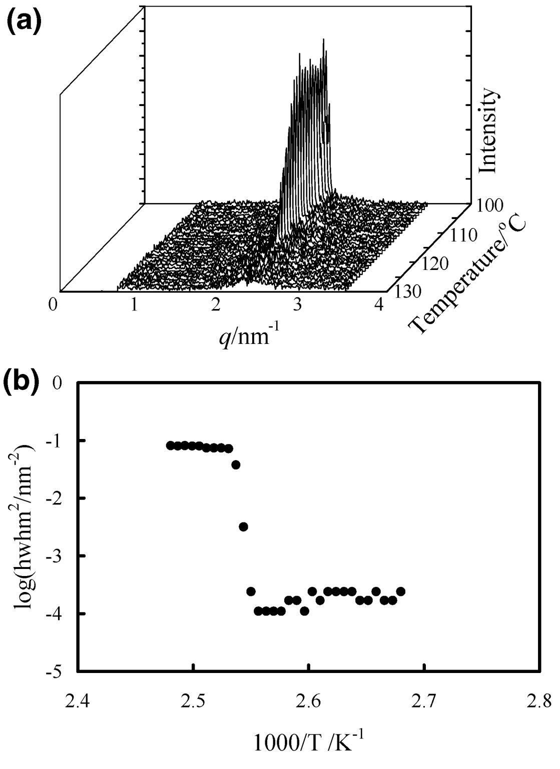


Figure 4. (a) Change of the SAXS profile of the AT-PMMA–DBSA mixture with elevating temperature. Order–disorder transition just like a block copolymer is observed in the AT-PMMA–DBSA mixture. (b) Plots of hwhm^2 against reciprocal temperature. The order–disorder transition temperature is determined as the temperature at which the hwhm^2 discontinuity changes.

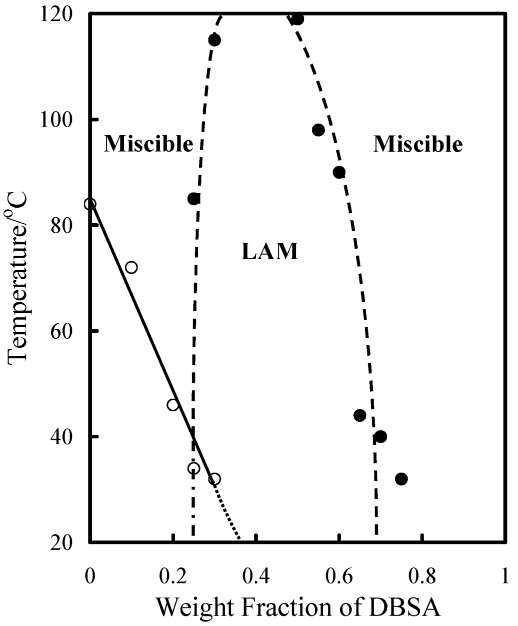


Figure 5. Phase diagram of AT-PMMA–DBSA mixtures. LAM indicates mesomorphic lamellar phase. Open circles represent glass transition temperatures determined by DSC measurements.

the lamellar structure as a function of reciprocal temperature (T^{-1}) for the AT-PMMA–DBSA(0.5) mixture, respectively. The intensity of the first-order diffraction peak of the lamellar structure of the AT-PMMA–DBSA(0.5) mixture is drastically decreased with elevating temperature above 110 °C. In addition, it is confirmed that this transition of the AT-PMMA–DBSA(0.5) mixture is thermoreversible. Therefore, this transition of the AT-PMMA–DBSA(0.5) mixture is thermodynamic phase transition. Since macroscopic phase separation is not observed in the AT-PMMA–DBSA mixtures in the temperature range of Figure 4, the phase transition in the AT-PMMA–DBSA(0.5) mixture is regarded as an order–disorder transition from mesomorphically ordered lamellar phase to the miscible state. Similar transitions with changing temperature are also observed in the other compositions of the AT-PMMA–DBSA($0.75 \geq \varphi \geq 0.25$) mixtures. The order–disorder transition temperatures (T_{ODT}) of the AT-PMMA–DBSA mixtures are determined as the onset temperature at which the hwhm^{2}s of the first-order diffraction peaks of the AT-PMMA–DBSA mixtures are discontinuously enlarged with elevating temperature in the plots of the hwhm^2 against T^{-1} as Figure 4b. This method can clearly indicate the T_{ODT} in block copolymer or comblike complex of polymer–surfactant systems in comparison with the other methods.[31,32]

Figure 5 shows a phase diagram of the AT-PMMA–DBSA mixtures. The closed and open circles in this figure indicate the T_{ODT} and glass transition temperature (T_g) of the AT-PMMA–DBSA mixtures. The phase diagram of the AT-PMMA–DBSA mixtures is divided into two regions. One is a disordered (miscible) state and the other a phase-separated state with the ordered lamellar morphology in nanospace. For the AT-PMMA–DBSA(0.6) mixture, the T_{ODT} is not observed in feasible temperature range because the T_{ODT} of the AT-PMMA–DBSA(0.6) mixture is higher than the initial temperature thermal decomposition (ca. 130 °C). As shown in Figure 3, the lamellar structures of the AT-PMMA–DBSA mixtures are well-ordered in the range of the weight fraction of the DBSA from 0.45 to 0.6. Because of the higher order of the lamellar structure, the T_{ODT} of the AT-PMMA–DBSA(0.6) mixture should not be observed in the feasible temperature range. As can be seen in Figure 5, the AT-PMMA–DBSA mixtures forms only lamellar structure in narrow composition range, and the morphologies of the ordered structures of the

AT-PMMA−DBSA mixtures are unchanged with variation of the composition. In our previous study, we have found that the nanoorganized morphologies of the polymer−surfactant mixtures, in which polymer and surfactant are connected at chain ends by ion−ion interaction, are changed from lamellar to sphere morphologies with decreasing the composition of the surfactant.[33] Since the binding energy of hydrogen bond is much weaker than that of ion−ion interaction, the connections between the end groups of AT-PMMA and DBSA in the AT-PMMA−DBSA mixtures can frequently repeat dissociation and recombination in comparison with ion−ion interactions in our previous study. Therefore, the AT-PMMA−DBSA mixtures can form the mesomorphically ordered lamellar structures which are the most stable shape in the organized structures regardless of composition.

Acknowledgment. SAXS measurements were performed the SPring-8 with the approved number 2003A0297-NL2-np and the Photon Factory with the approved number 2001G275. This work is supported by funding from the Japanese Ministry of ECSST via the Kitakyushu Knowledge-based Cluster Project.

References and Notes

(1) Kato, T. *Struct. Bonding (Berlin)* **2000**, *96*, 95.
(2) Kato, T. *Kobunshi* **2003**, *52*, 276.
(3) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Serimaa, R.; Mäkelä, T.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557.
(4) Ruokolainen, J.; ten Brinke, G.; Ikkala, O. *Adv. Mater.* **1999**, *11*, 777.
(5) Hamley, I. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1692.
(6) Akiba, I. *Seikeikakou* **2003**, *15*, 463.
(7) Thünemann, A. F.; Kubowicz, S.; Burger, C.; Watson, M. D.; Tchebotareva, N.; Mullen, K. *J. Am. Chem. Soc.* **2003**, *125*, 352.
(8) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interaction and the Miscibility of Polymer Blends*; Technomic: Lancaster, 1991.
(9) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(10) Hobbie, E. K.; Han, C. C. *J. Chem. Phys.* **1996**, *195*, 738.
(11) Akiba, I.; Ohba, Y.; Akiyama, S. *Macromolecules* **1999**, *32*, 1175.
(12) Akiyama, S.; Ishikawa, K.; Kawahara, S.; Akiba, I. *Polymer* **2001**, *42*, 6657.
(13) Akiba, I.; Seki, T.; Akiyama, S. *e-Polym.* **2002**, 008.
(14) Sato, A.; Kato, T.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 503.
(15) Tanaka, F.; Ishida, M.; Matsuyama, A. *Macromolecules* **1991**, *24*, 5582.
(16) Akiba, I.; Sakurai, K. *e-Polym.* **2002**, 053.
(17) Akiba, I.; Nomura, K.; Shikasho, K.; Jeong, Y.; Sakurai, K. *Macromolecules* **2003**, *36*, 8890.
(18) Akiba, I.; Akiyama, S. *Macromolecules* **1999**, *32*, 3741.
(19) Akiba, I.; Akiyama, S. *Mol. Cryst. Liq. Cryst.* **2000**, *339*, 209.
(20) Vikki, T.; Ruokolainen, J.; Ikkala, O.; Passiniemi, P.; Isotalo, H.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1997**, *30*, 4064.
(21) Ikkala, O.; Ruokolainen, J.; ten Brinke, G.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1995**, *28*, 7088.
(22) Ponomarenko, E. A.; Tirrell, D. A.; MacKnight, W. J. *Macromolecules* **1998**, *31*, 1584.
(23) Haraguchi, M.; Nakagawa, T.; Nose, T. *Polymer* **1995**, *36*, 2567.
(24) Haraguchi, M.; Inomata, K.; Nose, T. *Polymer* **1996**, *37*, 3611.
(25) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.
(26) Thünemann, A. F.; General, S. *Langmuir* **2000**, *16*, 9634. (b) Thünemann, A. F.; General, S. *Macromolecules* **2001**, *34*, 6978.
(27) *Hand Book of Analytical Chemistry*; Meites, L., Ed.; McGraw-Hill: New York, 1963.
(28) Oakes, J.; Gratton, P. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2563.
(29) Dirksen, A.; Zuidema, E.; Williams, R. M.; De Cola, L.; Kauffmann, C.; Vögtle, F.; Roque, A.; Pina, F. *Macromolecules* **2002**, *35*, 2743.
(30) Akiba, I.; Sakurai, K. *Polym. Prepr., Jpn.* **2003**, *52*, 2551.
(31) Ehlich, D.; Takenaka, M.; Hashimoto, T. *Macromolecules* **1993**, *26*, 492.
(32) Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Komanschek, E.; ten Brinke, G.; Ikkala, O. *Macromolecules* **1997**, *30*, 2002.
(33) Akiba, I.; Jeong, Y.; Sakurai, K. *Macromolecules* **2003**, *36*, 8433.

MA0356414