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Nanophase-Separated Supramolecular Assemblies of Two Functionalized Polymers via Acid−Base Complexation

Atsushi Noro,* Koji Ishihara, and Yushu Matsushita*

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

S Supporting Information

Microphase separation is the phase separation phenomenon at the microscopic scale for multicomponent soft materials, especially block copolymers,[1−7] and is being replaced with the term "nanophase separation"[8] in some literature because their actual size of phase separation is "nanoscopic". In order to achieve nanostructured materials with high performance and functionality, structures resulting from such nanophase separation in block copolymers have been investigated widely for the past several decades.[9−14]

Recently, incorporation of the supramolecular concept into multicomponent soft materials, in other words, combination of nanophase separation and supramolecular interactions in soft materials,[15−22] has been paid more and more attention since supramolecular interactions in nanophase-separated structures could bring higher performance and functionality into such materials. One of such typical studies is on "block supramacromolecules",[23] which are block copolymer-like supramolecular assemblies of different polymers. For instance, Russell et al. reported a very pioneering study on observation of nanophase-separated structures in block supramacromolecules composed of end-modified polymers in 1988.[24] In recent years, we and others have also reported some studies of block supramacromolecules, which were prepared on the basis of more precise molecular designs.[25−33] Preparation of block supramacromolecules, however, usually requires precise synthesis of end-modified polymers as building blocks. Moreover, the efficiency of the formation of block supramacromolecules from the blends of end-modified polymers is strongly influenced by stoichiometry between noncovalent bonding groups on each end-modified polymer.[34] If supramolecular assemblies could be built up from the blends of commercially available polymers, for instance, an end-modified polymer as one building block and a multifunctional polymer with many noncovalent bonding groups as the counterpart, this facile preparation approach could be widely useful to produce nanophase-separated structures of one-to-*n* ($n > 1$) supramolecular assemblies without maintaining severe restrictions of stoichiometry.[35]

Here in this Communication, we present a facile preparation approach of supramolecular assemblies of two homopolymers, which represent nanophase-separated structures due to acid−base complexation.[36] To build up supramolecular assemblies of polymers via acid−base complexation without utilizing time-consuming procedures, carboxyl-terminated poly(dimethylsiloxane) (PDMS-COOH, $M_n \sim 1450$, PDI ∼ 1.6, $T_g \sim -125$ °C, purchased from Shin-Etsu Chemical Co. Ltd.) for industrial use was selected as an end-modified polymer of one building block, while commercially available and branched polyethylenimine (PEI, $M_n \sim 1200$, $M_w \sim 1300$, $T_g \sim -56$ °C, purchased from Aldrich) was used as a multifunctional polymer (average number of amine per one PEI molecule is 28). Those chemical structures and the manner of their self-assembly are shown in Figure 1. These parent polymers are both liquids at room temperature. Mixing PDMS-COOH and PEI is expected to produce acid−base complexes between carboxylic acid on PDMS-COOH and many amino groups on PEI. To prepare homogeneous blend samples, these two polymers were blended in a mixed solvent of tetrahydrofuran/methanol (1:1 by volume). Then, the solvent was slowly evaporated from the solutions on a hot plate at 35 °C for 24 h, and the blend samples were further dried *in vacuo* for 48 h. The weight ratios of PDMS-COOH:PEI in the blends were varied as 50:*X*, where 10 samples with *X* (*X* = 1−10) were prepared in total, the blends being coded as DE-50:*X*. The neat PDMS-COOH was also called as DE-50:0 after the sample code of DE-50:*X*.

Figure 2 compares the appearance of two parent polymers as building blocks together with two blends. Although both parent samples (neat PDMS-COOH and neat PEI) are almost colorless, two blend samples have a yellow color which might be originated from the red shift of the absorption band in a UV−vis region due to acid−base complexation (see also Supporting Information.) As for the viscosity, though neat parent samples possess certain level of viscosity because of their molecular weights as polymers ($M_n \sim 1000$), they flow comparatively freely at room temperature as we can see in upside-down vials at the left for neat PDMS-COOH and the second left for neat PEI. On the other hand, the blend of DE-50:2 at the second right in Figure 2 apparently looks more viscous than both parent samples, even if the mass amount of PEI added to PDMS-COOH is small, probably due to acid−base complexation or hydrogen bonding between carboxylic acid and amine. This inclination of viscosity increase of the blends becomes more prominent for the sample DE-50:4, which looks like a gel and could flow very slowly at the speed of 1 cm per ∼30 s, maybe because of congestion of polymers in a confined nanospace.[37]

To reveal the interaction between PDMS-COOH and PEI in the blends, FT-IR measurements were carried out at room temperature under the reduced pressure. FT-IR spectra of 11 samples of DE-50:*X* are shown in Figure 3. There is a quite sharp peak at 1713 cm^{-1} on the spectrum of DE-50:0, indicating the characteristic absorption signal for C=O stretching vibration of

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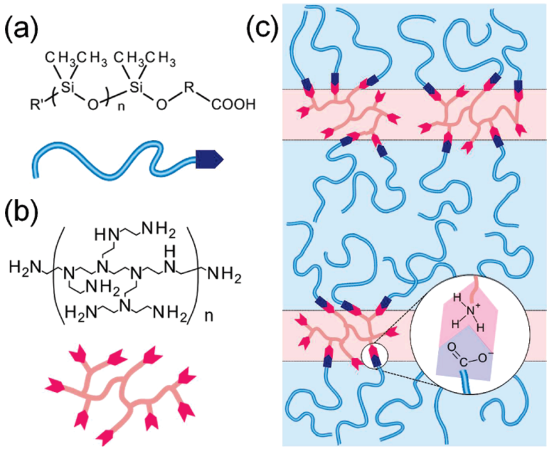

Figure 1. Schematic illustrations of nanophase-separated supramolecular assemblies and buliding blocks with their chemical structures. (a) PDMS-COOH. (b) PEI. (c) Supramolecular assemblies composed of PDMS-COOH and PEI. A primary ammonium ion is drawn as a representative for other ammonium ions in the enlarged acid−base complexed pair.

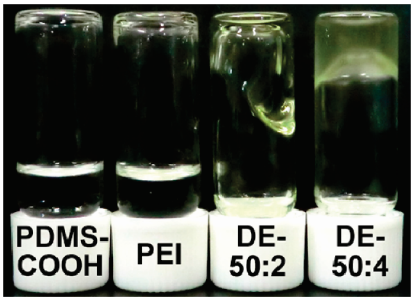

Figure 2. Comparison of appearance for two parent polymers and two blends of DE-50:*X* (*X* = 2 and 4) at room temperature.

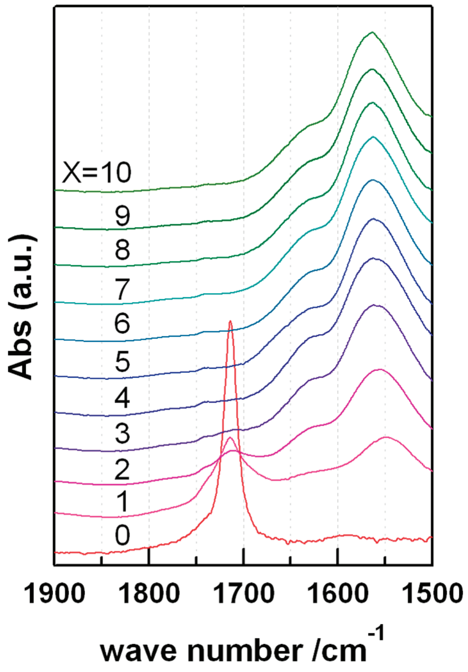

Figure 3. FT-IR spectra of 11 samples of DE-50:*X* ($0 \leq X \leq 10$). The spectra were displayed in the order of *X* from bottom (*X* = 0) to top (*X* = 10).

neutral COOH. There is also a small absorption peak of O═C−O$^-$ antisymmetric stretching vibration of ionized COOH at 1588 cm^{-1}, due to the presence of a little amount of dissociated carboxylic acid in neat PDMS-COOH. When the spectrum of DE-50:0 is compared with that of DE-50:1 which contains the small amount of PEI, however, the sudden decrease of the absorption at 1713 cm^{-1} as well as the increase in the absorption of ionized O═C−O$^-$ stretching around 1630 cm^{-1} can be recognized. On the basis of our molecular design of DE-50:1, this transformation in absorption spectra could be attributed to partial neutralization between carboxylic acid on PDMS-COOH and amine on added PEI (see also Supporting Information for more detailed analysis).

As *X* increases further, the absorption peak at 1713 cm^{-1} becomes smaller and smaller, and it vanishes at *X* = 3. The transformation in absorption spectra is very systematic. Paying attention to stoichiometry between carboxylic acid and amine, the stoichiometric balance should be attained at $X \sim 1.6$. Therefore, in DE-50:3, there exists already an excess amount of amine, which could neutralize all the acid in the blend promptly, resulting in the suppression of the absorption peak of neutral C═O stretching vibration at $X \geq 3$. The results suggest that all the blends give supramolecular assemblies composed of PDMS-COOH/PEI via acid−base complexation and that all the neutral COOH are consumed and turned into charged as COO$^-$ in the blends at $X \geq 3$.

To understand the morphological behavior of the blends at the nanoscopic scale, small-angle X-ray scattering (SAXS) measurements were conducted at room temperature at the beamline 15 A in the Photon Factory, Tsukuba, Japan. SAXS profiles of all DE-50:*X* samples are shown in Figure 4. The profile of neat PEI is also shown at the bottom in Figure 4. There are no peaks on the profiles of DE-50:0 and neat PEI, indicating no notable electron density difference in the neat samples. However, once both neat samples are blended, the shapes of profiles became totally different. The blends even with a small amount of PEI such as DE-50:1 and DE-50:2 show broad peaks at around 1.2 nm^{-1} on their profiles, representing correlation hole peaks[38] which might be originated from electron density difference between PDMS and PEI with the length scale of several nanometers. DE-50:3 also provides a large and broad peak on its profile at 0.9 nm^{-1}. In addition, the profile seems to possess the second-order peak at 1.8 nm^{-1}. Taking account of acid−base complexation between carboxylic acid on one end of PDMS-COOH and amino groups on PEI, the emergence of the second-order peak is possibly due to generation of the lamellar nanophase-separated structure between the PDMS phase and a newly created COOH/PEI acid−base complex phase in the blend. This interpretation is strongly supported by the profiles of the blends with $X \geq 4$. On the profile of DE-50:4, there are three sharp peaks at 0.85, 1.7, and 2.55 nm^{-1}, relative *q* values of 1, 2, and 3, indicating a clear lamellar nanophase-separated structure with domain spacing of 7.4 nm in the blend. Other profiles of DE-50:*X* ($X \geq 5$) have also sharp peaks at relative *q* values of 1, 2, and 3, but the location of peaks shifted to lower *q* values as the *X* value increases, representing domain spacing expansion probably due to the increase in the thickness of COOH/PEI phase in nanophase-separated structures.

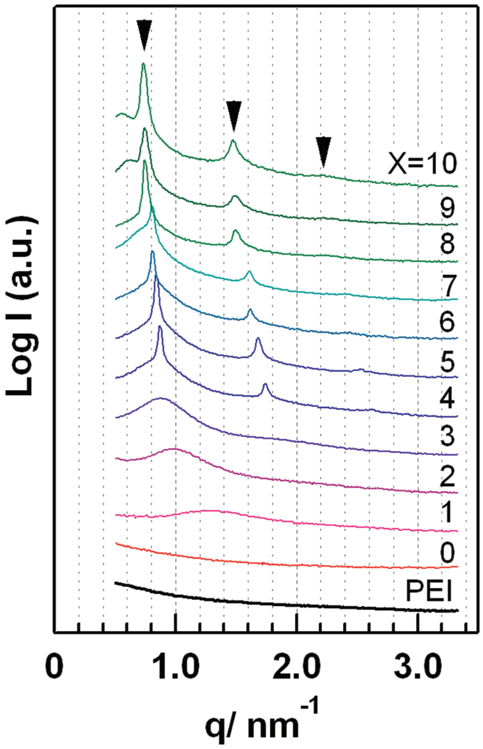

Figure 4. SAXS profiles of 11 samples of DE-50:*X* ($0 \le X \le 10$). The profile of neat PEI was displayed at the bottom. Profiles of DE-50:*X* were displayed in the order of *X* from the second bottom ($X = 0$) to top ($X = 10$).

As was supported in Figure 3, supramolecular assemblies of homopolymers was certainly generated in the blends of PDMS-COOH and PEI due to acid−base complexation between a carboxylic acid group (COOH) of PDMS-COOH and amino groups on PEI. Since the fraction of COOH and PEI is small in the blends (for example, 7.4 wt % of PEI in DE-50:4), spherical nanophase-separated structures between a PDMS phase and an acid−base COOH/PEI complex phase are expected to be observed in supramolecular assemblies if we remember the normal phase diagram of a diblock copolymer.[2,4,5] However, it was revealed by SAXS that DE-50:*X* ($X \ge 4$) represents lamellar nanophase-separated structures which probably consist of a hydrophobic PDMS phase and an ionically charged phase[39−41] of COOH/PEI, even though the fraction of COOH/PEI complex phase is fairly low. According to the theory by Semenov et al.,[42] the morphology formation of disklike multiplets and lamellae is more favored than spherical multiplets at so-called "superstrong segregation limit"[43] between a charged component and an uncharged component, regardless of the very small fraction of a charged component. Having this theory under consideration, our findings on DE-50:*X* ($4 \le X \le 10$), that is, formation of lamellar nanophase-separated structures without severe restrictions of acid/amine stoichiometry, are very reasonable.

In summary, we have demonstrated facile building-up of nanophase-separated supramolecular assemblies composed of commercially available polymers such as a pair of PDMS-COOH and PEI via acid−base complexation. FT-IR detected the ionized carboxylate (COO^-) which was neutralized by amine, representing acid−base complexation between carboxylic acid on PDMS-COOH and amine on PEI. Without severe restrictions of acid/amine stoichiometry, sharp peaks at relative *q* values of integer numbers up to the third order were observed for the blends of DE-50:*X* ($4 \le X \le 10$) by SAXS measurements, indicating the formation of lamellar nanophase-separated structures of supramolecular assemblies, whereas correlation hole peaks were observed for the blends of DE-50:*X* with $X \le 2$ due to the electron density difference between components. The formation of lamellar nanophase-separated structures was attained regardless of the small fraction of a charged component, probably due to superstrong segregation. Further studies of phase separation of supramolecular assemblies are now under investigation. In any case, such facile building-up of nanophase-separated supramolecular assemblies will be widely utilized for new applications of nanostructured soft materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yushu@apchem.nagoya-u.ac.jp (Y.M.); noro@nagoya-u.jp (A.N.).

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■ REFERENCES

(1) Matsuo, M.; Sagae, S.; Asai, H. *Polymer* **1969**, *10*, 79.
(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602–1617.
(3) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697–705.
(4) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525–557.
(5) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091–1098.
(6) Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204*, 265–273.
(7) Matsushita, Y. *Macromolecules* **2007**, *40*, 771–776.
(8) Masuda, J.; Takano, A.; Nagata, Y.; Noro, A.; Matsushita, Y. *Phys. Rev. Lett.* **2006**, *97*, 098301.
(9) Discher, B. M.; Won, Y. Y.; Ege, D. S.; Lee, J. C. M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284*, 1143–1146.
(10) Lin, Y.; Boker, A.; He, J. B.; Sill, K.; Xiang, H. Q.; Abetz, C.; Li, X. F.; Wang, J.; Emrick, T.; Long, S.; Wang, Q.; Balazs, A.; Russell, T. P. *Nature* **2005**, *434*, 55–59.
(11) Yang, S. Y.; Ryu, I.; Kim, H. Y.; Kim, J. K.; Jang, S. K.; Russell, T. P. *Adv. Mater.* **2006**, *18*, 709.
(12) Kang, Y.; Walish, J. J.; Gorishnyy, T.; Thomas, E. L. *Nature Mater.* **2007**, *6*, 957–960.
(13) Cho, J. H.; Lee, J.; Xia, Y.; Kim, B.; He, Y. Y.; Renn, M. J.; Lodge, T. P.; Frisbie, C. D. *Nature Mater.* **2008**, *7*, 900–906.
(14) Kim, K. T.; Cornelissen, J.; Nolte, R. J. M.; van Hest, J. C. M. *Adv. Mater.* **2009**, *21*, 2787.
(15) Ikkala, O.; ten Brinke, G. *Science* **2002**, *295*, 2407–2409.

(16) Noro, A.; Matsushita, Y.; Lodge, T. P. *Macromolecules* **2008**, *41*, 5839–5844.

(17) Tang, C. B.; Lennon, E. M.; Fredrickson, G. H.; Kramer, E. J.; Hawker, C. J. *Science* **2008**, *322*, 429–432.

(18) Feldman, K. E.; Kade, M. J.; Meijer, E. W.; Hawker, C. J.; Kramer, E. J. *Macromolecules* **2009**, *42*, 9072–9081.

(19) Zhao, Y.; Thorkelsson, K.; Mastroianni, A. J.; Schilling, T.; Luther, J. M.; Rancatore, B. J.; Matsunaga, K.; Jinnai, H.; Wu, Y.; Poulsen, D.; Frechet, J. M. J.; Alivisatos, A. P.; Xu, T. *Nature Mater.* **2009**, *8*, 979–985.

(20) Burnworth, M.; Tang, L. M.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* **2011**, *472*, 334–U230.

(21) Noro, A.; Hayashi, M.; Ohshika, A.; Matsushita, Y. *Soft Matter* **2011**, *7*, 1667–1670.

(22) Hunt, J. N.; Feldman, K. E.; Lynd, N. A.; Deek, J.; Campos, L. M.; Spruell, J. M.; Hernandez, B. Z.; Kramer, E. J.; Hawker, C. J. *Adv. Mater.* **2011**, *23*, 2327.

(23) Noro, A.; Nagata, Y.; Takano, A.; Matsushita, Y. *Biomacromolecules* **2006**, *7*, 1696–1699.

(24) Russell, T. P.; Jerome, R.; Charlier, P.; Foucart, M. *Macromolecules* **1988**, *21*, 1709–1717.

(25) Noro, A.; Yamagishi, H.; Matsushita, Y. *Macromolecules* **2009**, *42*, 6335–6338.

(26) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3825–3829.

(27) Pispas, S.; Floudas, G.; Pakula, T.; Lieser, G.; Sakellariou, S.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 759–763.

(28) Yang, X. W.; Hua, F. J.; Yamato, K.; Ruckenstein, E.; Gong, B.; Kim, W.; Ryu, C. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 6471–6474.

(29) Binder, W. H.; Bernstorff, S.; Kluger, C.; Petraru, L.; Kunz, M. J. *Adv. Mater.* **2005**, *17*, 2824.

(30) Huh, J.; Park, H. J.; Kim, K. H.; Park, C.; Jo, W. H. *Adv. Mater.* **2006**, *18*, 624.

(31) Feldman, K. E.; Kade, M. J.; de Greef, T. F. A.; Meijer, E. W.; Kramer, E. J.; Hawker, C. J. *Macromolecules* **2008**, *41*, 4694–4700.

(32) Ambade, A. V.; Yang, S. K.; Weck, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2894–2898.

(33) Qian, J.; Wu, F. P. *Chem. Mater.* **2009**, *21*, 758–762.

(34) Noro, A.; Tamura, A.; Wakao, S.; Takano, A.; Matsushita, Y. *Macromolecules* **2008**, *41*, 9277–9283.

(35) Ruokolainen, J.; Makinen, R.; Torkkeli, M.; Makela, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557–560.

(36) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345–6359.

(37) Noro, A.; Matsushita, Y.; Lodge, T. P. *Macromolecules* **2009**, *42*, 5802–5810.

(38) de Gennes, P.-G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(39) Mincheva, R.; Bougard, F.; Paneva, D.; Vachaudez, M.; Fustin, C.-A.; Gohy, J.-F.; Manolova, N.; Rashkov, I.; Dubois, P. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2105–2117.

(40) Dimitrov, I.; Jankova, K.; Hvilsted, S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2044–2052.

(41) Li, J.; He, W.-D.; He, N.; Han, S.-C.; Sun, X.-S.; Li, L.-Y.; Zhang, B.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1450–1462.

(42) Semenov, A. N.; Nyrkova, I. A.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 7491–7500.

(43) Li, Z. B.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98–101.