

## SHORT COMMUNICATIONS

## Novel Functional Polymers: Poly(dimethylsiloxane)–Polyamide Multiblock Copolymer VI.<sup>†</sup> A Transmission Electron Microscopic Study on Microphase-Separated Structure in Aramid-Silicone Resin

Tsutomu FURUZONO, Kazuhisa SENSHU,\* Akio KISHIDA, Takeo MATSUMOTO,\*\*  
and Mitsuru AKASHI<sup>††</sup>

*Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1–21–40 Korimoto, Kagoshima 890, Japan*

*\* R & D Center, Terumo Corporation, 1500 Inokuchi, Nakai-machi, Ashigarakami-gun, Kanagawa 259–01, Japan*

*\*\* Tsukuba Research Laboratory, NOF Corporation, 5–10, Tokodai, Tsukuba 300–26, Japan*

(Received October 11, 1996)

KEY WORDS    Multiblock Copolymer / Transmission Electron Microscopy Observation / Morphology  
/ Microdomain Structure /

The microphase-separated structures in bulk and the surface structures of block copolymers have been interesting subjects in recent years. The outcomes obtained from these studies have been utilized in the development of adhesives, composites, membranes, and biomedical materials. It is worthy of note that many advances in these studies are attributable to progress in techniques such as transmission electron microscopy (TEM),<sup>1</sup> small-angle X-ray scattering (SAXS),<sup>2</sup> X-ray photoelectron spectroscopy (XPS),<sup>3</sup> attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR),<sup>4</sup> ion scattering spectroscopy,<sup>5</sup> dynamic- or static-secondary ion mass spectrometry (SIMS),<sup>6</sup> atomic force microscopy,<sup>7</sup> laser scanning confocal microscopy,<sup>8</sup> and contact angle measurement.<sup>9</sup>

Recently, we have carried out investigations on the synthesis, characterization and functionalities of the multiblock copolymer (aramid-silicone resin; PAS)<sup>10–15</sup> consisting of polyamide (aramid) as the hard segment and poly(dimethylsiloxane) (PDMS) as the soft one (Figure 1). In our studies, the presence of a microphase-separated structure in PAS film is suggested from the electron probe micro analysis,<sup>10</sup> thermomechanical properties,<sup>14</sup> gas permeabilities<sup>14</sup> of PAS and cell adhesion onto a PAS surface.<sup>15</sup> In addition, the results of the XPS and contact angle measurements suggest that PDMS components fully cover the outermost surface of the PAS film.<sup>10</sup> The morphology and the periodicity of the microphase-separated structure of PAS film, however, are still unclear. In this report, in order to clarify the bulk and surface structure visually, we observed the morphology of the microdomains in the bulk and near the free surface by means of TEM.

### EXPERIMENTAL

PAS was synthesized by a low-temperature solution polycondensation through a two-step procedure according to the literature.<sup>10,16</sup> The PDMS-diamine (Shin-Etsu Chemical Co., Japan), number-average molecular weight (1680), was used in this procedure. The structure and

PDMS content of the resulting copolymers were confirmed as the proposed block copolymer by means of <sup>1</sup>H NMR (JEOL EX-90 Fourier transform spectrometer; JEOL Ltd., Japan) spectroscopy.<sup>10,13</sup>

The PAS films were cast from a 10 wt% *N,N'*-dimethylacetamide (DMAc) solution on a TEFLON<sup>®</sup> sheet. Then we evaporated the solvent at 60°C for 5 days. Finally, the films were dried at room temperature for 24 hours under a vacuum (2 mmHg), and PAS films with about 100 μm thickness were obtained. Test specimens (2 × 10 mm) were cut from the films and stained with a vapor of RuO<sub>4</sub><sup>17,18</sup> for 15–30 min. This was necessary to avoid structural change during the embedding process. The specimens were then embedded in epoxy resin (Quetol 812, Nisshin EM Ltd., Japan). Ultrathin sections (*ca.* 50–80 nm thickness) were made using an ultratome (2088V, LKB Ltd., Sweden) with a diamond knife at room temperature. TEM was done with a JEM 1200-EX transmission electron microscope (JEOL Ltd., Japan) at 80 kV accelerating voltage.

### RESULTS AND DISCUSSION

Table I shows the molecular weight of PDMS and aramid components in PAS. PAS possesses different values of

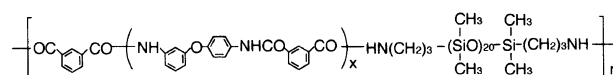


Figure 1. Chemical structure of aramid-silicone resin (PAS).

Table I. Molecular weight of PDMS and aramid components in PAS

Polymer	PDMS content <sup>a</sup>	<i>M<sub>n</sub></i>	
	wt%	PDMS	aramid (×) <sup>a</sup>
PAS-14	14	1,680	10,330 (30.9)
PAS-41	41	1,680	2,410 ( 6.9)

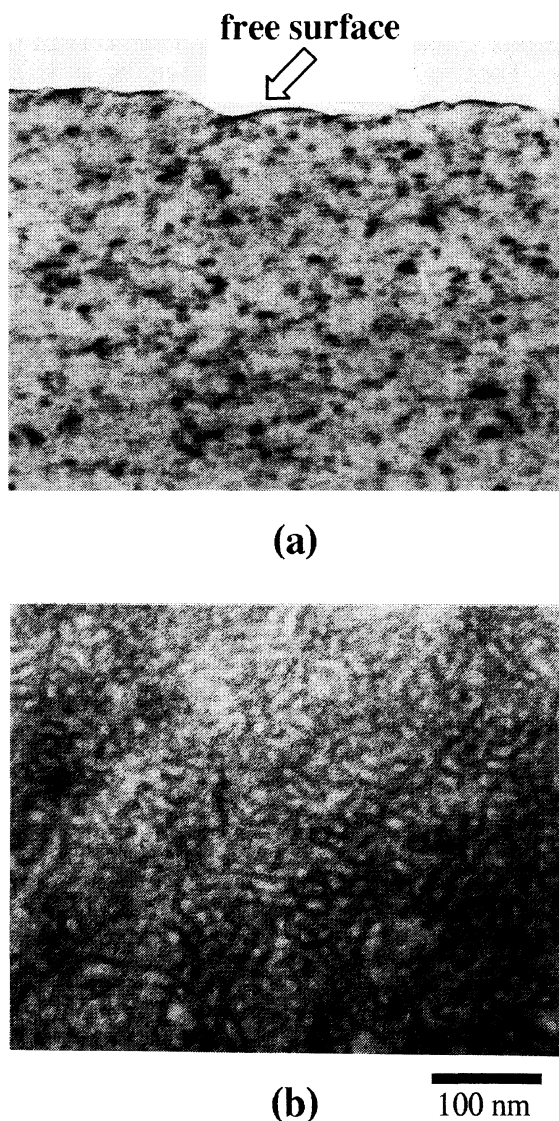
<sup>a</sup> Calculated from the Si-CH<sub>3</sub>/aromatic H ratio in the <sup>1</sup>H NMR spectrum.

<sup>†</sup> For Part I, *cf.* ref 10, for Part II, *cf.* ref 12, for Part III, *cf.* ref 13, for Part VI, *cf.* ref 14, for Part V, *cf.* ref 15.

<sup>††</sup> To whom correspondence should be addressed.

aramid segment's  $M_n$ . For molecular weight determination of PAS, gel permeation chromatographic measurement was attempted. However, we could not obtain reliable results about the molecular weight of PAS because of the poor solubility for the PDMS unit of PAS for *N,N'*-dimethylformamide as an eluent. From the results of the mechanical properties and moldability given elsewhere,<sup>10,12</sup> PAS might possess a high molecular weight.

Figure 2 shows the transmission electron micrographs of ultrathin sections of PAS-14 (PDMS/aramid = 1680/10330 by  $M_n$ ) and PAS-41 (PDMS/aramid = 1680/2410 by  $M_n$ ). We confirmed that the PDMS component was more easily stained with  $\text{RuO}_4$  than the aramid component. Thus, the black area indicates a PDMS domain, and the white area corresponds to an aramid domain. The PDMS layer (the thickness of the first PDMS layer at the outermost surface; *ca.* 10 Å) always occupied the free surface of PAS-14 film (Figure 2(a)). This is because the surface (which was exposed to air during the casting of the film), tended to minimize the surface free energy of the block copolymer. That is, the



**Figure 2.** Transmission electron micrographs of ultrathin sections of PAS-14 and 41 films. (a) Cross-section near the free surface of PAS-14 film. (b) Cross-section of the center region of PAS-41 film.

PDMS component should form the outermost layer at the free surface, since the critical surface tensions of wetting for PDMS and aramid are 22 and 46 dyn/cm, respectively.<sup>13</sup> In the cross-section near the free surface of PAS with 8 wt% of PDMS, the same phenomenon was also observed.<sup>19</sup> Moreover, the results of static-SIMS and angle-dependent XPS of the surfaces of PAS containing from 8 to 71 wt% of PDMS supported this phenomenon experimentally.<sup>19</sup> The surface enrichment of the PDMS component was also recognized in other block copolymers containing PDMS such as PDMS-polystyrene (PS)<sup>20</sup> and PDMS-Bisphenol A polycarbonate<sup>3</sup> block copolymers by XPS and ATR-FTIR. Unfortunately, ultrathin sections of PAS containing over 41 wt% of PDMS in the surface vicinity could not be perfectly obtained due to the flexibility of the films. The preparation of the cross-section near the free surface of PAS containing over 41 wt% of PDMS by means of a cryosectioning method is in progress.

In the bulk phase of PAS-14, discrete spherical regions of PDMS in an aramid matrix are shown (Figure 2(a)). The diameters of the spherical regions of PAS-14 were approximately 60–80 Å. The presence of PDMS spherical microdomains dispersed in an aramid matrix was quite reasonable from the volume fraction (0.19) of PDMS in PAS-14 which was obtained by using the group contribution calculation.<sup>21</sup> Hashimoto *et al.* have reported about the correlation between the thickness of the first layer at the outermost surface and the periodicity in bulk for polyisoprene-polystyrene block copolymer.<sup>22</sup> They suggested that the thickness of the first layer was half of the bulk periodicity for lamellae structures and that was one-third of radius for spherical structure. For PAS-14, the fraction between the thickness of PDMS surface layer and the radius of the PDMS spheres indicated almost the same value (1/3–1/4). This result was in agreement with Hashimoto's criterion.

Although we could not observe the near region of free surface for PAS-41, a transmission electron micrograph of the center region could be obtained (Figure 2(b)). The PDMS component formed cylindrical microdomains dispersed in an aramid matrix. The interdomain spacing from TEM observation was approximately 60–80 Å. In the morphology of the PDMS-related multiblock copolymer, the interdomain spacing of the PDMS-polysulphone (PSF) multiblock copolymer (PDMS/PSF = 6700/9700 by  $M_n$ , PDMS content = 41 wt%) was  $200 \pm 20$  Å by TEM and 240 Å by SAXS, and the PDMS-continuity was present.<sup>23</sup> The bulk morphology of PAS-41 observed by TEM was similar to that of the PDMS-PSF copolymer, although the interdomain spacing of PAS-41 was smaller than that of this PDMS-PSF copolymer. Also, we could observe the two-phase separated structure of PAS which was prepared by using an even smaller PDMS segment ( $M_n = 900$ ).<sup>19</sup> The phase separation displayed at such low block molecular weight levels, (such as PAS) seems to be unusual.<sup>14,24</sup> The presence of the two-phase separation of PAS at such low block molecular weight levels seems to depend on the results from the high degree of incompatibility of the nonpolar PDMS segment and the polar aramid segment. In a previous study, the oxygen permeation coefficient of PAS film was drastically increased to between a 0.43 and 0.55

volume fraction of PDMS.<sup>14</sup> In these fractions, a continuous PDMS domain should be formed in the bulk. The volume fraction of PDMS of PAS-41 was about 0.50 calculated by group contribution calculations.<sup>21</sup> Therefore, the gas permeability of PAS was consistent with the morphology in the bulk phase.

In conclusion, the surface and the bulk structures of aramid-silicone resin (PAS) were characterized by TEM. It was revealed that a PDMS component was condensed at the outermost surface, and PASs with 14 and 41 wt% of PDMS possessed the PDMS-spherical and -cylindrical microdomain structures in the bulk phase, respectively. Moreover, such surface enrichment well corresponds to the results of XPS and contact angle measurements.<sup>10</sup> We could visually reconfirm the surface structure of PAS film by TEM observation. This work is essential and very important so as to obtain a clue in order to clarify the relationships between the characteristics and the functionalities of the novel functional polymers (PASs).

*Acknowledgments.* T. Furuzono is indebted to the Japan Society for the Promotion of Science (JSPS Research Fellowships for Young Scientists) for research grants. This work was financially supported in part by a Grant-in-Aid for Scientific Research (No. 07558257) from the Ministry of Education, Science, and Culture of Japan, and a Grant-in-Aid for Research and Development Project of New Medical Technology in Artificial Organs from the Ministry of Health and Welfare, Government of Japan in 1995, and Ciba-Geigy Foundation (Japan) for the Promotion of Science. The authors would like to express their thanks to Professor Tadashi Komoto, Department of Materials Engineering, Gunma University, for his advice about the staining method with RuO<sub>4</sub>.

## REFERENCES AND NOTES

- H. Hasegawa and T. Hashimoto, *Macromolecules*, **18**, 589 (1985).
- R. L. Lescanec, D. A. Hajduk, G. Y. Kim, Y. Gan, R. Yin, S. M. Gruner, T. E. Hogen-Esch, and E. L. Thomas, *Macromolecules*, **28**, 3485 (1995).
- X. Chen, H. F. Lee, and J. A. Gardella, Jr., *Macromolecules*, **26**, 4601 (1993).
- E. R. Mittlefehldt and J. A. Gardella, Jr., *Appl. Spectrosc.*, **43**, 1172 (1989).
- R. L. Schmitt, J. A. Gardella, Jr., J. H. Magill, L. Salvati, Jr., and R. L. Chin, *Macromolecules*, **18**, 2675 (1985).
- D. G. Castner, B. D. Ratner, D. W. Grainger, S. W. Kim, T. Okano, K. Suzuki, D. Briggs, and S. Nakahama, *J. Biomater. Sci. Polym. Ed.*, **3**, 463 (1992).
- B. K. Annis, D. W. Schwark, J. R. Reffner, E. L. Thomas, and B. Wunderlich, *Makromol. Chem.*, **193**, 2589 (1992).
- H. Jinnai, Y. Nishikawa, T. Koga and T. Hashimoto, *Macromolecules*, **28**, 4782 (1995).
- J. H. Lee and J. D. Andrade, in "Polymer Surface Dynamics," J. D. Andrade, ed., Plenum Press, New York, N.Y., 1987, p 119.
- T. Furuzono, E. Yashima, A. Kishida, I. Maruyama, T. Matsumoto, and M. Akashi, *J. Biomater. Sci., Polym. Ed.*, **5**, 89 (1993).
- T. Furuzono, A. Kishida, M. Akashi, I. Maruyama, T. Miyazaki, Y. Koinuma, and T. Matsumoto, *Jpn. J. Artif. Organs*, **22**, 370 (1993).
- A. Kishida, T. Furuzono, T. Ohshige, I. Maruyama, T. Matsumoto, H. Itoh, M. Murakami, and M. Akashi, *Angew. Makromol. Chem.*, **220**, 89 (1994).
- T. Furuzono, K. Seki, A. Kishida, T. Ohshige, K. Waki, I. Maruyama, and M. Akashi, *J. Appl. Polym. Sci.*, **59**, 1059 (1996).
- T. Matsumoto, Y. Koinuma, K. Waki, A. Kishida, T. Furuzono, I. Maruyama, and M. Akashi, *J. Appl. Polym. Sci.*, **59**, 1067 (1996).
- T. Furuzono, A. Kishida, M. Yanagi, T. Matsumoto, T. Kanda, T. Nakamura, T. Aiko, I. Maruyama, and M. Akashi, *J. Biomater. Sci. Polym. Ed.*, **7**, 871 (1996).
- M. Kajiyama, M. Kakimoto, and Y. Imai, *Macromolecules*, **22**, 4143 (1989).
- J. S. Trent, J. I. Scheinbeim, and P. R. Couchman, *Macromolecules*, **16**, 589 (1983).
- J. S. Trent, *Macromolecule*, **17**, 2930 (1984).
- K. Senshu, T. Furuzono, N. Koshizaki, S. Yamashita, T. Matsumoto, A. Kishida, and M. Akashi, *Macromolecules*, in contribution.
- X. Chen, J. A. Gardella, Jr., and P. L. Kumler, *Macromolecules*, **25**, 6621 (1992).
- R. F. Fedors, *Polym. Eng. Sci.*, **9**, 147 (1974).
- H. Hasegawa and T. Hashimoto, *Polymer*, **33**, 475 (1992).
- D. Tyagi, J. L. Hedrick, D. C. Webster, J. E. McGrath, and G. L. Wilkes, *Polymer*, **29**, 833 (1988).
- A. Noshay, M. Matzner, and C. N. Merriam, *J. Polym. Sci., Part A-1*, **9**, 3147 (1971).