

# Syntheses of Poly(methyl methacrylate)/Poly(dimethyl siloxane) Graft Copolymers and Their Surface Enrichment of Their Blend with Acrylate Adhesive Copolymers

Yongjun Lee,<sup>1</sup> Isamu Akiba,<sup>2</sup> Saburo Akiyama<sup>1</sup>

<sup>1</sup>Department of Organic and Polymer Materials Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

<sup>2</sup>Faculty of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, Japan

Received 1 June 2001; accepted 9 December 2002

**ABSTRACT:** Several types of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers (PMMA-g-PDMS) were synthesized using macromonomer technology. Three types of PMMA-g-PDMS with different PDMS chain length were obtained. The effect of siloxane chain length on surface segregation of PMMA-g-PDMS/poly(2-ethylhexyl acrylate-

co-acrylic acid-co-vinyl acetate)[P(2EHA-AA-VAc)] blends was investigated. The blends of PMMA-g-PDMS with P(2EHA-AA-VAc) showed surface segregations of PDMS components. The surface enrichments of PDMS in the blends depended on the PDMS chain length, significantly. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1736–1740, 2002

## INTRODUCTION

The surface segregation behavior of block or graft copolymers is very important in fields of adhesive, coating, lubricants, and surface modification.<sup>1–5</sup> The surface segregations of copolymers or their blends are derived by the components with low-surface tension, such as Si-containing or F-containing copolymers. Because polysiloxanes and their copolymers especially have very interesting properties such as elastomeric behavior, good thermal, UV, oxidative stabilities, good weatherability, and so on, they should be useful materials to enhance surface segregation.

In our previous studies,<sup>7–11</sup> surface segregation and gradient domain structure of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) [P(2EHA-AA-VAc)]/poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] blends were investigated. It was found that the P(VDF-HFA) component enriched the surface and the P(2EHA-AA-VAc) component precipitated on the bottom (contact with substrate: poly(dimethylsiloxane)-coated paper) by using SEM, ATR-FTIR, XPS, etc.

Because surface tension of poly(dimethylsiloxane) is comparable with that of fluoro-polymers, such as P(VDF-HFA), blends of PDMS-containing copolymers with P(2EHA-AA-VAc) should indicate surface enrichment.

In this study, we prepared several types of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers.<sup>12–15</sup> Then we studied surface segregation of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers/P(2EHA-AA-VAc) blends.

## EXPERIMENTAL

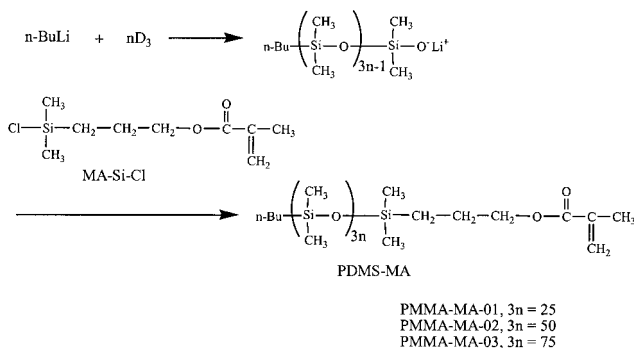
### Synthesis of 3-methacryloyloxypropyl polydimethylsiloxane (PDMS-MA) macromonomers

The PDMS-MA macromonomers were prepared by the anionic polymerization of hexamethylcyclotrisiloxane (D3) using *n*-BuLi as an initiator in a nitrogen atmosphere. D3 was dissolved in THF and then *n*-BuLi (1.6 N in hexane) was slowly added with stirring over a period 30 min. After all D3 was converted, then triethylamine and 3-methacryloyloxypropyldimethylchlorosilane (MA-Si-Cl) were added slowly. After 45 min mixing at room temperature, methanol was added and mixed 45 min. THF was removed under vacuum and the LiCl precipitate was removed by filtration. The PDMS-MA macromonomer was then purified by reprecipitation from THF into methanol/water mixture. Three types of PDMS-MA macromonomer, having different siloxane lengths, were prepared (Scheme 1).

### Synthesis of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers (PMMA-g-PDMS)

Free radical polymerization and copolymerization of the methyl methacrylate were conducted in toluene at

Correspondence to: S. Akiyama (akis@cc.tuat.ac.jp).



Scheme 1

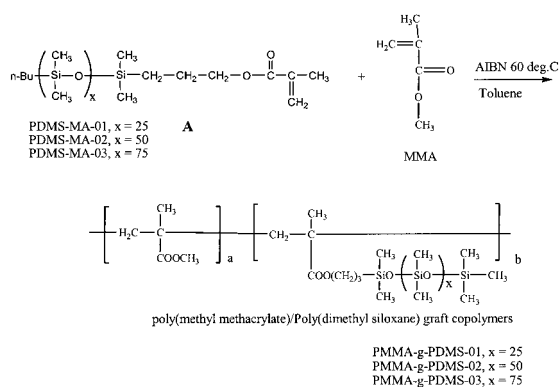
60°C using azo-isobutyronitrile as the initiator. Toluene was placed in a three- or four-neck flask in nitrogen atmosphere and heated to 60°C. Then the mixture of PDMS-MA-01 macromonomer, MMA(methyl methacrylate), and AIBN was added slowly. After 6 h mixing at 60°C, the reactants were precipitated into methanol. A solid sample was obtained after drying. Three types of PMMA-g-PDMS polymers were prepared using MS-MA macromonomer (Scheme 2).

### Preparation of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate [P(2EHA-AA-VAc)])

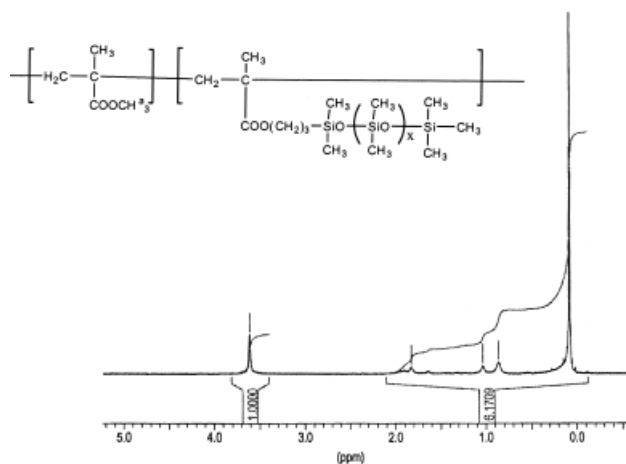
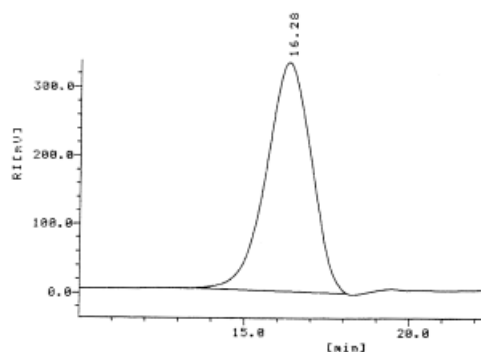
Poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate [P(2EHA-AA-VAc)]) was prepared by means of solution polymerization at 70°C for 7 h, using benzoyl peroxide as an initiator and mixtures of ethyl acetate (95%) with toluene (5%) as a solvent.

### DSC (differential scanning calorimeter) measurements

To evaluate the miscibility between components, the glass transition temperature ( $T_g$ ) of P(2EHA-AA-VAc)/PMMA-g-PDMS blends were determined using a 910 DSC with DuPont 990 system at a heating rate of 10°C/min under nitrogen gas.



Scheme 2

Figure 1  $^1\text{H-NMR}$  and GPC chart of PMMA-g-PDMS-02.

### ATR-FTIR

The ATR-FTIR measurements for surface of film specimens were carried out using a Nicolet 20SXB-FTIR with a prism of KRS-5 and two incidence angles of 45 and 90°.

## RESULT AND DISCUSSION

### Characterization of PMMA-g-PDMS

The  $^1\text{H-NMR}$  spectrum and GPC results of PMMA-g-PDMS-02 are shown in Figure 1. In addition, the characteristic data obtained by GPC and  $^1\text{H-NMR}$  for graft copolymers are shown in Table I. Because PMMA-g-PDMS-01 and -02 have relatively narrow molecular weight distribution (MWD) and reasonable integration ration of Si-CH<sub>3</sub> to H, syntheses of these polymers have been successfully performed. However, the PMMA-g-PDMS-03 had relatively wide (MWD). Therefore, only PMMA-g-PDMS-01 and -02 were used in the following sections. Table II shows molecular characteristics of PMMS-g-PDMS and P(2EHA-AA-VAc) used in this study.

### Miscibility and surface enrichment of P(2EHA-AA-VAc)/PMMA-g-PDMS blend films

Blend films were prepared by solution casting. Mixtures of PMMA-g-PDMS and P(2EHA-AA-VAc) were

TABLE I  
Characteristics of Poly(methyl methacrylate)/Poly(dimethyl siloxane) Graft Copolymers

	Integration ratio from <sup>1</sup> H-NMR		Molecular weight		
	H <sup>a</sup>	Si—CH <sub>3</sub>	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
PMMA-g-PDMS-01	1.00	1.96	7000	13,000	1.8
PMMA-g-PDMS-02	1.00	6.17	26,700	37,500	1.4
PMMA-g-PDMS-03	1.00	7.84	15,200	52,100	3.4

<sup>a</sup> Molecular weight equivalent to that of polystyrene by GPC.

dissolved in THF at 5% concentration. The solution was cast on the release liner[polydimethylsiloxane (PDMS), having a critical surface tension of wetting,  $\gamma_c \sim 24$  dyn/cm, is coated onto the liner]. The solution was allowed to stand for almost 2 days. The blend films were further dried at room temperature and reduced pressure for more than 1 day.

DSC thermograms for P(2EHA-AA-VAc)/PMMA-g-PDMS-02 blends films are shown at Figure 2. The blends films show two  $T_g$ s at  $-70$  and  $120^\circ\text{C}$ , which correspond to  $T_g$ s of P(2EHA-AA-VAc) and PMMA, respectively. Similar results were obtained for P(2EHA-AA-VAc)/PMMA-g-PDMS-01 blends. Therefore, the P(2EHA-AA-VAc)/PMMA-g-PDMS blends are immiscible. For these immiscible P(2EHA-AA-VAc)/PMMA-g-PDMS blends, ATR-FTIR measurements were performed to evaluate surface enrichment of PDMS.

Figure 3 shows ATR-FTIR spectra of the surface of P(2EHA-AA-VAc)/PMMA-g-PDMS-01 (50/50) and (30/70) blends, coated onto the release liner. When PDMS exists at surface of the films, the spectra show characteristic doublet between  $1100$  and  $1200\text{ cm}^{-1}$  attributed to absorbance of Si—O—Si. However,

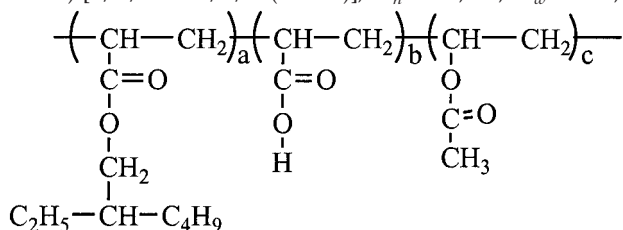
P(2EHA-AA-VAc)/PMMA-g-PDMS-01 (50/50) blend does not show any siloxane peak. In addition, the P(2EHA-AA-VAc)/PMMA-g-PDMS-01 (30/70) blend shows very weak doublet between  $1100$  and  $1200\text{ cm}^{-1}$ . Therefore, the PDMS component might be dispersed homogeneously in the blend films because the content and chain length of PDMS are not enough to cause segregating at the surface of the blend films.

Figure 4 shows ATR-FTIR spectra of P(2EHA-AA-VAc)/PMMA-g-PDMS-02 (50/50 and 30/70) blends coated onto the release liner. In these blends, the doublet between  $1100$  and  $1200\text{ cm}^{-1}$ , which is attributed to Si—O—Si, is clearly observed. Because the amount of Si—O—Si bonds is much less than that of C=O bonds, it is considered that intensity of the doublet of Si—O—Si should be much weaker than that of carbonyl stretching band at around  $1700\text{ cm}^{-1}$  as shown in Figure 3 when PDMS is homogeneously dispersed in the films. However, as shown in Figure 4, the intensity of the doublet of Si—O—Si is almost same as carbonyl stretching band at  $1700\text{ cm}^{-1}$ .

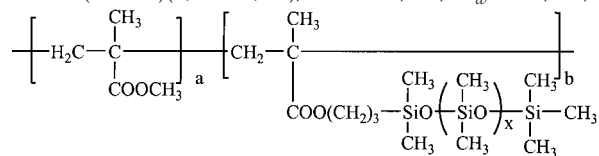
It is considered that the fraction of PDMS at the surface is higher than that predetermined by the blend composition in P(2EHA-AA-VAc)/PMMA-g-PDMS-02

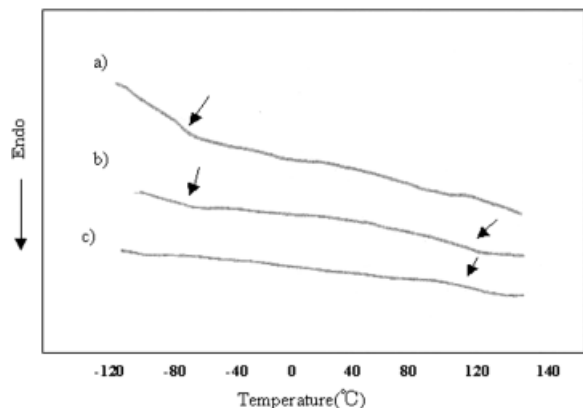
TABLE II  
Composition and Structure of PMMA-g-PDMS and P(2EHA-AA-VAc)

2-ethylhexyl acrylate/acrylic acid/vinyl acetate[P(2EHA-AA-VAc)]  
P(2EHA-AA-VAc) [a/b/c = 80/5/15(mol %)];  $M_n = 50,600$ ,  $M_w = 274,000$



Poly(methyl methacrylate)/Poly(dimethyl siloxane) Graft Copolymers  
PMMA-g-PDMS-01 ( $x = 25$ )(a/b = 50/50);  $M_n = 7000$ ,  $M_w = 13,000$ ,  $M_w/M_n = 1.8$   
PMMA-g-PDMS-02 ( $x = 50$ )(a/b = 50/50);  $M_n = 26,700$ ,  $M_w = 37,500$ ,  $M_w/M_n = 1.4$





**Figure 2** DSC Thermogram of (a) P(2EHA-AA-VAc), (b) P(EHA-AA-VAc)/PMMA-g-PDMS-02 = 50/50, (c) PMMA-g-PDMS-02.

blends. Depending on siloxane chain length in graft copolymer, different phase segregation behavior is observed. Inoue et al.<sup>2</sup> reported that the polysiloxane segments of polydimethylsiloxane-poly(methyl methacrylate) block copolymer and their PMMA blends accumulated on the air-side surfaces of the solution-cast film and surface segregation was significantly affected by siloxane chain length in block copolymers. Gorelova et al.<sup>6</sup> reported that the surface segregation of siloxane in blends of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers in poly(vinyl chloride) was influenced by the siloxane chain length. A similar result was reported by McGrath.<sup>17,18</sup> It was noticed that the siloxane surface segregation substantially depended on the block length of siloxane. These

results supported the fact that surface segregation of PMMA-g-PDMS took place in the P(2EHA-AA-VAc)/PMMA-g-PDMS blends, and was significantly influenced by the siloxane chain length in graft polymers.

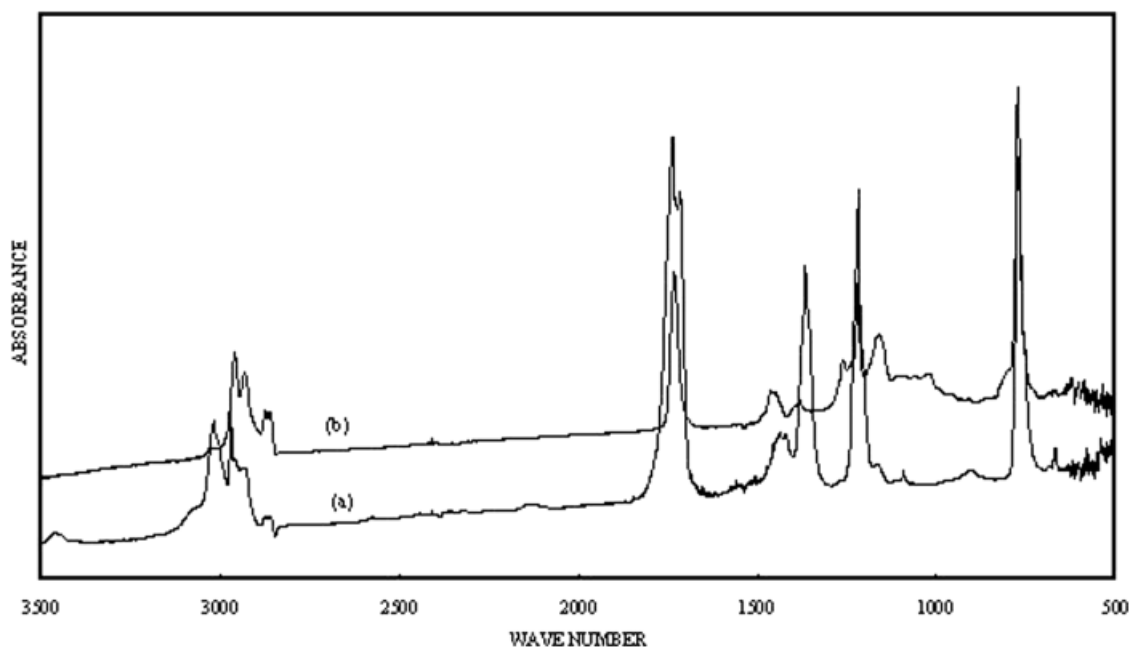
It is considered that composition of the PDMS varies with changing position in the blend film. Hence, it is expected that the ATR-FTIR spectra would vary when changing the incident angle of light source because the depth ( $d_p$ ) in ATR-FTIR measurement is calculated as<sup>16</sup>

$$d_p = \lambda / 2\pi \eta_A (\sin^2 \theta - \eta_{BA}^2)^{0.5},$$

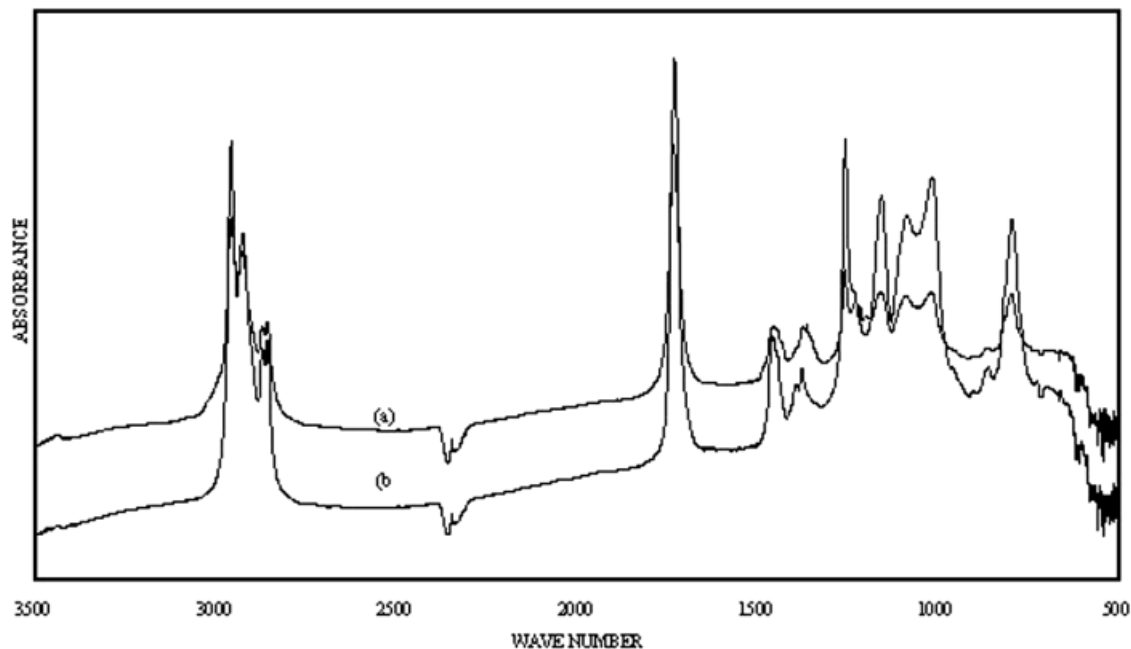
where  $\theta$  is the incidence angle,  $\pi$  is the circular constant,  $\lambda$  is infrared ray absorption wavelength, and  $\eta_A$  is the refractive index of prim, and  $\eta_{BA}$  is the refractive index of  $\eta_A/\eta_B$  ( $\eta_B$ , refractive index of sample).  $\eta_A$  of KRS-5 is around 2.37 and  $\lambda$  is  $1300 \text{ cm}^{-1}$ . In this study, the depth ( $d_p$ ) for P(2EHA-AA-VAc)/PMMA-g-PDMS was supposed to be 2.4 xmm at incident angle  $45^\circ$  and  $1.0 \mu\text{m}$  at incident angle  $90^\circ$ .

## CONCLUSION

Several types of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers were synthesized using macromonomer technology. The effect of siloxane chain length on surface segregation of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers (PMMA-g-PDMS)/poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) [P(2EHA-AA-VAc)] blends was investigated by ATR-FTIR. Surface



**Figure 3** ATR-FTIR spectra for P(2EHA-AA-VAc)/PMMA-g-PDMS-01 (incidence angle  $45^\circ$ , compositional change). (a) P(2EHA-AA-VAc)/PMMA-g-PDMS-01 = 50/50, (b) P(2EHA-AA-VAc)/PMMA-g-PDMS-01 = 30/70.



**Figure 4** ATR-FTIR spectra for P(2EHA-AA-VAc)/PMMA-g-PDMS-02 blends according to compositional change at the incidence angle 45°. (a) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 50/50, (b) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 30/70.

segregation was observed and significantly influenced by the siloxane chain length in graft copolymer. At the same blend compositions, surface segregation was significantly influenced by siloxane chain length and siloxane concentration at the surface of blends was increased as siloxane chain length was increased.

We are grateful for the financial supports on this work from Dow Corning Asia Co. Ltd. Japan.

## References

1. Kawakami, Y.; Yamashita, Y. *Makromol Chem* 1984, 185, 9.
2. Inoue, H.; Matsumoto, A.; Matsukawa, K.; Ueda, A.; Nagai, S. *J Appl Polym Sci* 1990, 40, 1917.
3. Chujo, Y.; Samukawa, H.; Yamashita, Y. *J Polym Sci Part A Polym Chem* 1980, 27, 1907.
4. Yang, J.; Hsiue, G. *J Appl Polym Sci* 1996, 61, 221.
5. Chang, T. C.; Liao, C. L.; Wu, K. W.; Wang, G. P.; Chiu, Y. S. *J Polym Sci Part A Polym Chem* 1998, 36, 2521.
6. Gorelova, M. M.; Pertsin, A. J.; Muzafarov, A. M.; Gritsenko, O. T.; Vasilenko, N. G. *J Appl Polym Sci* 1995, 55, 1131.
7. Kano, Y.; Akiyama, S.; Kasemura, T.; Kobayashi, S. *Polym J* 1995, 27, 339.
8. Kano, Y.; Ishikura, K.; Kawahara, S.; Akiyama, S. *Polym J* 1992, 24, 135.
9. Kano, Y.; Akiyama, S.; Kasemura, T. *J Appl Polym Sci* 1993, 50, 1619.
10. Kano, Y.; Akiyama, S.; Sano, H.; Yui, H. *J Electron Microsc* 1995, 44, 344.
11. Kano, Y.; Akiyama, S. *Kobunshi* 1992, 41, 774.
12. Gordon Cameron, G.; Chisholm, M. S. *Polymer* 1985, 26, 437.
13. Kawakami, Y.; Yamashita, Y. *ACS Symp Ser* 1985, 286, 245.
14. Oshibe, Y.; Ohmura, H.; Yamamoto, T. *J Adhesion* 1994, 47, 3.
15. Smith, S. D.; Long, T. E.; McGrath, J. E. *J Polym Sci Part A Polym Chem* 1994, 32, 1747.
16. Eva, M.; Smartt, L. M. *Appl Spectros* 1995, 49, 513.
17. Dwight, D. W.; McGrath, J. E.; Beck, A. R.; Riffle, J. S. *Polym Prepr Am Chem Soc Div Polym Chem* 1979, 20, 702.
18. Patel, N. M.; Dwight, D. W.; Hedrick, J. W.; Webster, D. C.; McGrath, J. E. *Macromolecules* 1988, 21, 2689.