

SHORT COMMUNICATIONS

Novel Functional Polymers. Poly(dimethylsiloxane)-Polyamide Multiblock Copolymers X.[†] ¹H NMR Analysis on Fine Structure of Aramid-Silicone Resin

Eui-Chul KANG and Mitsuru AKASHI^{*,††}

Tsukuba Research Laboratory, NOF Corporation, 5–10 Tokodai, Tsukuba, Ibaraki 300–2635, Japan

*Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1–21–40 Korimoto, Kagoshima 890–0065, Japan

(Received December 17, 2001; Accepted April 8, 2002)

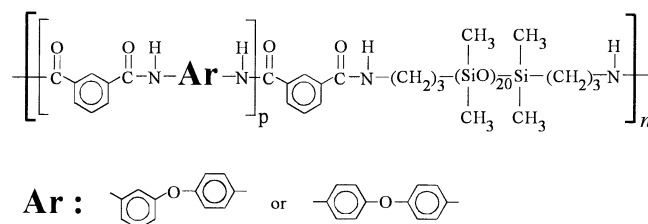
KEY WORDS Nuclear Magnetic Resonance (NMR) / Block Copolymer / Poly(dimethylsiloxane) / Aramid / Polycondensation /

Poly(dimethylsiloxane) (PDMS) has unique physical and chemical properties such as high thermal stability, oxidative stability, ultraviolet resistance, low surface energy, good electrical properties, and high gas permeability.^{1–3} Although PDMS has several favorable properties, the weak mechanical strength is a serious problem to overcome to use in the medical field. In 1986, Imai *et al.* reported the synthesis of aramid-silicone multiblock copolymer (PAS) consisted of an aromatic polyamide (aramid) as a hard segment and PDMS as a soft segment.^{4,5} In the previous reports, we studied the synthesis and characteristics of PAS from the point of view of a novel biomaterial.^{6–15} In that study, PAS exhibited many of the desirable properties of aramid and PDMS for medical applications. The interactions between biomolecules such as protein, cell, and tissue and PAS surfaces were found to be equal or relatively low compared with SILASTIC 500-1.¹¹ Moreover, surface structure and properties were also investigated in some details. We observed the microphase-separated structures of PAS films under TEM.^{12,14} Although the microphase-separated structures in bulk were different according to the PDMS content in PAS, XPS static SIMS analyses suggested that the free surface of all PAS films were predominantly covered with a PDMS thin layer.¹⁴ In this paper, we report the detailed ¹H NMR characterization of PAS, because the regularity of chemical structure of copolymer such as PAS, which seem to be strongly influenced by the molding method, play an important role in their functionality, especially in medical applications.

RESULTS AND DISCUSSION

The random and regular PASs (Scheme 1) were synthesized with a mixture solvent of THF/DMAc (2/1, v/v) by one-, two- and three-step polycondensation with PDMS-diamine ($M_n = 1680$), isophthaloyl chloride (IPC), 3,4'-diaminodiphenylether (3,4'-DAPE), and 4,4'-diaminodiphenylether (4,4'-DAPE). ¹H NMR spectra were measured at 25°C in DMF-*d*₇/CCl₄ (3/7, v/v) by using a JEOL JNM-EX270 spectrometer.

The ¹H NMR spectra of amide groups in the aromatic region of regular and random PASs are shown in Figure 1. The amide proton peaks of aramid prepared with 3,4'-DAPE and IPC showed a single peak at 10.32 ppm (Figure 1A). The amide proton of the aromatic region in regular PAS (p-RPAS1673) prepared with symmetrical diamine (4,4'-DAPE) showed a single peak at 10.20 ppm (Figure 1B). The amide proton of amide linkage between PDMS-diamine and IPC showed at 8.27 ppm. The peak at 10.20 ppm corresponds to the amide proton of amide linkage between 4,4'-DAPE



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

[†]For Part I, *cf.* ref 6, for Part II, *cf.* ref 8, for Part III, *cf.* ref 9, for Part IV, *cf.* ref 10, for Part V, *cf.* ref 11, for Part VI, *cf.* ref 12, for Part VII, *cf.* ref 13, for Part VIII, *cf.* ref 14, for Part IX, *cf.* ref 15.

^{††}To whom correspondence should be addressed (Tel: +81-99-285-8320, Fax: +81-99-255-1229, E-mail: akashi@apc.kagoshima-u.ac.jp).

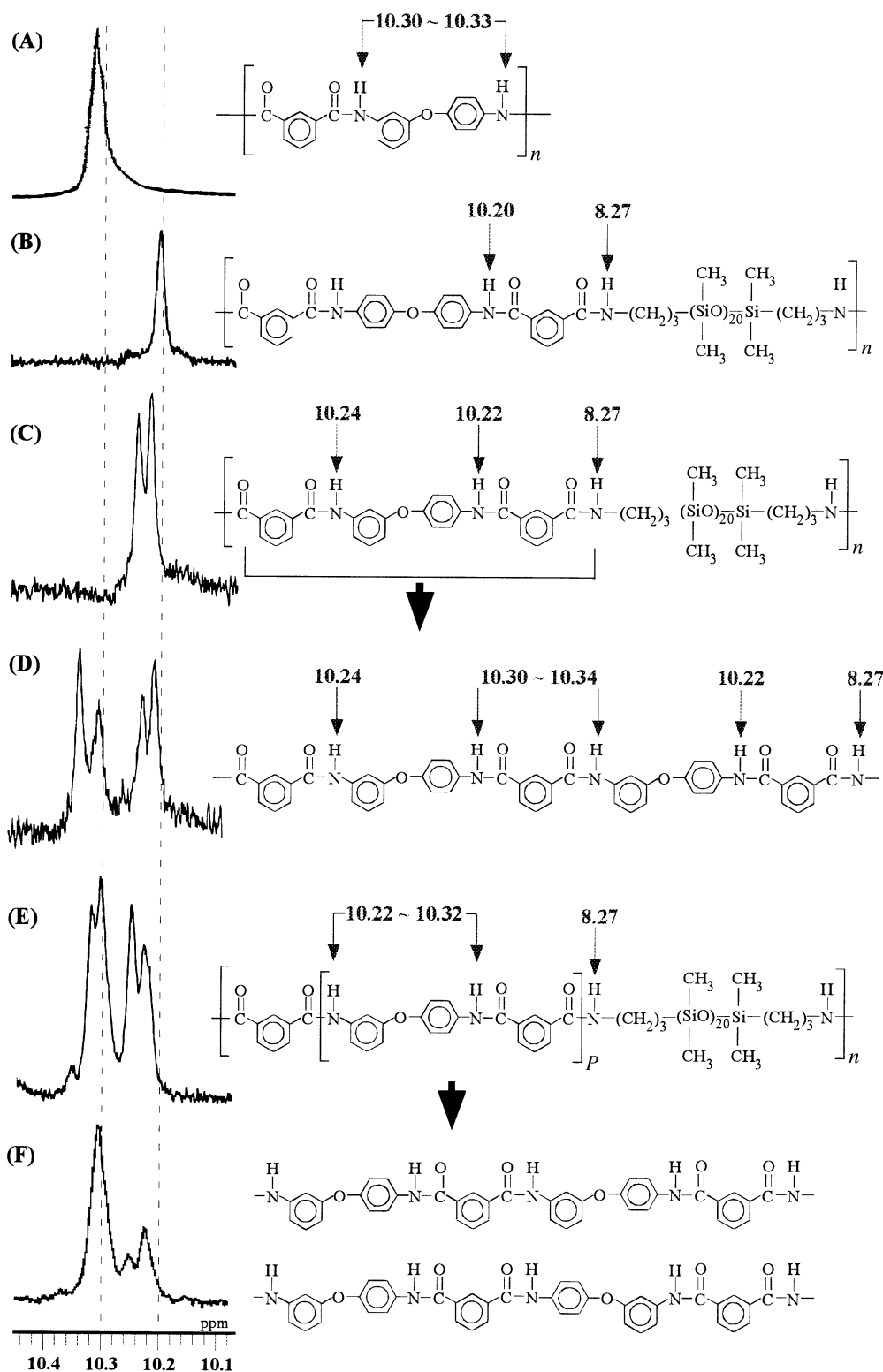


Figure 1. ^1H NMR spectra of amide proton peaks of PAS in $\text{DMF-}d_7/\text{CCl}_4$ (3/7, v/v) at 25°C . The PDMS contents of all PASs were 73%. (A): poly(IPC-co-DAPE), (B): p-RPAS1673, (C): m-RPAS1673, (D): m-RPAS1663 (PDMS content 63%), (E): PAS1673, and (F): TPAS 1673.

and IPC. Those of regular PAS (m-RPAS1673) prepared with 3,4'-DAPE showed two peaks at 10.22 and 10.24 ppm due to the unsymmetrical diamine in aromatic ring (Figure 1C). The integration ratio of amide peaks observed at 10.22 and 10.24 ppm was 1:1. On the other hand, in the case of regular PAS (m-RPAS1663)

with 63% PDMS content, four amide proton peaks were observed at 10.22, 10.24, 10.30, and 10.34 ppm (Figure 1D). The peaks at 10.30 and 10.34 ppm correspond to the amide protons of the central amide linkage in the aramid parts of PAS. The integration ratio of amide proton peaks observed at 10.22 and 10.24 ppm,

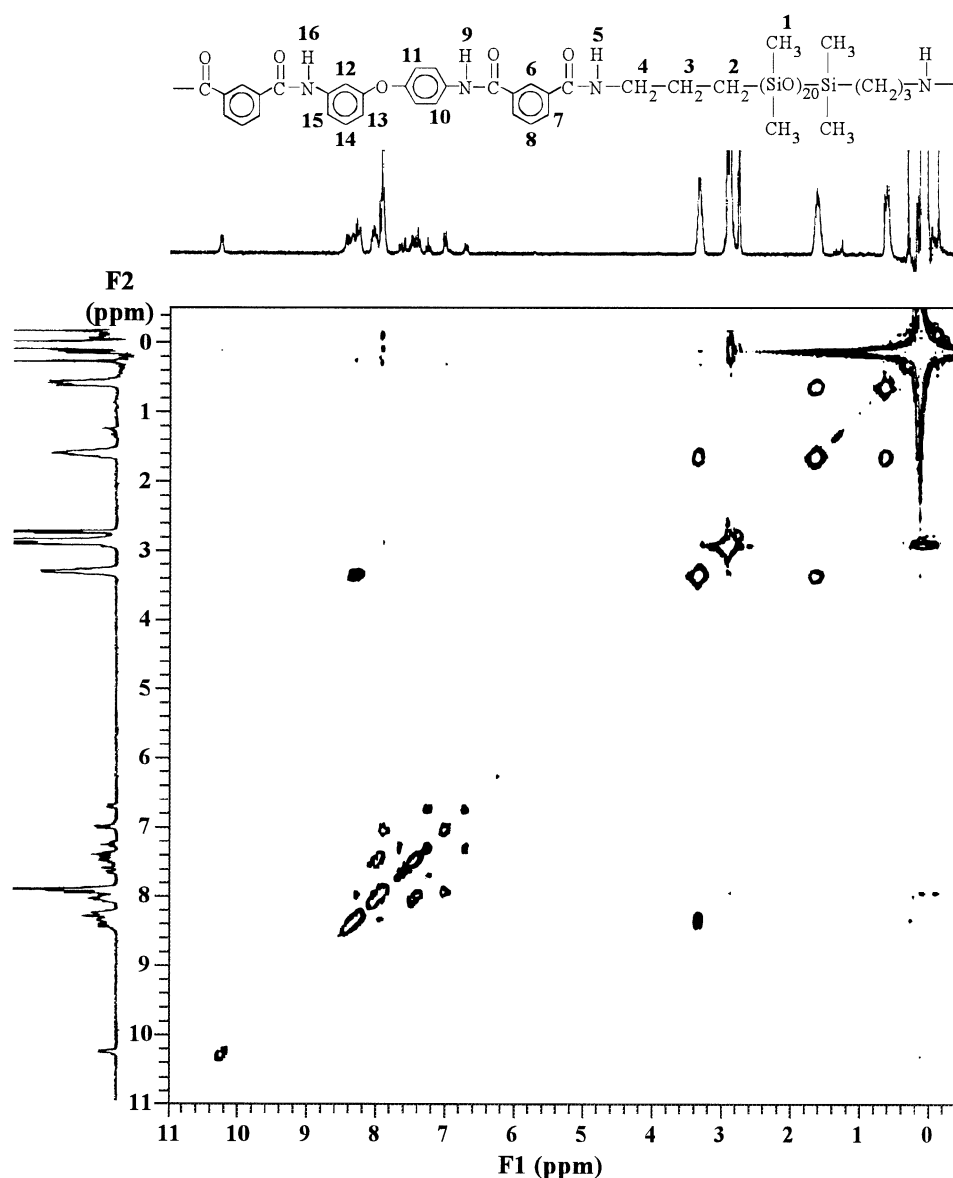


Figure 2. 2D ^1H - ^1H COSY NMR spectrum at 25°C for the regular PAS (m-RPAS1673).

10.30 and 10.34 ppm was 1:1. The integration values of amide proton peaks at 10.30 and 10.34 ppm indicated the length of aramid parts in PAS. In the case of random PAS (PAS1673) with 73% PDMS content prepared by one-step method, the four amide proton peaks were observed at 10.22, 10.24, 10.30, and 10.32 ppm (Figure 1E). From comparison of ^1H NMR spectra of regular and random PASs, the length of aramid parts of random PAS1673 showed slightly longer than that of regular m-RPAS1673 with the same content of PDMS. The integration ratio of amide peaks observed at 10.22 and 10.24 ppm, 10.30 and 10.32 ppm was approximately 1:1. As a result of integration ratio, the length of aramid parts of random PAS1673 was almost identical to that of regular m-RPAS1663. On the other hand, in random PAS (TPAS1673) prepared with THF only as a solvent, three amide proton peaks obtained at 10.22, 10.24, and 10.30 ppm, the integral ratio

of 10.22–10.24 ppm and 10.30 ppm was approximately 1:2 (Figure 1F). This result indicated that the length of aramid of random TPAS1673 prepared with THF was much longer than that of regular PAS, m-RPAS1673, and of random PAS1673 prepared with a mixture solvent of THF/DMAc (2/1, v/v). It is indicated that the polycondensation reactions of PAS is unevenly proceed in a single solvent such as THF or CHCl_3 .

In the polycondensation of 3,4'-DAPE ($\text{NH}_2\text{-Ph-O-Ph-NH}_2$) with IPC (Cl-Ph-Cl), the amino group linked to the para position of the aromatic ring (head group) is slightly reactive than the amino group linked to the meta position of the aromatic ring (tail group).¹⁶ The structure of aramid parts in PAS is consisted of symmetrical diamines containing head-to-head and/or tail-to-tail arrangement and unsymmetrical diamines containing head-to-tail arrangement (Figure 1F). Thus, the amide proton peaks of aramid parts in random PAS1673

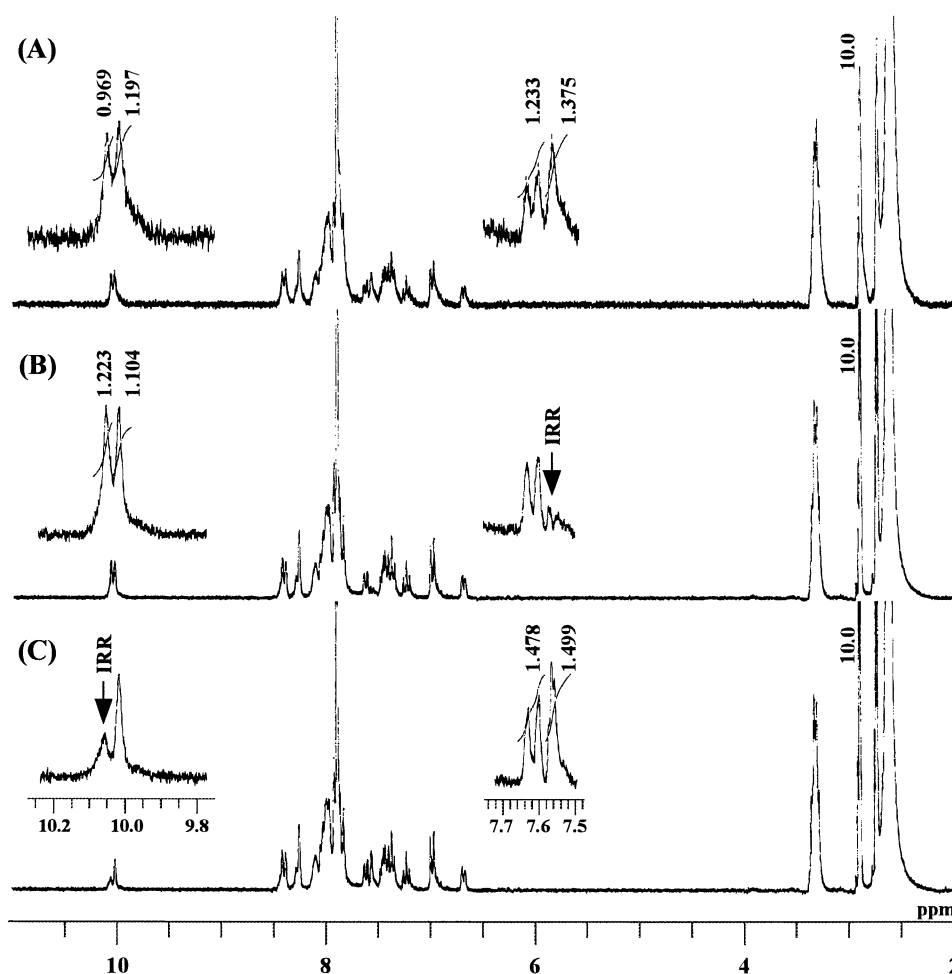


Figure 3. The NOE experiments. (A): ^1H NMR spectrum of m-RPAS1673 at 60°C . (B): ^1H NMR spectrum of m-RPAS1673 at 60°C with irradiation of 7.57 ppm. (C): ^1H NMR spectrum of m-RPAS1673 at 60°C with irradiation of 10.05 ppm (NH).

and TPAS1673 exhibited broad and partially overlapping peaks at 10.3 ppm.

In the previous report,⁶ the ^1H NMR spectrum for PAS showed at 0.0794 ppm (s, H_1 , SiCH_3), 0.61 ppm (t, H_2), 1.62 ppm (m, H_3), 3.32 ppm (m, H_4), 6.5–8.6 ppm (aromatic proton groups), and 10.2–10.4 ppm (amide proton groups). To study the assignment of the aromatic and the amide proton peaks in more detail, the 2D ^1H – ^1H COSY NMR and the nuclear Overhauser effect (NOE) experiments were carried out at 25 and 60°C , respectively, in $\text{DMF-}d_7/\text{CCl}_4$ (3/7 by vol.). The results of 2D ^1H – ^1H COSY NMR spectrum at 25°C for the regular PAS (m-RPAS1673) are shown in Figure 2. The resonances found coupled to each other were differentiated further splitting patterns and integration areas. Therefore, it can be assumed that the 2D ^1H – ^1H COSY NMR spectrum showed at 6.70 ppm (d, H_{13}), 6.96 ppm (d, H_{11}), 7.24 ppm (t, H_{14}), 7.39 ppm (t, H_8), 7.56 ppm (s, H_{12}), 7.62 ppm (d, H_{15}), 7.94 ppm (d, H_{10}), 8.07 ppm (dd, H_7), 8.28 ppm (s, H_5), 8.41 ppm (s, H_6), and 10.22 ppm (d, H_9 , H_{16}). The nuclear Overhauser effect (NOE) experiments are based on the decoupling between nuclear dipoles. The NOE results in

the enhancement of intensity, which can be detected by integration. The NOE experiments were carried out at 60°C to use the reference standard of the integration value of solvent peaks. Figure 3 shows the ^1H NMR spectra of m-RPAS1673 at 60°C with or without irradiation of 7.57 ppm (H_{12}) and 10.05 ppm (NH). By increased temperature, the amide proton peaks of 10.22 ppm at 25°C shifted to upfield, 10.05 ppm, at 60°C (Figure 3A). When the H_{12} proton was irradiated, the enhancement of the NH peak signal strength of 10.05 ppm was observed in Figure 3B. Reversely, when the amide proton of 10.05 ppm was irradiated, the enhancement of the signal strength of H_{12} and H_{15} protons at 7.56 ppm and 7.62 ppm, respectively, were observed in Figure 3C. Consequently, from the results of 2D ^1H – ^1H COSY NMR and NOE experiments, the amide proton peaks at 10.01 and 10.05 ppm can be assigned to H_9 and H_{16} , respectively.

The analyses of chemical structure of random and regular PASs were achieved by performing ^1H NMR experiments in $\text{DMF-}d_7/\text{CCl}_4$ (3/7, v/v). The present study suggested that the controlled chemical structure of PASs is more effectively obtained by using a mixture

solvent of THF/DMAc (2/1, v/v) than a single solvent such as THF or CHCl₃.

REFERENCES

1. R. Rudolph, J. Abraham, T. Vechione, S. Guber, and M. Woodward, *Plast. Reconstr. Surg.*, **62**, 185 (1978).
2. W. Lynch, "Handbook of Silicone Rubber Fabrication", Van Nostrand Reinhold, New York, N.Y., 1988.
3. L. C. Hartman, R. W. Bessette, R. E. Baier, A. E. Meyer, and J. Wirth, *J. Biomed. Mater. Res.*, **22**, 475 (1988).
4. M. Kajiyama, Y. Nishikata, M. Kakimoto, and Y. Imai, *Polym. J.*, **18**, 735 (1986).
5. M. Kajiyama, M. Kakimoto, and Y. Imai, *Macromolecules*, **22**, 4143 (1989).
6. T. Furuzono, E. Yashima, A. Kishida, I. Maruyama, T. Matsumoto, and M. Akashi, *J. Biomater. Sci., Polym. Ed.*, **5**, 89 (1993).
7. T. Furuzono, A. Kishida, M. Akashi, I. Maruyama, T. Miyazaki, Y. Koinuma, and T. Matsumoto, *Jpn. J. Artif. Organs*, **22**, 370 (1993).
8. A. Kishida, T. Furuzono, T. Ohshige, I. Maruyama, T. Matsumoto, H. Itoh, M. Murakami, and M. Akashi, *Angew. Makromol. Chem.*, **220**, 89 (1994).
9. T. Furuzono, K. Seki, A. Kishida, T. Ohshige, K. Waki, I. Maruyama, and M. Akashi, *J. Appl. Polym. Sci.*, **59**, 1059 (1996).
10. T. Matsumoto, Y. Koinuma, K. Waki, A. Kishida, T. Furuzono, I. Maruyama, and M. Akashi, *J. Appl. Polym. Sci.*, **59**, 1067 (1996).
11. 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).
12. T. Furuzono, K. Senshu, A. Kishida, T. Matsumoto, and M. Akashi, *Polym. J.*, **29**, 201 (1997).
13. T. Matsumoto, T. Uchida, A. Kishida, T. Furuzono, I. Maruyama, and M. Akashi, *J. Appl. Polym. Sci.*, **64**, 1153 (1997).
14. K. Senshu, T. Furuzono, N. Koshizaki, S. Yamashita, T. Matsumoto, A. Kishida, and M. Akashi, *Macromolecules*, **30**, 4421 (1997).
15. A. Kishida, T. Kanda, T. Furuzono, I. Maruyama, and M. Akashi, *J. Appl. Polym. Sci.*, **78**, 1059 (2000).
16. J. A. Moore and S. Kaur, *Macromolecules*, **33**, 3585 (2000).