Synthesis of polyurethane–polysiloxane graft copolymer using uniform-size poly(dimethylsiloxane) with a diol end group

Hideki Kazama, Tatsuya Ono, Yasuyuki Tezuka* and Kiyokazu Imai*
Department of Material Science and Technology, Technological University of Nagaoka, Kamitomioka, Nagaoka, Niigata 940–21, Japan
(*Received 26 May 1988; revised 8 July 1988; accepted 25 July 1988*)

A series of uniform-size poly(dimethylsiloxane)s (PDMS) containing a diol end group were synthesized by hydrosilylation of PDMS containing a silane end group with 3-allyloxy-1,2-propanediol. The polyurethane–polysiloxane graft copolymer was then synthesized by two different methods: polyaddition of uniform-size PDMS having a diol end group with 4,4′-diphenylmethanediisocyanate (MDI), followed by chain extension with 1,4-butanediol (BD); and polyaddition of BD and MDI, followed by chain extension with uniform-size PDMS having a diol end group.

(Keywords: polyurethane; poly(dimethylsiloxane); graft copolymer; macromonomer; polyaddition; telechelic polymer)

INTRODUCTION

Uniform-size polymers possessing suitably reactive end groups are considered to be important as macromolecular synthetic building blocks for well characterized multiphase and multidimensional polymer structures. We have recently reported uniform-size poly(tetrahydrofuran)[1–3] and poly(dimethylsiloxane) (PDMS)[4,5] with a variety of reactive end groups and their use for the synthesis of multidimensional[1,3] and multiphase polymers[4,5]. As an extension of the preceding studies, we describe in the present paper the synthesis of polyurethane–PDMS graft copolymer making use of uniform-size PDMS with a diol end group as the macromonomer.

The macromonomer technique has been extensively studied in the last decade for the synthesis of graft copolymers with well defined graft segment[6]. A variety of PDMS macromonomers possessing radically copolymerizable end groups, namely styrene[7,8], (meth)acrylate[7,9] and recently also vinylsilane derivatives[10], for copolymerization with a non-conjugated monomer like vinyl acetate are now available. Nevertheless, reports of macromonomers designed for polyaddition to give polyurethane or polyamide copolymers with well defined graft segment have been limited since those of Yamashita and Chujo[11–13].

In the present study, polyurethane–polysiloxane graft copolymers with uniform-size polysiloxane graft segment are described. Block and graft copolymers consisting of PDMS as a segment component have gained increasing attention owing to the unique properties of these inorganic/organic hybrid polymers both in bulk and at the surface[14,15]. For example, segmented polyurethane or poly(urethane urea) copolymers containing PDMS as soft-segment component are considered as possible candidates for biomedical materials[16–18]. Also it will become important to develop the reaction system in order to provide block and graft copolymers containing uniform-size PDMS segment component because the microphase separation morphology of multiphase polymers is known to be strongly influenced not only by molecular weight but also by the molecular-weight distribution of the polymer segment component.

EXPERIMENTAL

Reagents

Hexamethylcyclotrisiloxane (D_3) and dimethylchlorosilane (both from Toshiba Silicone Co.) were purified by distillation over CaH_2. 3-Allyloxy-1,2-propanediol (Tokyo Kasei Co.) was used after distillation. Pt/C (5% Pt, Japan Engelhard Co.) was used as received. 1,4-Butanediol (BD) and 4,4′-diphenylmethanediisocyanate (MDI) were used after distillation. Tin(II) octylate (Nakarai Chemicals Co.) was used as received. Tetrahydrofuran (THF) and toluene were distilled from a blue solution of sodium/benzophenone. *N*,*N*-Dimethylacetamide (DMAc) was distilled over CaH_2. Other reagents were purified by the usual methods.

Synthesis of uniform-size PDMS with a diol end group

PDMS with a diol end group was synthesized by the hydrosilylation reaction of PDMS containing a silane end group[4] with 3-allyloxy-1,2-propanediol as follows. Twenty grams of PDMS with a silane end group were dissolved in 20 ml of dry toluene and 0.33 g of Pt/C was introduced under dry nitrogen. Then a large excess of 3-allyloxy-1,2-propanediol (1/50–1/150 in moles) was added by a syringe and stirred in a thermostated bath at a predetermined temperature. After Pt/C was removed by filtration, the reaction product was isolated and purified by precipitation into a methanol/water mixture (4/1 in volume), and finally freeze-dried from benzene solution.

Synthesis of polyurethane–PDMS graft copolymer

Synthesis of polyurethane–PDMS graft copolymer was performed by a slightly modified method reported by

---

* To either of whom correspondence should be addressed

0032-3861/89/030553–05$03.00
© 1989 Butterworth & Co. (Publishers) Ltd.

Cooper *et al.*[19] with the two different procedures described below. Polyurethane homopolymer was produced by the equimolar reaction of MDI and BD in THF/DMAc (3/1 in volume) at 50°C for 6.5 h.

Procedure A. To 40 ml THF/DMAc mixture (3/1 in volume) solutions containing a weighed amount of PDMS with a diol end group and MDI, 1 wt% of tin(II) octylate and triethylamine were added by a syringe and heated at 50°C for 1 h. Thereafter the prescribed amount of BD was added under dry nitrogen and the reaction was further continued for 6.5 h. After evacuating THF, the reaction mixture was poured into methanol to isolate the product and finally dried *in vacuo* at 60°C.

Procedure B. In this case, BD and MDI were mixed first and heated at 50°C for 1 h in the presence of tin(II) octylate and triethylamine. Then a weighed amount of PDMS with a diol end group in 40 ml THF/DMAc (3/1 in volume) solution was added. The reaction was continued for a further 6.5 h and the product was isolated in the same way as described in procedure A.

Fractionation of PDMS–polyurethane graft copolymer

To 0.5 g of the graft copolymer placed in an Erlenmeyer flask, 20 ml of THF was added and stirred for 12 h at 23°C. Filtration of the resultant suspension mixture through a G4 glass filter allowed one to separate the sample into soluble and insoluble parts. The fractionated sample was dried *in vacuo* at 60°C.

Measurements

270 MHz ^{1}H n.m.r. spectra were recorded by means of a JEOL JNM-GX270 apparatus. Chemical shifts were calibrated using $CHCl_3$ (7.30 ppm) or DMSO (2.50 ppm) as internal standard. G.p.c. measurements were carried out using a Toyo Soda model 803C High Speed Liquid Chromatograph equipped with a TSK G4000 HXL column and THF as eluent. V.p.o. measurements were carried out using a Corona model 114 apparatus in toluene solution at 70°C. Silicon elemental analyses were carried out according to the method described by Kipping and Lloyd[20]. D.s.c. measurements were carried out on a Seiko I&G DSC 20 apparatus with a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Synthesis of uniform-size PDMS with a diol end group

We have recently reported[4,5] the synthesis of PDMS with a silane end group through the reaction of living PDMS with dimethylchlorosilane. Subsequent hydrosilylation with a variety of allylic compounds like allyl alcohol and *N,N*-dimethylallylamine provided hydroxyl and dimethylamino groups, respectively, at the PDMS chain end. These uniform-size telechelic PDMS were used for the synthesis of block copolymers with well characterized polysiloxane segment.

In the present study, we carried out the hydrosilylation reaction of PDMS having a silane end group with 3-allyloxy-1,2-propanediol. The selective and quantitative hydrosilylation reaction took place regardless of the molecular weight of PDMS prepolymer when the reaction was performed at 50°C or higher, as summarized in *Table 1.*

Figure 1 shows the 270 MHz ^{1}H n.m.r. spectrum of the obtained PDMS with a diol end group. The signals due to

Table 1 Synthesis of PDMS with a diol end group[a]

Run	$\bar{M}_n$	Temp. (°C)	Time (h)	Yield of diol end group[b] (mol%)
1	2200	70	6	100
2		50	18	100
3		20	6	0
4	3600	70	6	100
5		50	18	100
6		20	6	0
7	6800	70	6	100
8		50	18	100
9		20	6	0

[a] PDMS with a silane end group, 20.0 g; 3-allyloxy-1,2-propanediol, 56.6 g; Pt/C, 0.33 g; toluene, 80 ml

[b] Determined by ^{1}H n.m.r. spectroscopy

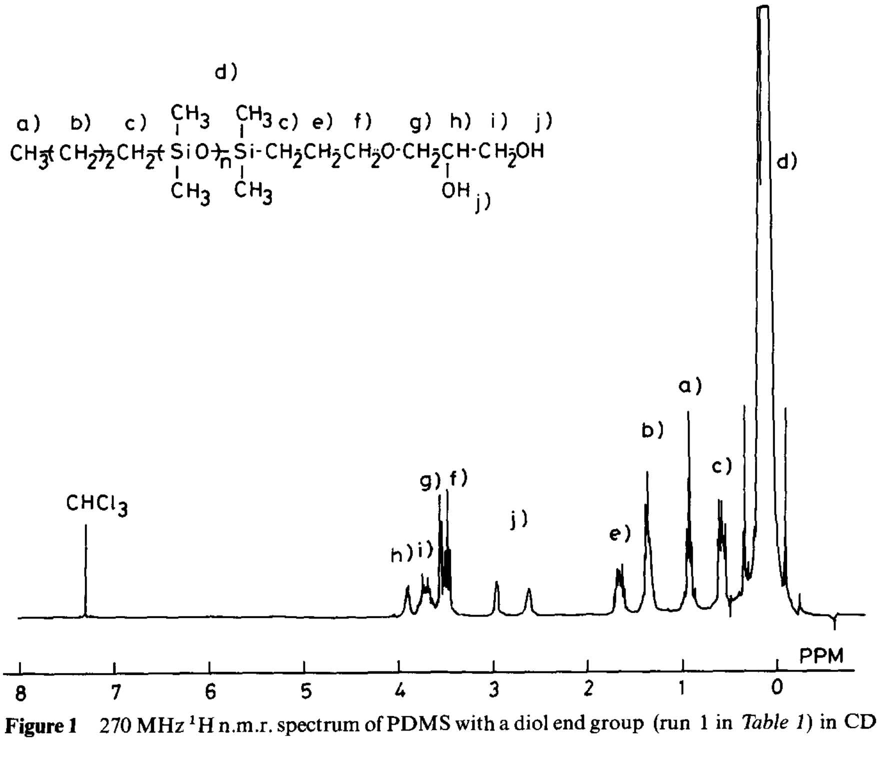


Figure 1 270 MHz ^{1}H n.m.r. spectrum of PDMS with a diol end group (run 1 in *Table 1*) in $CDCl_3$

the glycol methylene protons at 3.55 ppm and the methyne proton at 3.90 ppm were observed along with other signals compatible with anti-Markovnikov addition of the silane end group of PDMS with 3-allyloxy-1,2-propanediol. The signals due to another end group, namely n-butyl, also appeared at 0.60, 0.95 and 1.35 ppm. The molar ratio between n-butyl and glycol groups was found to be unity, indicating that the hydrosilylation reaction took place quantitatively.

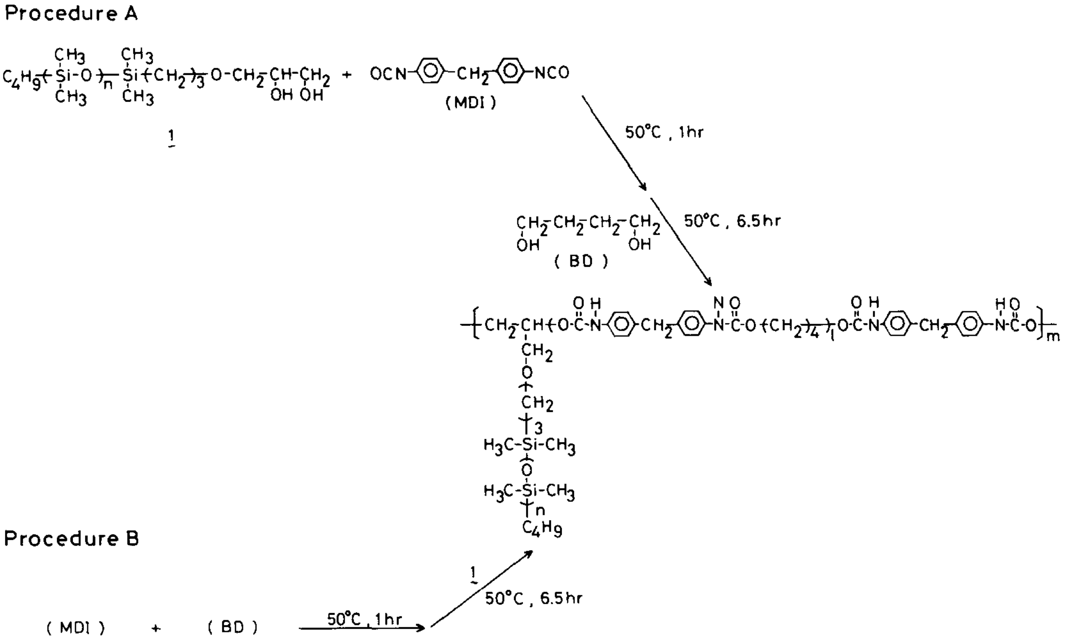
Synthesis of polyurethane–PDMS graft copolymer

Polyurethane synthesis making use of the above uniform-size PDMS having a diol end group was carried out by reaction with 4,4′-diphenylmethanediisocyanate (MDI) and subsequently with 1,4-butanediol (BD) as chain extender:

As shown in *Scheme 1*, two different procedures were employed: (A) polyaddition of PDMS having a diol end group with MDI, followed by chain extension with BD; and (B) addition of MDI and BD, followed by chain extension with PDMS containing a diol end group.

A series of polyurethane–PDMS graft copolymers with well defined graft chain length were obtained in both procedures, as summarized in *Table 2*. The siloxane contents in the graft copolymers produced were found to agree with the feed siloxane contents.

Figure 2 shows the 270 MHz ^{1}H n.m.r. spectrum of the polyurethane–PDMS graft copolymer. The signal due to the PDMS main-chain protons at 0.10 ppm was present in addition to those of the polyurethane sequence, namely phenyl-ring protons at 7–8 ppm, diphenylmethylene



Scheme 1

Table 2 Synthesis of polyurethane–PDMS graft copolymer[a]

Run[b]	$\bar{M}_n$ of PDMS	Molar ratio PDMS/MDI/BD	PDMS feed content (wt%)	Yield (%)	PDMS content (wt%) N.m.r.[c]	PDMS content (wt%) Elem. anal.[d]
A-1	2300	1/3/2	73	82	–	65
A-2		1/10/9	43	86	45	36
A-3		1/100/99	6.8	93	5.1	5.8
A-4	3700	1/3/2	80	78	–	77
A-5		1/10/9	53	88	63	51
A-6		1/50/49	18	94	12	16
A-7		1/100/99	9.8	97	9.9	8.9
A-8		1/200/199	5.2	95	4.6	4.9
A-9	6900	1/3/2	88	66	–	82
A-10		1/10/9	70	89	77	64
A-11		1/100/99	18	96	21	21
B-1	2300	1/2/1	81	72	–	70
B-2		1/3/2	73	82	–	64
B-3		1/10/9	43	83	31	31
B-4		1/100/99	6.8	92	6.6	5.8
B-5	3700	1/10/9	53	88	41	47
B-6		1/100/99	9.8	94	9.4	8.8
B-7	6900	1/10/9	70	92	75	63
B-8		1/100/99	18	98	18	17

[a] In THF/DMAc (3/1 in volume), triethylamine (1 wt%), tin(II) octylate (1 wt%), 50°C
[b] A-1 to A-11, procedure A; B-1 to B-8, procedure B; see also 'Experimental'
[c] Determined by ^{1}H n.m.r. spectroscopy
[d] Determined by silicon elemental analysis

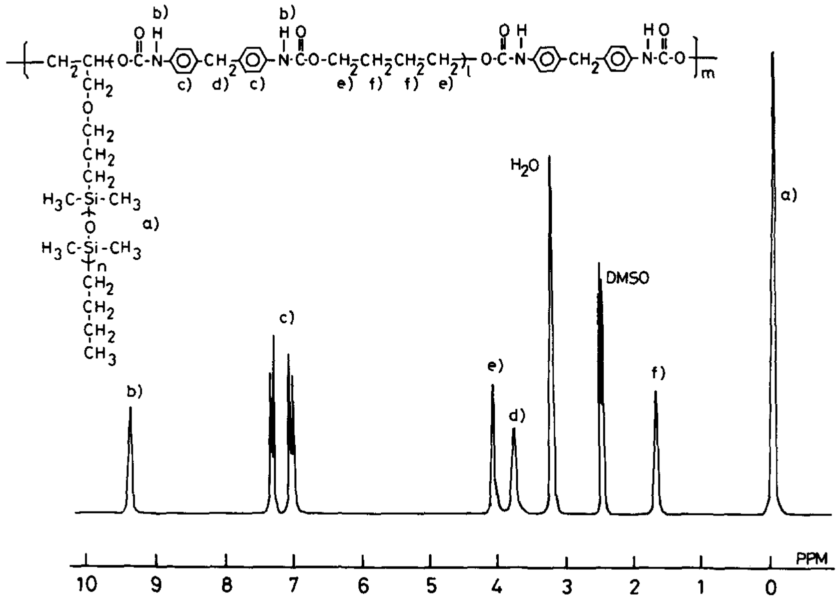


Figure 2 270 MHz ^1H n.m.r. spectrum of polyurethane–PDMS graft copolymer (run A-2 in *Table 2*) in DMSO-d_6

Table 3 Fractionation of polyurethane–PDMS graft copolymer[a]

	Soluble part			Insoluble part		
		DMS content (wt%)			DMS content (wt%)	
Sample[b]	Yield (g)	N.m.r.[c]	Elem. anal.[d]	Yield (g)	N.m.r.[c]	Elem. anal.[d]
A-2	0.32	46	44	0.16	25	21
A-3	0.06	11	8.6	0.41	3.6	4.6
A-5	0.47	63	49	none		
A-7	0.07	22	–	0.43	8.8	8.6
A-10	0.47	–	60	none		
A-11	0.13	29	22	0.18	14	18
B-3	0.18	60	53	0.30	17	18
B-4	0.20	10	8.3	0.30	4.3	4.7
B-5	0.15	–	49	0.35	–	37
B-6	0.46	11	8.6	0.04	4.1	4.6
B-7	0.34	–	68	0.10	–	45
B-8	0.07	–	39	0.42	9.4	12
C-1[e]	0.09			0.41		

[a] 0.5 g of graft copolymer in 20 ml THF; stirred for 12 h
[b] See also *Table 2*
[c] Determined by ^1H n.m.r. spectroscopy
[d] Determined by silicon elemental analysis
[e] Polyurethane homopolymer

protons at 3.75 ppm and methylene protons of BD at 1.70 and 4.10 ppm, together with a urethane proton at 9.35 ppm, confirming that the polyaddition reaction was proceeding. The formation of polyurethane was also indicated by the i.r. absorption at 1700 cm^{-1} for the urethane carbonyl function in the reaction product.

In order to inspect compositional differences in the polyurethane–PDMS graft copolymers obtained by procedures A or B, fractionation of the graft copolymer sample was carried out for separation into THF-soluble and -insoluble parts. It will be presumed that the PDMS-rich graft copolymer is soluble in THF while the polyurethane-rich graft copolymer is not. As summarized in *Table 3*, the siloxane contents in the graft copolymer determined by either n.m.r. or silicon elemental analysis agreed with each other, and the ratio of the THF-soluble fraction was found to be higher in procedure A than in procedure B. This shows the presence of a notable compositional difference presumably based on the number of PDMS graft segments and their distribution in the present polyurethane–PDMS graft copolymers synthesized by procedures A or B, even though the bulk products happen to give almost identical siloxane contents.

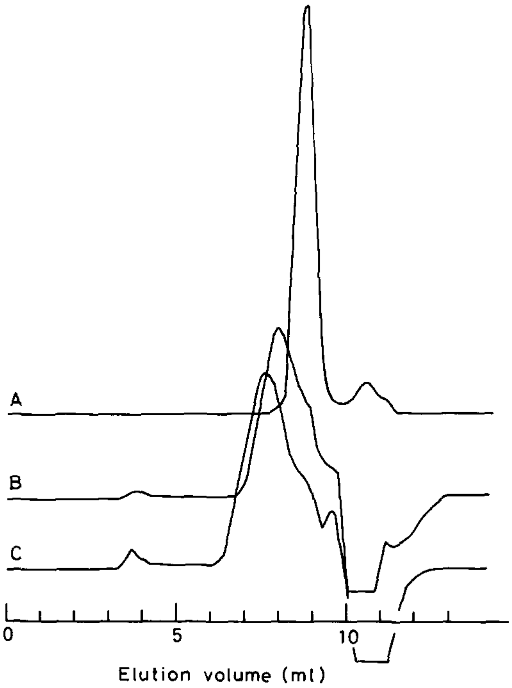


Figure 3 G.p.c. traces of (A) PDMS with a diol end group (run 2 in *Table 1*); (B) polyurethane–PDMS graft copolymer by procedure A (run A-2 in *Table 2*); and (C) polyurethane–PDMS graft copolymer by procedure B (run B-3 in *Table 2*) (column, TSK G4000HXL; eluent, THF, 1.0 ml min^{-1})

G.p.c. traces of the THF-soluble fraction of polyurethane–PDMS graft copolymers are shown in *Figure 3* along with that of the starting PDMS having a diol end group. The graft copolymers show significantly higher molecular weight, namely $(1.5–2.5) \times 10^4$ calibrated with polystyrene, than the parent PDMS prepolymer, again confirming the occurrence of the polyaddition reaction. The graft copolymer produced in procedure B was observed to possess a slightly higher molecular weight than that produed in procedure A.

D.s.c. analysis of polyurethane–PDMS graft copolymer

Polyurethane graft copolymers possessing uniform-size PDMS graft length are considered to be suitable model polymers for elucidating properties as a function of graft length. From such a viewpoint, d.s.c. measurements were carried out on a series of polyurethane–PDMS graft copolymers with different PDMS segment lengths and siloxane contents. In *Figure 4*, typical examples are given together with the parent PDMS with a diol end group. A melting endotherm of the PDMS segment was observed at around $-50°C$, slightly lower than that of the PDMS homopolymer, in a series of graft copolymer samples with long PDMS graft segment. On the other hand, graft copolymer samples with short PDMS graft segment of $MW = 2300$ and siloxane content of $36\,wt\%$ failed to exhibit any clear melting endotherm though PDMS homopolymer of the same molecular weight does show one. As for the directly relevant multiphase structure containing PDMS component, Wang and Krause[21] have recently made a similar observation in a polystyrene–PDMS block copolymer, where PDMS segment of $MW < 3500$ failed to show the melting endotherm when it is incorporated in the block copolymer.

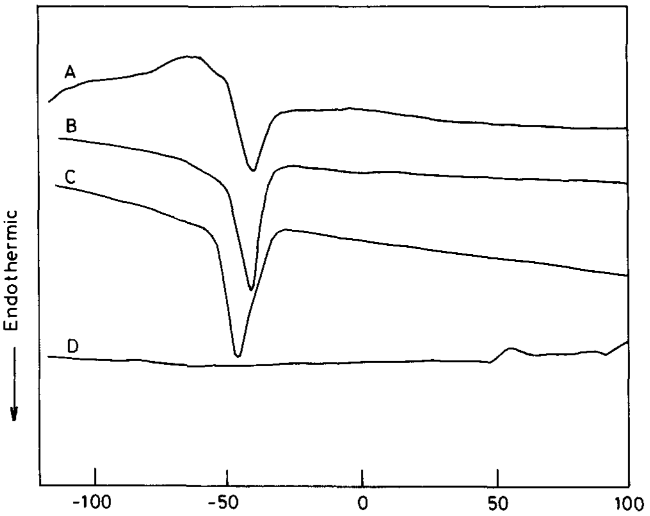


Figure 4 D.s.c. curves of (A) PDMS with a diol end group (run 8 in *Table 1*) and (B–D) polyurethane–PDMS graft copolymers (B, run A-10; C, run B-7; and D, run A-2; in *Table 2*)

ACKNOWLEDGEMENTS

We are grateful to Toshiba Silicone Co. for the gift of D_3 and dimethylchlorosilane. Financial support from the Ministry of Education, Science and Culture (Nos. 62604551 and 63604539) is also acknowledged.

REFERENCES

1 Tezuka, Y. and Goethals, E. J. *Eur. Polym. J.* 1982, **18**, 991
2 Tezuka, Y. and Goethals, E. J. *Makromol. Chem.* 1987, **188**, 783
3 Tezuka, Y. and Goethals, E. J. *Makromol. Chem.* 1987, **188**, 791
4 Kazama, H., Tezuka, Y. and Imai, K. *Polym. J.* 1987, **19**, 1091
5 Kazama, H., Tezuka, Y. and Imai, K. *Makromol. Chem.* 1988 in press
6 Rempp, P. F. and Franta, E. *Adv. Polym. Sci.* 1984, **58**, 1
7 Kawakami, Y., Miki, Y., Tsuda, T., Murthy, R. A. N. and Yamashita, Y. *Polym. J.* 1982, **14**, 913
8 Cameron, G. G. and Chisholm, M. S. *Polymer* 1985, **26**, 437
9 Cameron, G. G. and Chisholm, M. S. *Polymer* 1986, **27**, 1420
10 Tezuka, Y., Fukushima, A. and Imai, K. *Makromol. Chem.* 1985, **186**, 685
11 Yamashita, Y., Chujo, Y., Kobayashi, H. and Kawakami, Y. *Polym. Bull.* 1981, **5**, 361
12 Chujo, Y., Tatsuda, T. and Yamashita, Y. *Polym. Bull.* 1982, **8**, 239
13 Chujo, Y., Kobayashi, H. and Yamashita, Y. *Polym. Commun.* 1984, **25**, 278
14 Noshay, A. and McGrath, J. E. 'Block Copolymers: Overview and Critical Survey', Academic Press, New York, 1977
15 Tezuka, Y., Fukushima, A., Matsui, S. and Imai, K. *J. Colloid Interface Sci.* 1986, **114**, 16
16 Mileshkevich, V. P., Novikova, N. F. and Korlin, A. V. *Vysokomol. Soedin. (B)* 1972, **14**, 682; *Chem. Abstr.* 1973, **78**, 44717d
17 Yilgor, I., Shaaban, A. K., Steckle, W. P., Jr, Tyagi, D., Wilkes, G. L. and McGrath, J. E. *Polymer* 1984, **25**, 1800
18 Tyagi, D., Yilgor, I., McGrath, J. E. and Wilkes, G. L. *Polymer* 1984, **25**, 1807
19 Yu Xue-Hai, Vagarajan, M. R., Grasel, T. G., Gibson, P. E. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 2319
20 Kipping, F. S. and Lloyd, L. L. *J. Chem. Soc.* 1901, **79**, 449
21 Wang, B. and Krause, S. *Macromolecules* 1987, **20**, 2201