

Synthesis of polyurethane-based graft copolymers with uniform-size polyether and polyamine segments

Hideki Kazama, Michiaki Hoshi, Hiroshige Nakajima, Daniel Horák*, Yasuyuki Tezuka† and Kiyokazu Imai†

Department of Material Science and Technology, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-21, Japan

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Poly(tetrahydrofuran) (poly(THF)) and poly(*N*-*t*-butylaziridine) (poly(TBA)) having diol end-groups were synthesized through the reactions of living poly(THF) and of living poly(TBA), both initiated by methyl trifluoromethanesulphonate, with diethanolamine. The subsequent polyaddition reaction of poly(THF) and poly(TBA) with 4,4'-diphenylmethanediisocyanate followed by chain extension with 1,4-butanediol produced polyurethane/polyether and polyurethane/polyamine graft copolymers possessing uniform-size poly(THF) and poly(TBA) graft segments.

(Keywords: polyurethane; poly(tetrahydrofuran); poly(*N*-*t*-butylaziridine); macromonomer; graft copolymer; diol end-group; uniform-size polymer)

INTRODUCTION

Although the macromonomer technique has been extensively studied in the last decade for the synthesis of graft copolymers with well defined structures¹, reports on macromonomers designed for polyaddition and polycondensation reactions to give polyurethane or polyamide copolymers have been relatively limited until recently²⁻⁴.

We have recently reported⁵ the synthesis of polyurethane-polysiloxane graft copolymers by making use of uniform-size poly(dimethylsiloxane) with a diol end-group as the macromonomer. As the extension of a preceding study, we report in the present paper on the synthesis of polyurethane-based graft copolymers having uniform-size poly(tetrahydrofuran) (poly(THF)) and poly(*N*-*t*-butylaziridine) (poly(TBA)) graft segments, respectively.

Polyurethane-based graft copolymers having a variety of well defined graft segments may be regarded as model polymers for polyurethane-based hybrid materials currently applied for artificial cardiovascular devices due to their favourable mechanical and antithrombogenic properties⁶. Indeed, surface studies on polyurethane-polysiloxane block^{7,8} and graft^{5,9} copolymers having uniform-size polysiloxane block and graft segments revealed that the mode, i.e. block or graft, and the length of polysiloxane segment as well as the total siloxane content in the copolymer strongly influenced the environmentally induced surface rearrangement behaviour during the change of the contacting medium from air to water.

Thus, polyurethane-poly(THF) and polyurethane-poly(TBA) graft copolymers are considered to be useful model polymers to examine the influence of the type of graft segment on the surface behaviour, since a poly(THF) segment is thought to be less flexible compared to the

polysiloxane counterpart under ambient conditions, while a poly(TBA) segment becomes soluble in the acidic medium after protonation.

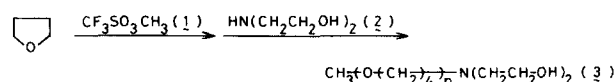
EXPERIMENTAL

Reagents

THF (Nacalai Tesque) was distilled from blue solution of sodium/benzophenone. TBA was synthesized¹⁰ and distilled twice over CaH₂. Methyl trifluoromethanesulphonate (methyl triflate (1)) was distilled just before use. Diethanolamine (2) was distilled over CaH₂. 4,4'-Diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) were used after distillation over CaH₂. Tin(II) octylate was used as received. Triethylamine, dimethylacetamide (DMAc) and hexamethylphosphoramide (HMPA) were distilled over CaH₂. Other reagents were purified by the usual methods.

Synthesis of uniform-size poly(THF) with a diol end group (3)

To 50 ml of dry THF placed in a 100 ml flask, the required amount of (1) was added by means of a microsyringe under vigorous stirring at 20°C. After a prescribed time, compound (2) (in the ratio (1)/(2) = 1/20 mol/mol) was introduced by syringe against a current of dry nitrogen. The reaction mixture was allowed to stand overnight under stirring at 20°C. The reaction product was isolated and purified by precipitation from THF/cold water and freeze-dried from benzene solution.



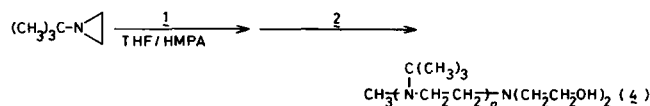
Synthesis of uniform-size poly(TBA) with a diol end-group (4)

To 160 ml of THF and 28 ml of HMPA solution

* On leave from Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences

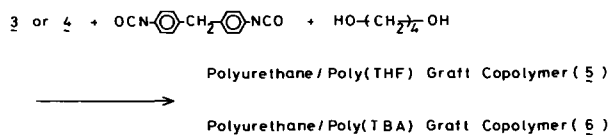
† To either of whom correspondence should be addressed

mixture containing 9.9 g (0.1 mol) of TBA, the required amount of (1) was added under a dry nitrogen atmosphere. The reaction mixture was stirred for 20 min at 15°C. Thereafter 20 times excess of (2) was added, and the solution was retained at 50°C for 5 h. The reaction product was then isolated and purified by precipitation into methanol and dried *in vacuo* at room temperature.



Synthesis of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers by use of (3) and (4)

Syntheses of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers were carried out by using the method described in the synthesis of polyurethane/polysiloxane graft copolymer⁵. A weighed amount of MDI and (3) was dissolved in 40 ml of THF/DMAc, while MDI and (4) were dissolved in 60 ml of benzene/HMPA mixture solution (vol. ratio 3/1) containing 1 wt% of tin(II) octylate and of triethylamine. The mixture was heated to 60°C, and stirred for 1 h. A predetermined amount of BD was then added by syringe and stirred for 6.5 h. The reaction products were isolated by precipitation into methanol after the concentration of the reaction solution by evacuation, and finally dried *in vacuo* at 60°C.



Measurements

The 270 MHz ¹H n.m.r. spectra were recorded by means of a Jeol JNM-GX270 apparatus. Chemical shifts were calibrated using CHCl₃ (7.30 ppm) and dimethylsulphoxide (2.50 ppm) as internal standards. G.p.c. measurements were carried out using a Tohso model CCPH High Liquid Chromatograph equipped with TSK G3000HXL and G4000HXL as columns and THF as eluent. V.p.o. measurements were carried out by means of a Corona model 114 apparatus in toluene solution at 70°C. I.r. spectra were taken on a Hitachi 260-10 Infrared Spectrophotometer. Differential thermal analysis (d.t.a.) measurements were carried out on a Seiko I&E TG/DTA 20 apparatus at a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

Synthesis of uniform-size poly(THF) (3) and poly(TBA) (4) macromonomers with diol end-groups

THF is known to polymerize in a living character by appropriate initiators such as methyl triflate (1) or triethyloxonium tetrafluoroborate¹¹. The modification reaction of a living oxonium end-group by suitable nucleophiles could introduce polymerizable end-groups, namely styryl¹², methacryl¹³ and vinylsilyl¹⁴ groups. The modification reaction with *N*-alkylazetidines could also produce uniform-size poly(THF) having azetidinium end-groups, and they were used as convenient prepolymers for the synthesis of various well defined multiphase and multidimensional polymers¹⁵⁻¹⁸.

TBA is also known to polymerize by (1) to give a living poly(TBA) having an aziridinium end-group¹⁹. The subsequent termination reaction of a living aziridinium end-group with methacrylic acid could provide a polyamine macromonomer having a methacryl end-group²⁰.

In the present study, we carried out the reaction of a living poly(THF) and of a living poly(TBA) with diethanolamine (2) to produce uniform-size polyether (3) and polyamine (4) having diol end-groups. They are considered as macromonomers for the polyaddition reaction. The relevant polysiloxane macromonomer having a diol end-group was recently synthesized and used for the synthesis of polyurethane-based graft copolymers⁵.

Figures 1 and 2 show 270 MHz ¹H n.m.r. spectra of the resulting poly(THF) (3) and poly(TBA) (4) macromonomers having diol end-groups. In both spectra, signals of methyl protons due to the initiator were observed at 3.33 and 2.27 ppm, respectively. Also those of methylene protons adjacent to nitrogen and oxygen derived from diethanolamine were observed at 2.71 and 3.65 ppm, in addition to the overflowed main-chain signals of poly(THF) (1.53 and 3.35 ppm) and of poly(TBA) (1.09 and 2.50 ppm). A quantitative termination reaction was confirmed by comparing the signal intensities of the initiator and the terminator fragments.

A series of poly(THF) (3) and poly(TBA) (4) macromonomers having different molecular weights with narrow molecular-weight distributions were synthesized as shown in Table 1. The polydispersity (\bar{M}_w/\bar{M}_n) of produced poly(THF) (3) and poly(TBA) (4) macromonomers was estimated by g.p.c. analysis with reference to standard polystyrene samples of known polydispersity values, and was always less than 1.10. Experimental molecular-weight values determined by v.p.o. and by g.p.c. were found to agree well with calculated ones from polymer yield/initiator concentration ratios, confirming the living character of THF and TBA polymerizations.

Synthesis of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers

The uniform-size poly(THF) (3) and poly(TBA) (4) having diol end-groups thus obtained were allowed to react with MDI and BD in various reactant ratios, to produce polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers possessing well defined graft segment length and graft content. The results are collected in Table 2.

Polyurethane/poly(THF) graft copolymers (5) were synthesized in a THF/DMAc solution mixture at 60°C, while polyurethane/poly(TBA) graft copolymers (6) were synthesized in a benzene/HMPA solution mixture at 60°C. In both cases, polyaddition reactions were found to take place to produce graft copolymers in almost quantitative yields. Poly(THF) and poly(TBA) graft contents in products were in close agreement with those in the feed.

Figures 3 and 4 show 270 MHz ¹H n.m.r. spectra of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers, respectively. Signals due to the polyurethane sequence, namely phenyl-ring protons at 6.9-7.5 ppm, diphenyl methylene protons at 3.80 ppm, butanediol methylene protons at 1.72 and 4.11 ppm and a urethane proton for polyurethane/poly(THF) at 9.27 ppm as well as for polyurethane/poly(TBA) at 9.00 ppm, are

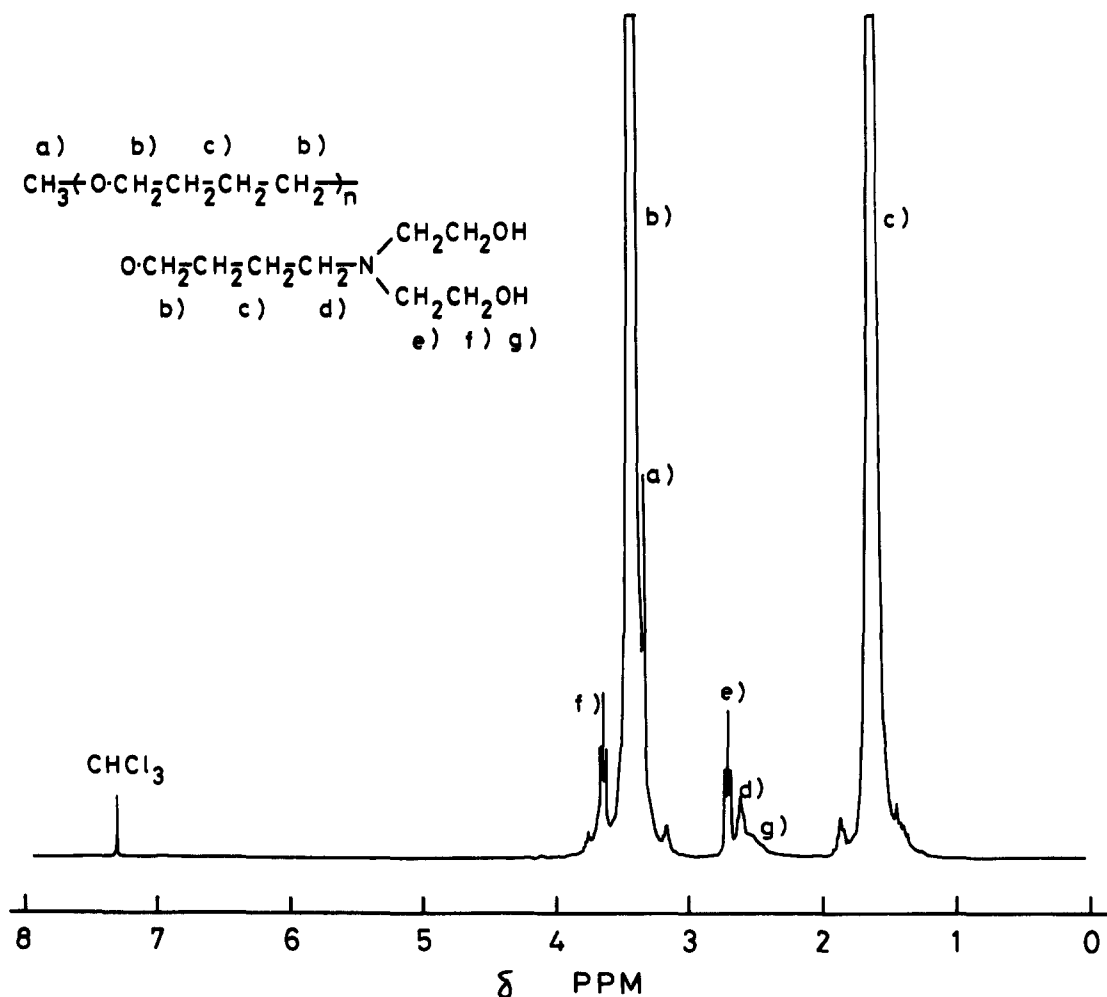


Figure 1 270 MHz ¹H n.m.r. spectrum of poly(THF) macromonomer having a diol end-group (3) (run A-1 in Table 1) in CDCl₃ at 40°C

Table 1 Synthesis of poly(THF) (3)^a and poly(TBA) (4)^b macromonomers with diol end-groups

No.	Type	Monomer (mol)	1 (mmol)	2 (mmol)	Time (min)	Yield (%)	\bar{M}_n		
							Calc. ^c	G.p.c. ^d	V.p.o.
A-1	THF	0.62	2.87	57.4	20	15.5	2400	2900	2700
A-2		0.62	2.20	44.0	40	30.3	6100	5700	5400
A-3		0.62	1.83	36.6	60	30.0	7300	7800	7900
B-1	TBA	0.10	3.96	79.2	20	92.5	2400	—	3200
B-2		0.12	2.45	49.0	20	79.6	4000	—	4900

^a In bulk, 20°C

^b In THF/HMPA (3/1 in vol), 15°C

^c A series: $\bar{M}_n(\text{calc.})$ of poly(THF) = Yield(g)/CF₃SO₃CH₃(mol)

B series: $\bar{M}_n(\text{calc.})$ of poly(TBA) = $\frac{\text{TBA}(\text{mol})}{\text{CF}_3\text{SO}_3\text{CH}_3(\text{mol})} \times \frac{\text{Yield}(\%)}{100} \times 99$

+ 119(molecular weight of -CH₃ and -N(CH₂CH₂OH)₂)

^d $M_n(\text{g.p.c.}) = M_n$ (estimated from standard polystyrene) × 0.556²¹

present together with those due to the graft sequence, namely for poly(THF) protons at 1.53 and 3.35 ppm and for poly(TBA) protons at 1.09 and 2.50 ppm, respectively.

The i.r. analysis of reaction products also confirmed the formation of polyurethane-based graft copolymers from the urethane absorption at 1700 cm⁻¹.

The g.p.c. traces of THF-soluble fractions of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6)

graft copolymers are shown in Figures 5 and 6, respectively, together with those of the starting poly(THF) (3) and poly(TBA) (4) macromonomers. Both graft copolymer samples appeared to possess significantly higher molecular weight, (2.5–3.5) × 10⁴ calibrated with polystyrene, compared to the corresponding macromonomers, indicating the formation of polyurethane-based graft copolymers.

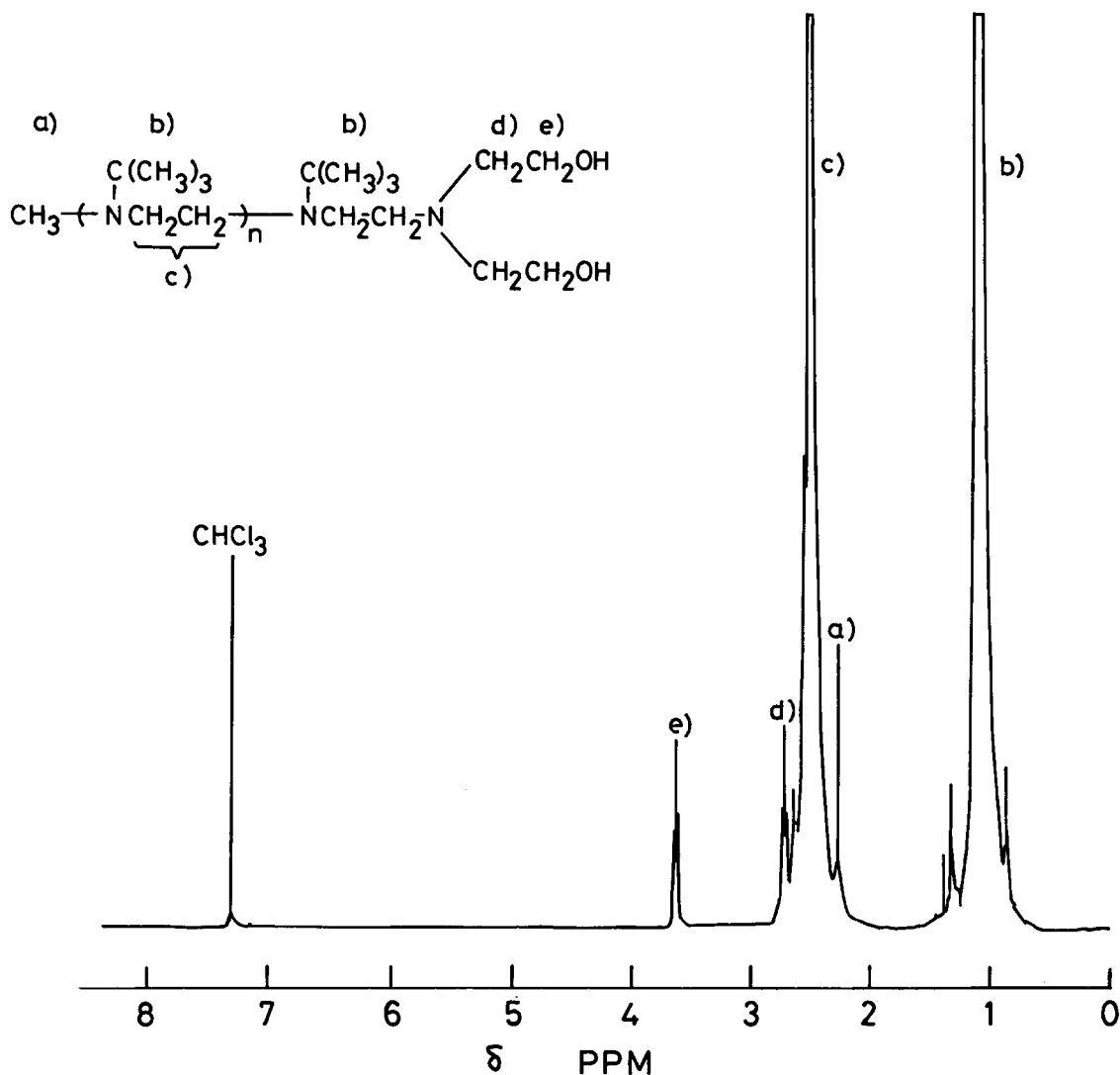


Figure 2 270 MHz ¹H n.m.r. spectrum of poly(TBA) macromonomer having a diol end-group (4) (run B-1 in Table 1) in CDCl₃ at 40°C

Table 2 Synthesis of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers

Run ^a	\bar{M}_n of macromonomer	Molar ratios		Feed content of graft segment (wt%)	Yield (%)	Graft segment content (wt%) ^b	
		Macromonomer/MDI	BD				
A-1	2700	1	10	9	44.9	62.8	42.9
A-2		1	50	49	13.8	90.4	11.8
A-3		1	100	99	8.0	96.3	6.2
A-4	5400	1	3	2	85.1	77.4	87.2
A-5		1	50	49	24.2	64.6	25.0
A-6		1	100	99	13.7	91.8	15.5
A-7		1	200	199	7.4	91.2	8.6
A-8	7800	1	3	2	89.3	70.7	87.2
A-9		1	50	49	31.8	64.2	25.0
A-10		1	100	99	18.9	92.6	20.2
A-11		1	200	199	10.4	91.7	9.9
B-1	3200	1	10	9	54.7	88.6	56.1
B-2		1	50	49	15.1	94.8	14.5
B-3		1	100	99	10.5	95.4	9.9
B-4	4900	1	10	9	60.1	94.7	51.4
B-5		1	50	49	22.8	91.7	21.2
B-6		1	100	99	12.8	97.8	14.0

^a A series: polyurethane/poly(THF) graft copolymer (5), in THF/DMAc (3/1 in vol), triethylamine (1 wt%), tin(II) octylate (1 wt%), 60°C

B series: polyurethane/poly(TBA) graft copolymer (6), in benzene/HMPA (3/1 in vol), triethylamine (1 wt%), tin(II) octylate (1 wt%), 60°C

^b Determined by ¹H n.m.r. spectrum

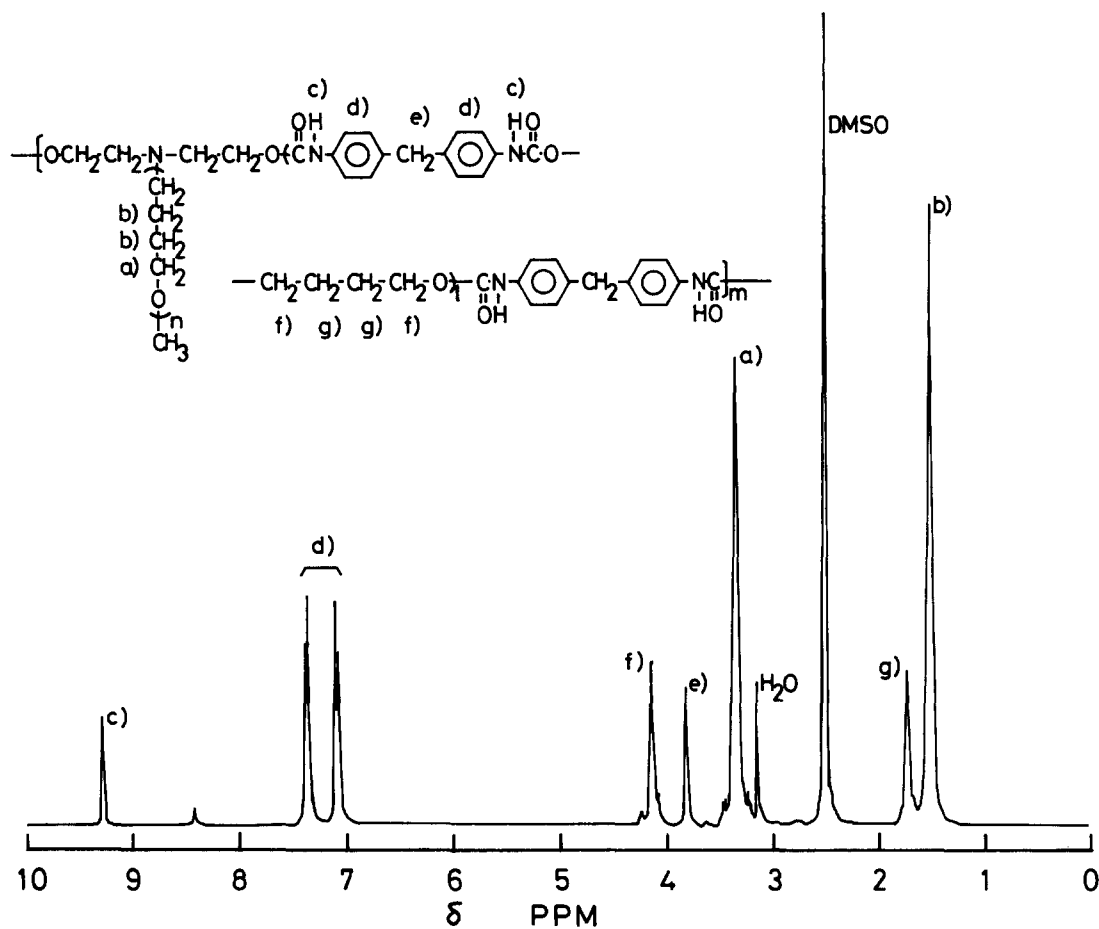


Figure 3 270 MHz ¹H n.m.r. spectrum of polyurethane-poly(THF) graft copolymer (5) (run A-1 in Table 2) in DMSO-d₆ at 60°C

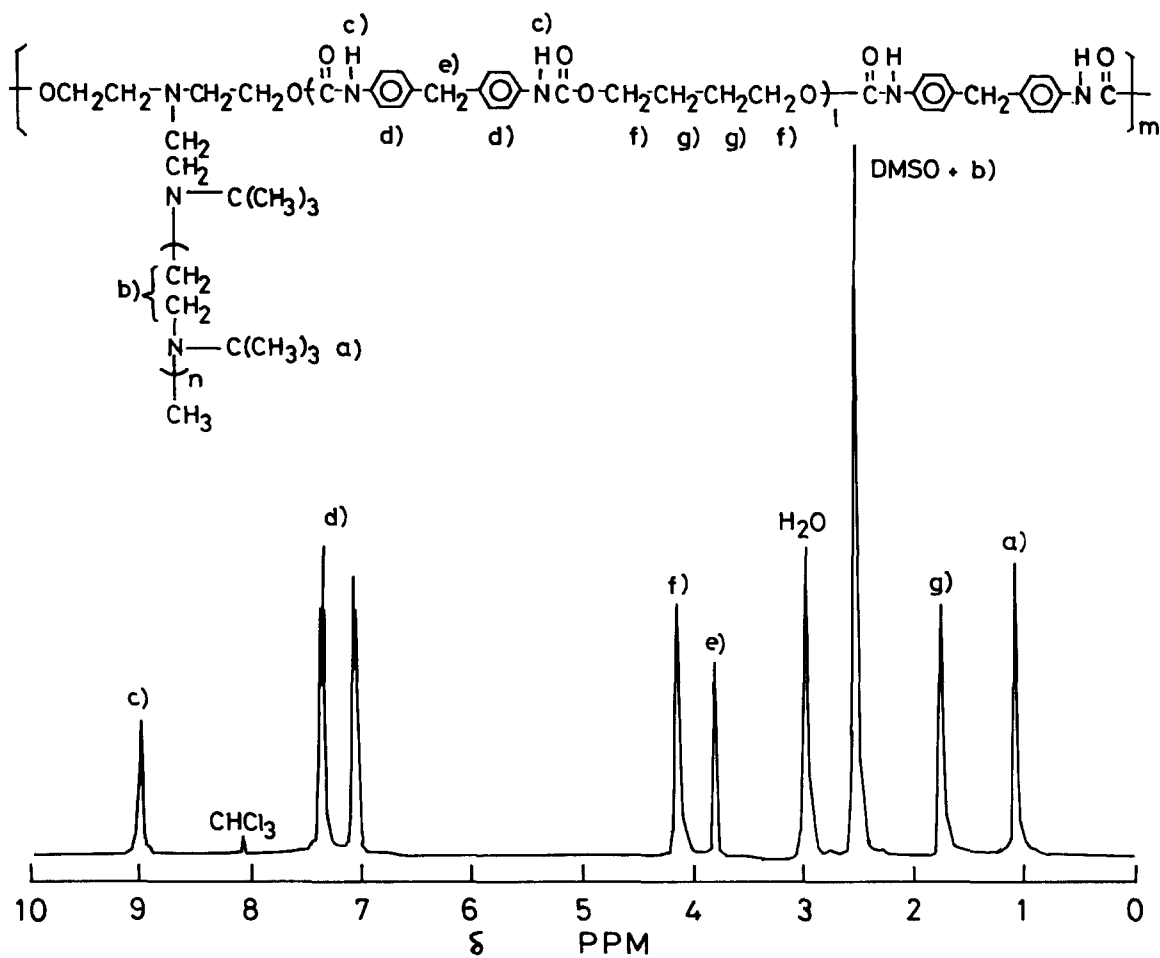


Figure 4 270 MHz ¹H n.m.r. spectrum of polyurethane-poly(TBA) graft copolymer (6) (run B-1 in Table 2) in DMSO-d₆/CDCl₃ (1/1 in vol) at 100°C

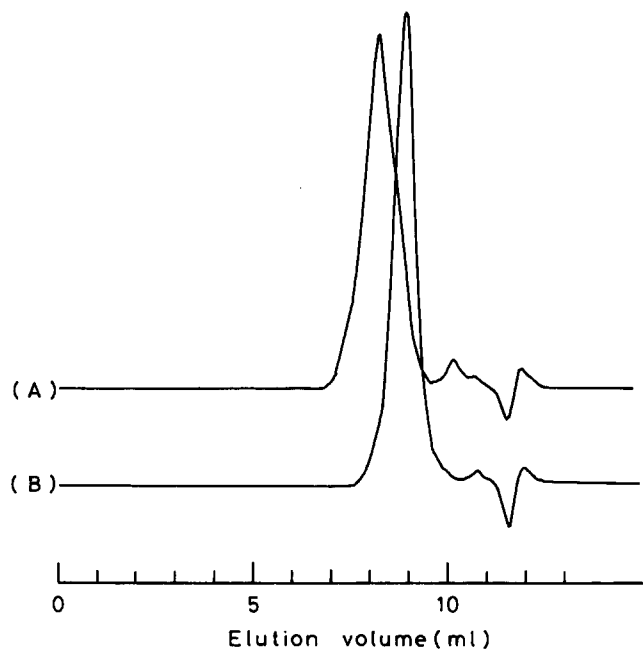


Figure 5 G.p.c. traces of (A) polyurethane-poly(THF) graft copolymer (5) (run A-8 in Table 2) and (B) poly(THF) macromonomer having a diol end-group (3) (run A-3 in Table 1). Column, TSK G4000HXL; eluent, THF; 1.0 ml min^{-1}

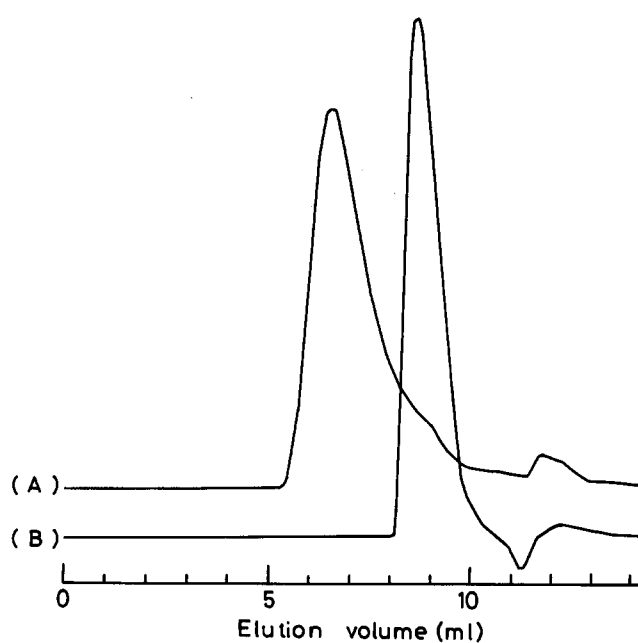


Figure 6 G.p.c. traces of (A) polyurethane-poly(TBA) graft copolymer (6) (run B-2 in Table 2) and (B) poly(TBA) macromonomer having a diol end-group (4) (run B-1 in Table 1). Column, TSK G3000HXL; eluent, THF; 1.0 ml min^{-1}

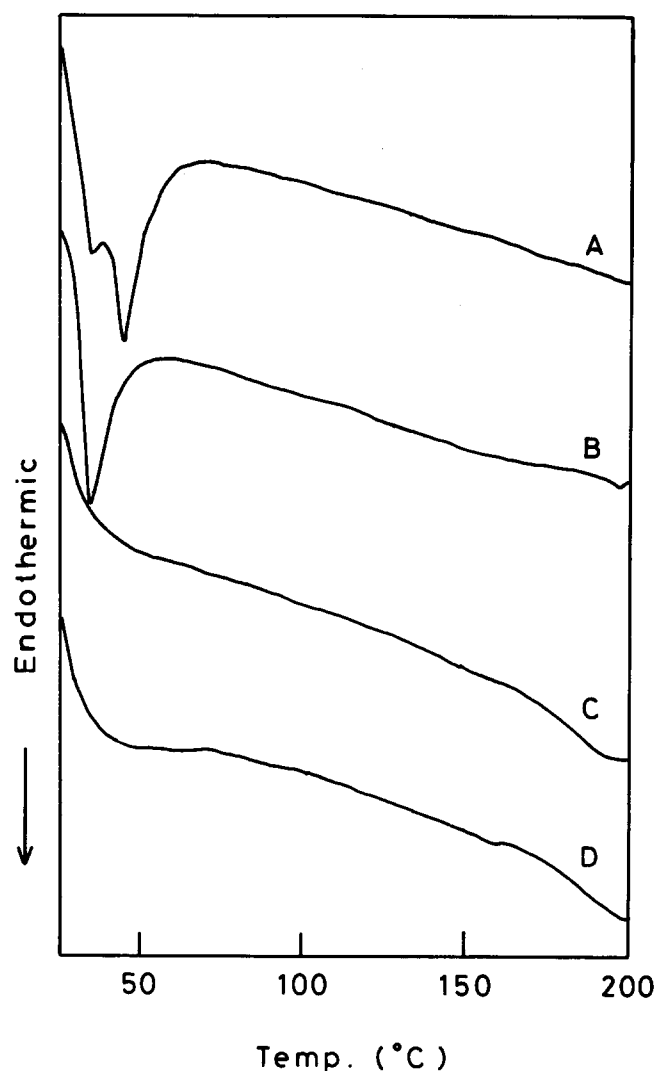


Figure 7 D.t.a. curves of (A) poly(THF) macromonomer having a diol end-group (3) (run A-3 in Table 1) and (B)-(D) polyurethane/poly(THF) graft copolymers (5) (B, run A-4, C, run A-9, D, run A-1 in Table 2)

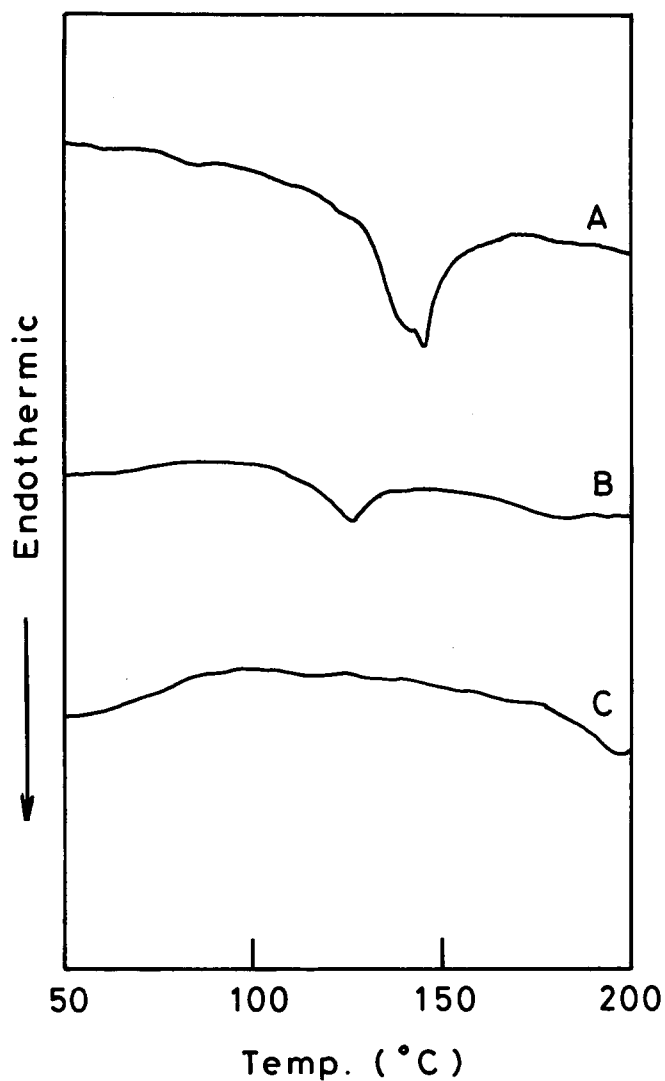


Figure 8 D.t.a. curves of (A) poly(TBA) macromonomer having a diol end-group (4) (run B-2 in Table 1) and (B), (C) polyurethane/poly(TBA) graft copolymers (6), (B, run B-1, C, run B-3 in Table 2)

Thermal analyses of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers

A series of polyurethane/poly(THF) (5) and polyurethane/poly(TBA) (6) graft copolymers possessing uniform-size graft segments were subjected to d.t.a. analysis together with the corresponding poly(THF) (3) and poly(TBA) (6) macromonomers. Part of the results are shown in *Figures 7* and *8*, respectively. Melting endotherms of poly(THF) at around 40°C and of poly(TBA) at around 140°C were only observed for graft copolymer samples of a high graft content. Similar results were previously observed for poly(vinyl alcohol)-poly(THF)¹⁴ and polyurethane/polysiloxane⁵ graft copolymers. This may be explained by a considerable phase mixing of poly(THF) or poly(TBA) segments into polyurethane phase, preventing the crystallization of poly(THF) or poly(TBA) graft segments in the graft copolymer matrix.

CONCLUSIONS

Polytetrahydrofuran and poly(*N*-*t*-butylaziridine) with diol end-groups were synthesized by reactions of the corresponding living polymers with diethanolamine. The reaction of these macromonomers with 4,4'-diphenylmethanediisocyanate followed by chain extension with butanediol produced polyurethane/poly(THF) and polyurethane/poly(TBA) graft copolymers possessing uniform-size graft segments.

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