Synthesis of polyurethane–polystyrene graft copolymer using uniform-size polystyrene with a diol end-group

Yasuyuki Tezuka* and Akitoshi Araki
Department of Material Science and Technology, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-21, Japan
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Uniform-size polystyrenes (PSs) having a diol end-group **2** were synthesized through the reaction of a living PS with a chlorosilane derivative having a trimethylsilyl-protected diol function, i.e. 3-chlorodimethylpropoxy-1,2-bis(trimethylsiloxy)propane **1**, and the subsequent deprotection by precipitation into an acidic methanol solution. The polyaddition reaction of **2** with 4,4'-diphenylmethanediisocyanate followed by the chain extension with 1,4-butanediol produced polyurethane–PS graft copolymers **3** with a controlled graft segment length and graft content.

(Keywords: polyurethane; polystyrene; macromonomer)

INTRODUCTION

Polyurethane-based graft copolymers having well-defined graft segment structures are of significant interest as model polymers for polyurethane-based composite materials currently applied in artificial cardiovascular devices owing to their favourable mechanical and antithrombogenic properties[1]. In this context, we have synthesized a series of polyurethane-based graft copolymers having either poly(dimethylsiloxane)[2], poly(tetrahydrofuran)[3] or poly(t-butyl aziridine)[3] segments by means of a macromonomer technique, by which a graft copolymer of well-defined graft segment length as well as graft content can be obtained.

Although the macromonomer technique has been extensively studied in the last decade for the synthesis of graft copolymers of well-controlled structures[4], reports on macromonomers have mostly been limited to those applicable for a chain polymerization mechanism, and scarce examples designed for a step polymerization mechanism, i.e. polyaddition and polycondensation reactions to give polyurethane or polyamide copolymers[5–8]. Hence, the synthesis of uniform-size macromonomers for this purpose is thought to provide a unique opportunity to control the multicomponent structure in polyurethane-based graft copolymers produced by the polyaddition mechanism.

The subsequent surface studies on these polyurethane-based graft copolymers[9–11] and their block-type analogues[12] revealed that a significant accumulation of the lower surface energy graft component, namely the poly(dimethylsiloxane) or poly(tetrahydrofuran) segment, took place at the dry sample film surface during the casting procedure, and a remarkable restructuring occurred at the surface when the contacting medium was changed from air to water. In addition, the dynamics of the surface response process were found to be related to various structural parameters of the graft copolymer, such as the nature of the surface-accumulated segment, the mode (i.e. graft or block) of the segment linkage and the length of the graft segments as well as the total graft segment content.

As an extension of the preceding studies, we report in the present paper on the synthesis of polyurethane-based graft copolymers having a polystyrene (PS) graft segment, which is characterized as being hydrophobic and glassy (T_g is above ambient temperature) in contrast to the hydrophobic and rubbery (T_g is below ambient temperature) poly(dimethylsiloxane) and poly(tetrahydrofuran) graft segments reported previously[2,3].

EXPERIMENTAL

Reagents

Styrene (Nacalai Tesque), dried over CaH_2 and distilled under reduced pressure, was passed through a column packed with aluminium oxide (Merck, aluminium oxide 90) and stored over CaH_2 in a refrigerator; it was distilled again under reduced pressure just before use[13]. n-Butyllithium (Nacalai Tesque, 1.6 $mol\,l^{-1}$ in n-hexane) was filtered with a G-4 glass filter and used after titration with 2,5-dimethoxybenzyl alcohol[14]. THF and benzene (Nacalai Tesque) were distilled from sodium/benzophenone just before use. 3-Allyloxy-1,2-propanediol (Tokyo Kasei) was refluxed over CaH_2 and distilled under reduced pressure. Chlorodimethylsilane (Toshiba Silicone Co.) and triethylamine (Nacalai Tesque) were distilled over CaH_2. Pt/C (5 wt%, N. E. Chemcat) was used as received. 4,4'-Diphenylmethanediisocyanate (MDI), 1,4-butanediol (BD) and dimethylacetamide (DMAc) were refluxed over CaH_2 and distilled under reduced pressure. Tin(II) octylate (Nacalai Tesque), chlorotrimethylsilane and pyridine (Nacalai Tesque) were used as received.

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* To whom correspondence should be addressed

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Procedures

Synthesis of 3-allyloxy-1,2-bis(trimethylsiloxy)propane. In a 1 l three-necked flask equipped with a dropping funnel, a reflux condenser and a mechanical stirrer, 3-allyloxy-1,2-propanediol (50.0 g, 0.379 mol) and pyridine (89.8 g, 1.137 mol) were mixed in 400 ml of dichloromethane. Thereupon, chlorotrimethylsilane (123.4 g, 1.137 mol) was added under stirring at 0°C and the reaction was carried out for 1 h at ambient temperature and for 3 h at 40°C. The precipitate formed in the reaction mixture was separated by filtration and subsequent distillation under reduced pressure (112–115°C/22 mmHg) yielded 93.0 g (89% yield) of a trimethylsilyl-protected diol product.

Synthesis of 3-chlorodimethylsilylpropoxy-1,2-bis(trimethylsiloxy)propane 1. In a 200 ml three-necked flask equipped with a dropping funnel, a reflux condenser and a three-way stopcock, 3-allyloxy-1,2-bis(trimethylsiloxy)propane (30.0 g, 0.109 mol) and Pt/C (0.09 g, 2.2×10^{-2} mmol) were mixed under a dry N_2 atmosphere. Thereupon, chlorodimethylsilane (30.9 g, 0.327 mol) was added under stirring with a magnetic stirrer at 60°C and the reaction was allowed to continue for 5 h. The reaction solution was then subjected to an evaporation procedure to remove unreacted chlorodimethylsilane and finally distilled under reduced pressure (130–132°C/2 mmHg) to yield 24.2 g (60% yield) of **1**. ^1H n.m.r. ($CDCl_3$) δ (ppm): 0.12 (s, 9H), 0.18 (s, 9H), 0.89 (t, 2H), 1.70 (m, 2H), 3.31–3.66 (overlapped, 6H), 3.85 (m, 1H). ^{13}C n.m.r. ($CDCl_3$) δ (ppm): −0.6, 0.3, 1.5, 15.3, 23.3, 64.5, 72.5 (two overlapping peaks), 73.3. I.r. (neat) (cm^{-1}): 840, 1110, 1255, 2950.

Synthesis of uniform-size PSs with a diol end-group 2. A living PS was prepared by the method detailed elsewhere[13]. Thus, styrene was polymerized in a 25 ml THF/benzene (2/1 v/v) mixture for 30 min at −50°C using n-butyllithium as the initiator with a monomer/initiator ratio of 52.3. Under these polymerization conditions, styrene was consumed quantitatively[13]. A five-fold excess of **1** was subsequently added and allowed to react for 2 h at ambient temperature. The reaction product was recovered by pouring the reaction solution into a pre-cooled (< 10°C) 1 l methanol solution containing 100 ml of 0.1 N aqueous HCl and purified by reprecipitation twice from THF using a pre-cooled methanol/water (9/1 v/v) mixture. Finally, the product was freeze dried from a benzene solution.

Synthesis of polyurethane–PS graft copolymers 3 by use of 2. Synthesis of polyurethane–PS graft copolymers was carried out using a similar method to that reported for the syntheses of polyurethane–poly(dimethylsiloxane)[2] and polyurethane–poly(tetrahydrofuran)[3] graft copolymers. Thus, in a 50 ml round-bottomed flask equipped with a three-way stopcock, a solution containing a weighed amount of MDI, DMAc (15 ml), tin(II) octylate and triethylamine (both 1 wt% of the total weight of MDI and **2**) was prepared under a N_2 atmosphere. Thereupon, a 15 ml DMAc solution containing a prescribed amount of **2** was introduced to react under stirring for 1 h at 60°C, followed by addition of a weighed amount of BD to continue the reaction for a further 7 h. The reaction product was recovered by pouring the mixture into 1 l of methanol and purified by reprecipitation from a DMAc/methanol system. The product was finally dried *in vacuo* for more than 24 h at 60°C. The fractionation of the products was performed first by means of a Soxhlet apparatus with cyclohexane for 10 h. The products of more than 30 wt% PS content were totally soluble in hot cyclohexane; thus, they were precipitated from DMAc solution (10–15 ml containing ca. 1.0 g of the product) into a 1 l benzene/methanol (1/1 v/v) mixture to separate the PS homopolymer fraction.

Measurements

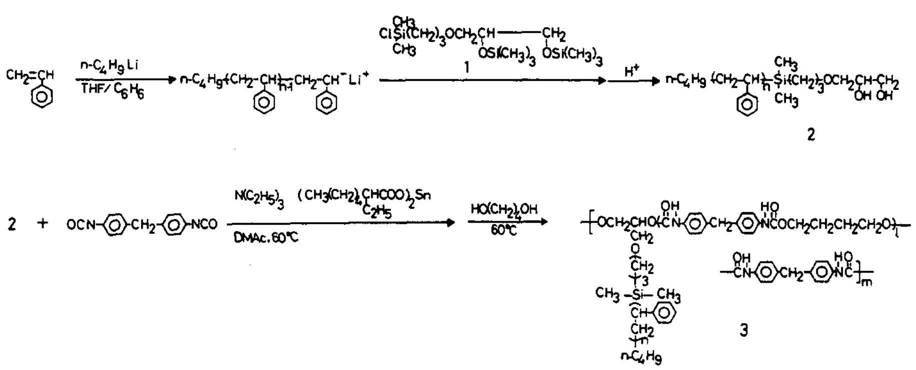
^1H and ^{13}C n.m.r. spectra were recorded by means of a JEOL JNM-GX 270 apparatus at 40°C in $CDCl_3$ or at 60°C in DMSO-d_6. Chemical shift values were referenced from a residual proton signal in either $CDCl_3$ (7.30 ppm) or DMSO-d_6 (2.50 ppm), or from the central carbon signal of $CDCl_3$ (77.0 ppm). Gel permeation chromatography (g.p.c.) measurements were performed using a Tohso model CCPD equipped with a reflective index detector RI 8000, and using a G3000HXL as the column and THF as eluent with a flow rate of 1.0 ml min^{-1}. I.r. spectra were taken on a Shimadzu 8100 *FT*i.r. apparatus using cast film samples from either chloroform or DMAc solution on a NaCl plate. Differential scanning calorimetry (d.s.c.) measurements were carried out on a Seiko DSC-20 apparatus with a Seiko SSC/580 thermal controller at a heating rate of 10°C min^{-1}. Samples (ca. 20 mg) were annealed by heating to 240°C at a heating rate of 10°C min^{-1} and then slowly cooled to ambient temperature. A thermogram of each sample was then obtained at a heating rate of 10°C min^{-1}. Polyurethane homopolymer for the i.r. and d.s.c. measurements was prepared by the identical procedure to the graft copolymers with equimolar amounts of MDI and BD over 6 h at 60°C.

RESULTS AND DISCUSSION

Synthesis of uniform-size PSs with a diol end-group 2

Although polyurethane-based graft copolymers have been commonly prepared by either a 'graft from' technique, such as the initiation of anionic polymerization from pre-metallated polyurethanes[15–17], or a 'graft onto' technique, such as the polymer–polymer coupling reaction with the use of pre-metallated polyurethanes[15,18,19] or the radical addition of olefinic groups introduced into the polyurethane chain[20–28], the application of the macromonomer technique with the use of pre-polymers having a diol group has been explored only recently[2,3,7,8].

In the present study, we employed a macromonomer technique by which a graft copolymer of controlled graft segment length and graft content can be obtained (see *Scheme 1*). Thus, PSs having a diol end-group were prepared by the quantitative end-capping reaction of a living carbanion with a chlorosilane derivative having a trimethylsilyl-protected diol group, namely 3-chlorodimethylsilylpropoxy-1,2-bis(trimethylsiloxy)propane **1**, which was prepared through the hydrosilation reaction of 3-allyloxy-1,2-bis(trimethylsiloxy)propane with chlorodimethylsilane in the presence of Pt/C as a catalyst. Monofunctional living PSs, prepared by a 'syringe and flask' procedure in a THF/benzene mixture at −30 to −50°C[13], were subjected to reaction with **1**. Isolation of the reaction products by precipitation into methanol



Scheme 1 Reactions used in the preparation of the polyurethane–PS graft copolymers

Table 1 Synthesis of PS macromonomers with a diol end-group **2**

Run	[Styrene] (mmol)	[n-C_4H_9Li] (mmol)	THF/benzene (v/v)	Temperature (°C)	Yield (wt%)	M_n Calculated[a]	M_n G.p.c.[b]	M_w/M_n[c]	End-capping efficiency[d] (%)
1	29.0	1.76	1/1	−30	83	2000	2900	1.07	93
2	28.8	0.84	2/1	−50	89	3800	4200	1.09	88
3	28.6	0.60	2/1	−50	90	5200	6000	1.06	85

[a] $M_n = 104$ ([Styrene]/[n-C_4H_9Li]) + 248 [molecular weights of $(CH_2)_3CH_3$ and $Si(CH_3)_2(CH_2)_3OCH_2CH(OH)CH_2(OH)$]
[b] Calibrated using standard polystyrene
[c] Determined by g.p.c.
[d] Calculated from ^{1}H n.m.r.

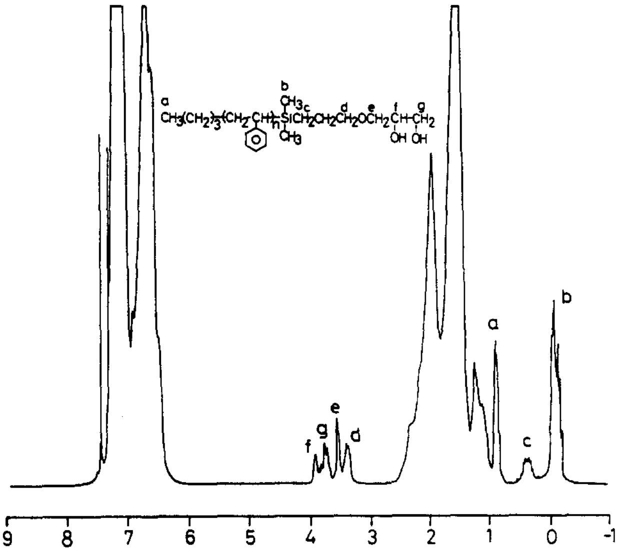


Figure 1 270 MHz ^{1}H n.m.r. spectrum of a PS macromonomer with a diol end-group **2** (run 1 in *Table 1*) in $CDCl_3$ at 40°C

containing a small amount of HCl, enabling simultaneous deprotection of the trimethylsilyl groups on the diol function, produced uniform-size PSs with a diol end-group **2**.

Figure 1 shows the 270 MHz ^{1}H n.m.r. spectrum of **2**. In addition to the strong main-chain signals of PS at around 1.0–2.5 ppm and 6.5–7.5 ppm, methyl protons from the initiator (n-butyllithium) fragment are observed at 0.89 ppm together with methyl and methylene protons adjacent to silicon at around −0.1 ppm and 0.39 ppm, respectively. Also methylene and methyne protons adjacent to the ether and hydroxy oxygens at around 3.4–3.9 ppm are visible. The signal splitting of the methyl protons on silicon is ascribed to the presence of stereoisomeric sequences in the adjacent styrene monomer units[29]. The high end-capping efficiency was confirmed by comparing the proton signal area of the methyl group from the initiator with the signal areas of the methylene and methyne groups from the end-capping reagent (*Table 1*).

As listed in *Table 1*, PS macromonomers having different molecular weights with narrow molecular weight distributions ($M_w/M_n < 1.10$) were produced in high yields. The molecular weights estimated by g.p.c. were found to be slightly higher than those calculated from the monomer/initiator ratio, suggesting the loss of the lower-molecular-weight portion during the isolation procedure.

Synthesis of polyurethane–PS graft copolymers 3

The PS macromonomers **2** were then subjected to the reaction with diphenylmethanediisocyanate (MDI), followed by chain extension with butanediol (BD) in various MDI/BD ratios to produce polyurethane–PS graft copolymers **3**.

Figure 2 shows the 270 MHz ^{1}H n.m.r. spectrum of **3**. In addition to the signals due to the PS segment, those assignable to the polyurethane segment are visible, i.e. a urethane proton at 9.33 ppm, phenyl ring protons at 7.34 ppm, and tetramethylene protons at 1.81 ppm and 4.21 ppm.

The results of the i.r. inspections of **3** and the relevant PS and polyurethane homopolymers are shown in *Figure 3*. The absorptions both from the PS segment, i.e. 3030, 1600 and 700 cm^{-1}, and from the polyurethane segment, i.e. 3330, 1703, 1530 and 1083 cm^{-1}, are observed in the spectrum of **3**.

The results on the synthesis of **3** are collected in *Table 2*. The recovered yield of the product was found to increase with increasing feed content of MDI against **2**, and the PS contents in the recovered products were nearly equal to those in the feed. Thus, both primary and secondary hydroxy groups in **2** appeared to react with MDI during the first stage of the polyaddition reaction, as in the case of poly(dimethylsiloxane) macromonomer reported elsewhere[2].

G.p.c. inspection of the product obtained with the high feed content of **2**, on the other hand, showed a shoulder peak relevant to the unreacted macromonomer **2**, as shown in *Figure 4*. This indicates that unreacted PS macromonomer fraction still remained in the isolated product after precipitation into methanol, particularly in those products obtained with high feed contents of **2**. Therefore, a Soxhlet extraction treatment was performed using cyclohexane, which can remove PS homopolymer and presumably also any graft copolymer with a high PS segment content. As summarized in *Table 3*, no homopolymer was extracted from products containing less than 13 wt% PS, while those containing more than 30 wt% PS were found to be totally soluble in hot cyclohexane. Then, the cyclohexane-soluble products were precipitated in a benzene/methanol (1/1 v/v) mixture, which dissolves PS homopolymer but is a non-solvent for polyurethane homopolymer. As a result, the PS homopolymer fraction was mostly removed from the crude products, as evidenced by g.p.c. inspection of the products (*Figure 4*), though a part of the graft copolymer with high PS content was also lost during the procedure (*Table 3*).

D.s.c. measurements for a series of **3** were performed to elucidate the phase structure of this polymeric material and the results are shown in *Figure 5*. The observed T_g values for the graft copolymer samples were 94–101°C, close to those of the homopolymers of PS (85°C) and polyurethane (94°C). Multiendothermic peaks at 192, 215 and 230°C for the crystalline domains of the polyurethane

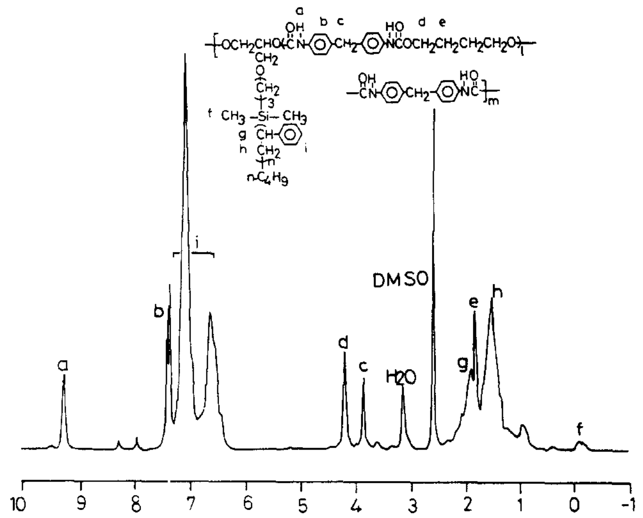


Figure 2 270 MHz ^{1}H n.m.r. spectrum of a polyurethane–PS graft copolymer **3** (run 6 in *Table 3*) in DMSO-d_6 at 60°C

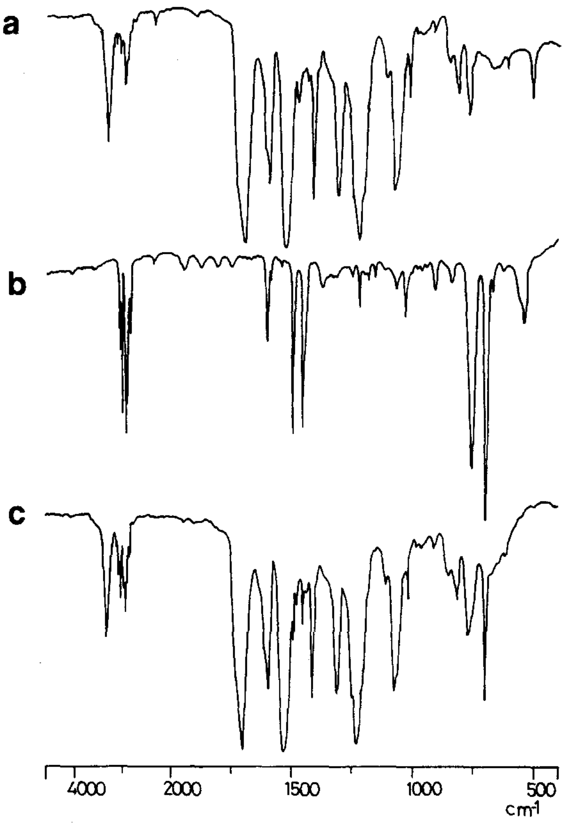


Figure 3 I.r. spectra of (a) polyurethane homopolymer, (b) PS homopolymer (run 1 in *Table 1*) and (c) a polyurethane–PS graft copolymer **3** (run 7 in *Table 3*)

Table 2 Synthesis of polyurethane–PS graft copolymers **3**[a]

Run	M_n of macromonomer	Molar ratio Macromonomer/MDI/BD	Feed content of segment (wt%)	Yield (wt%)	PS segment content in crude graft copolymer[b] (wt%)
1	2900	1/60/59	12.9	89.3	13.0
2		1/120/119	6.9	93.6	4.8
3	4200	1/10/9	43.0	87.6	41.6
4		1/50/49	12.9	91.8	12.6
5		1/100/99	6.9	95.3	6.3
6	6000	1/5/4	87.2	60.0	95.1
7		1/30/29	37.2	70.7	32.5
8		1/100/99	15.0	84.7	11.8
9		1/200/199	8.1	89.9	9.3

[a] DMAc, 25 ml; triethylamine, 1 wt%; tin(II) octylate, 1 wt%; 60°C
[b] Determined by ^{1}H n.m.r. (see Experimental)

Table 3 Fractionation of polyurethane–PS graft copolymers

Run	M_n of macromonomer	PS segment content of crude graft copolymer (wt%)	Soxhlet procedure[a] PS content (wt%)	Soxhlet procedure[a] Recovery yield (wt%)	Precipitation procedure[b] PS content (wt%)	Precipitation procedure[b] Recovery yield (wt%)
1	2900	13.0	12.9	98	–[c]	–[c]
2		4.8	4.9	100	–[c]	–[c]
3	4200	41.6	Totally soluble		40.2	75.2
4		12.6	12.9	100	–[c]	–[c]
5		6.3	6.2	100	–[c]	–[c]
6	6000	95.1	Totally soluble		84.1	60.0
7		32.5	Totally soluble		31.6	74.4
8		11.8	11.5	100	–[c]	–[c]
9		9.3	8.8	98	–[c]	–[c]

[a] Soxhlet extraction with cyclohexane
[b] Precipitation in benzene/methanol (1/1 v/v) mixture
[c] Not performed

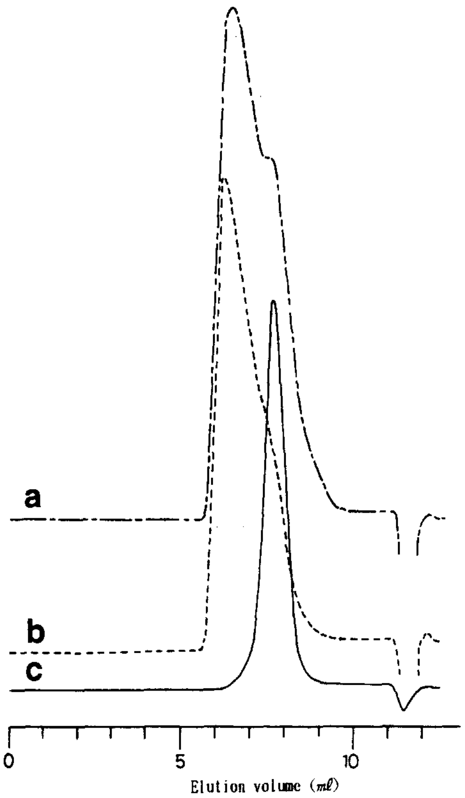


Figure 4 G.p.c. traces of a polyurethane–PS graft copolymer **3** (a) before (run 7 in *Table 2*) and (b) after (run 7 in *Table 3*) fractionation and (c) the starting PS macromonomer **2** (run 3 in *Table 1*)

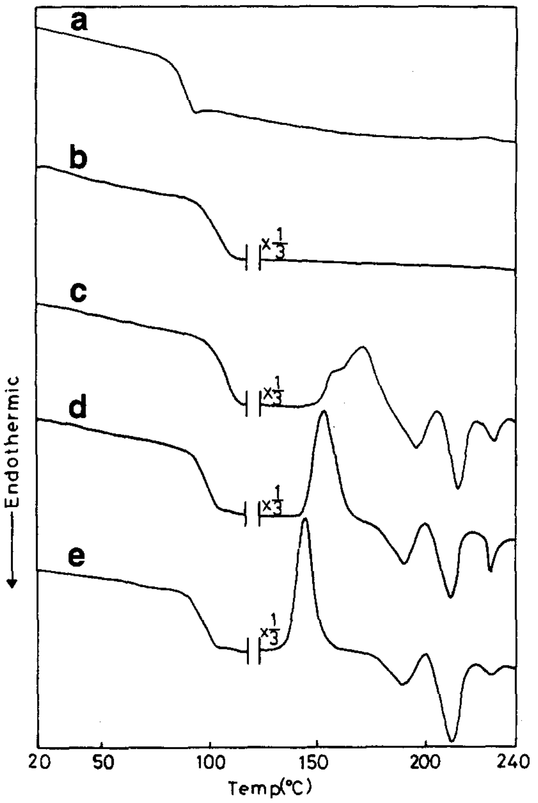


Figure 5 D.s.c. thermograms of (a) PS homopolymer (run 3 in *Table 1*), (b–d) polyurethane–PS graft copolymers **3** of different PS contents (b, run 7: c, run 8; and d, run 9; *Table 3*) and (e) polyurethane homopolymer

segment produced from MDI and BD[29–31] were absent from the scan for the graft copolymer with 31.6 wt% PS content. In addition, the exothermic crystallization peaks at around 140–170°C were noticeably affected by the introduction of the PS graft segment. Thus a phase mixing between PS and polyurethane domains is envisaged in the present graft copolymers.

A study of the surface properties, including the environmental response behaviour, of these new polyurethane-based graft copolymers is now in progress and will be reported elsewhere.

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