Alternating block copolymers of aromatic poly(ether sulphone) and poly(dimethylsiloxane) by hydrosilylation

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(Received 2 September 1986; accepted 30 October 1986)

Alternating block copolymers of aromatic poly(ether sulphone) (PSU) and poly(dimethylsiloxane) (PDMS) were prepared via Pt-catalysed hydrosilylation of α,ω-di(vinylbenzyl)PSU or α,ω-di(allylether)PSU with α,ω-di(silane)PDMS. The vinyl functionalized PSUs were prepared by Williamson phase transfer catalysed (PTC) etherification of α,ω-di(hydroxyphenyl)PSU with *p*-chloromethylstyrene or allyl bromide (chloride), respectively. The block copolymers prepared were characterized by nuclear magnetic resonance (n.m.r.), gel permeation chromatography (g.p.c.), differential scanning calorimetry (d.s.c.) and membrane osmometry. These block copolymers showed good degrees of chain extension and phase separation into rubbery PDMS and glassy PSU domains.

(Keywords: α,ω-di(vinyl)PSU; α,ω-di(silane)PDMS; hydrosilylation; alternating block copolymers; phase separation)

INTRODUCTION

Block copolymers represent an interesting class of materials whose unique molecular architecture can lead to useful product properties[1,2]. Various methods for block copolymer synthesis have been described[1-4]. Especially interesting are combinations of rubbery and thermoplastic polymers, which when combined into block copolymers constitute a family of materials known as thermoplastic elastomers. The properties of these materials depend not only on the polymers chosen but also on their respective sequence lengths and ability to form discrete rubbery and glassy domains. Combination of a very low T_g rubber with a high T_g thermoplastic could yield a material with a very broad useful temperature range. One such combination would be aromatic poly(ether sulphone) (PSU, $T_g \approx 190°C$) and poly(dimethylsiloxane) (PDMS, $T_g = -120°C$). It was the purpose of the work described here to synthesize alternating block copolymers, i.e. $(PSU\text{–}PDMS)_n$, from these two precursor polymers.

Alternating block copolymers of PSU and PDMS have been previously prepared. Their synthesis was described by Noshay *et al.*[5] and involved the coupling of α,ω-di(hydroxyphenyl)PSU with α,ω-di(dimethylamine) PDMS. This reaction was shown to proceed well, and yielded high molecular weight block copolymers with segment lengths sufficient to attain good phase separation. The linkages formed between these blocks were of the Si–O–C type. Although the authors showed that, in this case, the hydrolytic stability of these Si–O–C linkages was good[5], generally these types of bonds are avoided due to their susceptibility to hydrolysis[6,7].

For a different system, the use of Pt-catalysed hydrosilylation (addition of ≡Si–H groups to double bonds) to produce alternating block copolymers of α,ω-di(vinylsilane) polystyrene (PS) and α,ω-di(silane)PDMS was shown to be feasible by Chaumont *et al.*[8-10]. This type of reaction led to PS–PDMS block copolymers with hydrolytically stable[7] Si–C linkages between blocks. Investigation of model systems for this hydrosilylation reaction of PS and PDMS[9] showed that, typically, very high reactant concentrations were needed for high degrees of conversion. In the block copolymer synthesis, concentrations as high as 50 wt% were employed[10]. At these high concentrations, the reaction mixtures were often heterogeneous at first due to the incompatibility of the two precursor polymers. With reaction time, however, the reaction usually became homogeneous as the block copolymerization reactions progressed. Degrees of chain extension between 3 and 9, and moderate to high block copolymer molecular weights, were obtained for a range of precursor molecular weights[10].

The use of Pt-catalysed hydrosilylation was first applied to the synthesis of PSU–PDMS alternating block copolymers by Gagnebien *et al.*[11,12] and involved either coupling of α,ω-di(hydroxyphenyl)PSU with α,ω-di(epoxy)PDMS (produced from hydrosilylation of 1-allyloxy-2,3-epoxypropane with α,ω-di(silane)PDMS[11], or coupling of α,ω-di(1-allyloxy-2-hydroxypropyl)PSU[13] with α,ω-di(silane)PDMS[12]. In both cases, hydrolytically stable Si–C linkages[7] were formed between the two blocks. The reactions were typically performed at high concentrations of PSU in diglyme with slow additions of small quantities of PDMS, demixing (due to drastic incompatibility) and slow homogenization following each addition. The viscosities of the reaction mixtures became very high as the reaction progressed,

0032–3861/87/081407–11$03.00

leading to difficulties in stirring. The degrees of chain extension reported for both methods, however, were low (*DP* in the range 2–3), considering the short block lengths employed ($\bar{M}_n \leqslant 1500$ for both), owing to stirring difficulties; the molecular weights of the reported block copolymers reached only to $\bar{M}_n = 6000$[11,12]. The segment lengths were also not of sufficient molecular weight to yield good phase separation into glassy and rubbery domains, a necessary condition for desired product properties. Further, the reaction of α,ω-di(hydroxyphenyl)PSU with either 1-allyloxy-2,3-epoxypropane to yield α,ω-di(1-allyloxy-2-hydroxypropyl)PSU[13] or with α,ω-di(epoxy)PDMS[11] can produce side products owing to the formation of the secondary alcohol group upon opening of the epoxy ring[11,13]. This secondary alcohol group can further react to open an epoxy ring, resulting in branched structures[11,13]. It is also possible that the secondary alcohol group might react with the ≡Si–H end groups of α,ω-di(silane)PDMS during the hydrosilylation reaction at elevated temperatures, as noted elsewhere for alcoholic solvents[9,14], resulting in a decrease in the PDMS functionality.

In previous work in our laboratory[15,16] we have shown that Williamson phase transfer catalysed (PTC) etherification of α,ω-di(hydroxyphenyl)PSU with chloromethylstyrene (ClMS) results in quantitative functionalization of the PSU phenol chain ends and gives α,ω-di(vinylbenzyl)PSU. This oligomeric PSU has styrene-type double bonds as chain ends. In this paper, we also describe the synthesis of α,ω-di(allylether)PSU by PTC etherification of α,ω-di(hydroxyphenyl)PSU with allyl bromide (chloride), producing a PSU with allyl-type double bonds as chain ends. Both types of PSU oligomers containing end-standing vinyl functions can be reacted with α,ω-di(silane)PDMS in the presence of a Pt-catalyst to yield alternating block copolymers with Si–C linkages between blocks. This hydrosilylation method is, of course, similar to that of Gagnebien *et al.*[12], except that both these vinyl-terminated PSUs can be prepared and reacted without the aforementioned drawbacks associated with the epoxy group[11–13].

In subsequent work[17–19] we described the synthesis and properties of thermally reactive oligomers of PSU containing PDMS segments. The oligomers were prepared via Pt-catalysed hydrosilylation of α,ω-di(vinylbenzyl)PSU with α,ω-di(silane)PDMS using a 2/1 excess of PSU to PDMS[17,18]. This method yielded statistically a 'triblock' copolymer with, on average, one PDMS segment incorporated between two PSU segments. The chain ends of these 'triblocks' consisted of thermally reactive vinylbenzyl (styrene-type) groups due to the 2/1 excess of PSU to PDMS. Because of the drastic incompatibility of these two polymers, which makes the reaction particularly difficult[11,12], a method was developed whereby the reaction was performed in initially diluted solution, which was then concentrated as the reaction proceeded[18]. This method led to the expected degrees of conversion for higher molecular weight precursor pairings for which the methods of Chaumont *et al.*[10] for PS–PDMS and Gagnebien *et al.*[12] applied to this system did not produce the desired conversions. Although Pt-catalysed hydrosilylation reactions can be accompanied by side reactions of the PDMS ≡Si–H end groups[20–23], these side reactions are typically much slower than the addition reaction[20]. It was shown by 200 MHz proton nuclear magnetic resonance (n.m.r.) spectroscopy[18] that, with the good reactivity of styrene towards hydrosilylation and the 2/1 excess of vinylbenzyl to ≡Si–H in the 'triblock' system, essentially quantitative conversion of ≡Si–H into Si–C linkages could be achieved.

Since the quantitative functionalization of α,ω-di(hydroxyphenyl)PSU with ClMS or allyl bromide (chloride) under PTC conditions readily leads to α,ω-di(vinyl)PSUs with good functionality, these oligomers were considered good candidates for alternating multiblock copolymer synthesis via hydrosilylation with α,ω-di(silane)PDMS. This, of course, is simply an extension of the 'triblock' synthesis mentioned above except that stoichiometric amounts of the two precursor polymers are used. In this case, however, side reactions of ≡Si–H may become important due to the necessity of strict stoichiometry for the production of high molecular weight block copolymers. It was the aim of the work described here to investigate the feasibility of the hydrosilylation reaction for the production of PSU–PDMS alternating block copolymers of high molecular weight with segment lengths sufficient to allow good phase separation.

EXPERIMENTAL

Materials

Bisphenol A (BPA, Aldrich) and 4,4′-dichlorodiphenyl sulphone (DCDPS, Fluka) were recrystallized several times from toluene. α,ω-Di(silane)PDMS was obtained from Petrarch Chemicals (sample 1) and Wacker Chemie, F.R.G. (all others) and was used as received. *p*-Chloromethylstyrene (*p*-ClMS) was prepared and purified according to a method reported by Kondo *et al.*[24]. Allyl bromide (Aldrich) was dried with $CaCl_2$, filtered, and then distilled before use. Chlorobenzene (ClBz, Aldrich) for use in hydrosilylation reactions was dried over P_2O_5 and distilled; otherwise it was used as received. Potassium carbonate (Fischer) was pulverized in a blender and then dried at 120°C for several days before use. The platinum catalyst was either an organic platinum compound obtained from Wacker Chemie (SLM-86003, data undisclosed) or Pt-divinyltetramethyldisiloxane in xylenes (PC072, Petrarch) diluted to 1 wt% Pt (called PC072′ in the text). All other solvents and reagents (Aldrich) were used as received.

Techniques

Number average molecular weights of the precursor oligomers were determined by ^1H n.m.r., vapour pressure osmometry (v.p.o.), and gel permeation chromatography (g.p.c.). Proton n.m.r. spectra were obtained with Varian XL-200, Bruker WH-250, or Bruker WH-90 *FT*n.m.r. instruments with $CDCl_3$ as solvent and TMS as internal standard. No TMS was used for samples containing PDMS. V.p.o. measurements were performed using Wescan 233 or Perkin–Elmer 115 instruments ($CHCl_3$, 36°C). G.p.c. was performed with PL Gel columns of 10^5, 10^4, 10^3, 5×10^2 and 10^2 Å (column set 1) or 10^6, 10^5, 10^4 and 10^3 Å (column set 2) using THF (for PSU and blocks) or toluene (for PDMS) as the mobile phase at a flow rate of 1.0 ml min^{-1}. Detection was u.v. and r.i. (THF) or only r.i. (toluene). Both column sets were calibrated with polystyrene standards. Differential scanning calorimetry (d.s.c.) measurements were performed on Perkin–Elmer DSC 2, 4 or 7 instruments at a heating rate of

10°C min^{-1}. Repeated scans were performed to verify the reproducibility of the thermal transitions. Temperature calibration was performed with various thermal standards (e.g. cyclohexane, Hg, Ga, In, Sn). Infrared spectra were measured by a Perkin–Elmer 1330 spectrophotometer from polymer thin films on KBr discs. Membrane osmometry measurements were performed using a Hewlett–Packard instrument (THF, 30°C).

Synthesis of α,ω-di(hydroxyphenyl)PSU (PSU-OH)

These oligomers, with molecular weights in the range 1000–7000, were prepared as reported in a previous publication[18].

Synthesis of α,ω-di(vinylbenzyl)PSU (PSU-VB)

These styrene-terminated PSUs were prepared by Williamson PTC etherification of PSU-OH with *p*-ClMS using tetrabutylammonium hydrogen sulphate (TBAH) as phase transfer catalyst, as previously described[18]. Characterization of these oligomers is presented in *Table 1.*

Synthesis of α,ω-di(allylether)PSU (PSU-AE)

A typical synthesis is illustrated in the following example. Five grams of PSU-2-OH ($\bar{M}_n = 2000$ by v.p.o., 2.5×10^{-3} moles, 5.0×10^{-3} moles –OH groups) were dissolved in 25 ml of chlorobenzene. To the stirring solution, 1.7 g (5×10^{-3} moles) TBAH and 2.4 g allyl bromide (2.0×10^{-2} moles) were added. After several minutes of stirring, 4 ml (5.0×10^{-2} moles OH) of a 12.5 N aqueous NaOH solution were added and the reaction was allowed to proceed at room temperature overnight. Afterwards, the organic layer was separated from the aqueous, washed with distilled water, washed several times with dilute aqueous HCl, and then again with distilled water. The organic phase was then diluted with chloroform and precipitated into slightly acidified (HCl) methanol. Two additional purifications were performed by dissolution of the polymer in chloroform, filtration of the solution when necessary, and precipitation into slightly acidified methanol. The polymer was dried at 40°C under vacuum to constant weight. Recovered yields were normally $\geq 90\%$. One sample (PSU-4-AE) was prepared by reaction of PSU-4-OH with allyl chloride under similar reaction conditions except that the reaction temperature was 40°C.

Synthesis of alternating block copolymers of PSU and PDMS

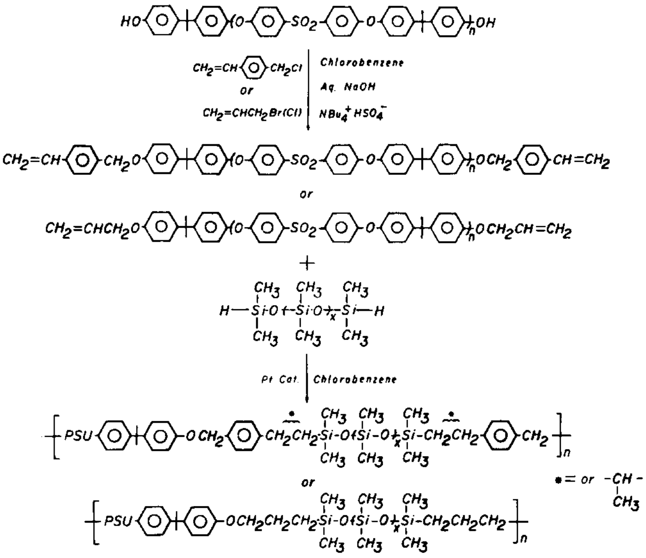
One gram (total polymer weight) of PSU-VB (or PSU-AE) and α,ω-di(silane)PDMS in a 1/1 mole/mole ratio (based on their v.p.o. $\bar{M}_n$) was dissolved in just enough ClBz (as given in *Table 3*) to obtain an optically homogeneous solution. With PSU-VB a small amount ($\leq 10\%$ of PSU vinyl groups) of hydroquinone was added to prevent the thermal polymerization of the styrene groups. The reaction vessel was a flat-bottomed cylindrical tube equipped with a nitrogen inlet and outlet and a magnetic stir bar just smaller than the diameter of the tube. The dimensions of the tube were chosen to maximize stirring and facilitate solvent removal. The solution was purged well with nitrogen, either under stirring at ambient temperature or under heating to the reaction temperatures listed in *Table 3.* After thorough purging at the specified reaction temperature, one drop ($\approx$ 10–20 μl) of the catalyst solution (either SLM 86003 or PC072′) was added. Typically, it was desired to concentrate the solution as fast and as much as possible while maintaining homogeneity[18], so the reaction mixture was sparged with a steady stream of nitrogen to remove excess solvent. Usually the reaction mixture was concentrated to 2–3 ml ClBz per gram of polymer, the viscosity of the reaction mixture being the limiting factor. Solvent was removed until the point where effective stirring became seriously hampered by the solution's viscosity. The reaction was allowed to proceed for the times given in *Table 3.* After cooling (if the reaction was performed at high temperature), the reaction mixture was diluted with chloroform, and precipitated into slightly acidified (HCl) methanol. A second purification was carried out by dissolution of the polymer in chloroform, filtration of the solution, and precipitation into a slightly acidified (HCl) mixture of acetone/methanol (75/25, v/v). The polymer was dried under vacuum at room temperature. Note that based on 200 MHz proton n.m.r. analyses (to be discussed later) the stoichiometry of the system was varied in subsequent experiments in order to obtain the highest block copolymer molecular weight.

Table 1 Characterization of α,ω-di(vinylbenzyl)PSU and α,ω-di(allylether)PSU

Sample	End group[a]	$\bar{M}_n$ Theor.[b]	$\bar{M}_n$ v.p.o.	$\bar{M}_n$ n.m.r.[c]	G.p.c.[c] $\bar{M}_n$	G.p.c.[c] $\bar{M}_w$	G.p.c.[c] $\bar{M}_w/\bar{M}_n$	T_g (°C) (d.s.c.)
1	VB	830	1200	1300[d]	1250	1750	1.4	75
2	VB	1500	2100	2500[d]	2700	3500	1.3	113
	AE	1350	2150	2200[e]	2700	3500	1.3	109
3	VB	3100	3200	3900[d]	4400	8100	1.8	139
	AE	2950	3500	4000[d]	4500	8200	1.8	142
4	VB	4100	3800	5200[d]	5500	11 000	2.0	147
	AE[f]	3950	4400	4700[e]	5900	12 000	2.0	151
5	VB	6200	5600	7500[d]	7400	17 000	2.3	162
	AE	6050	5700	7000[e]	7600	17 500	2.3	163
6	VB	8200	6900	10 200[d]	10 000	21 000	2.1	167
	AE	8050	6800	9400[e]	9800	21 000	2.1	169

[a] AE, allylether; VB, vinylbenzyl
[b] Based on mole ratio of BPA to DCDPS and including end groups
[c] Column set 2
[d] $\bar{M}_n$ determined by 200 MHz ^{1}H n.m.r. spectroscopy
[e] $\bar{M}_n$ determined by 90 MHz ^{1}H n.m.r. spectroscopy
[f] Prepared by reaction with allyl chloride

The necessary PSU/PDMS ratios needed to accomplish this are listed in *Table 3*. The synthetic route is outlined in *Scheme 1*.



Scheme 1 Synthesis of PSU–PDMS alternating block copolymers

RESULTS AND DISCUSSION

Figures 1, 2 and *3* present 200 MHz proton n.m.r. spectra of PSU-OH, PSU-VB, and PSU-AE, respectively, together with proton assignments. The quantitative nature of the PTC etherification of PSU-OH chain ends with *p*-chloromethylstyrene to yield PSU-VB was previously discussed[18]. PTC etherification of PSU-OH with allylbromide (or chloride) to give PSU-AE (*Figure 3*) results in similar quantitative downfield shifts of the signals 1, 2 and 3 from PSU-OH (*Figure 1*) after etherification, as was noted for PSU-VB (*Figure 2*), proving quantitative etherification of the phenol chain ends with these allyl halides. Additionally, the signals of the allylether chain ends (signals o, p, q and r, *Figure 3*) are clearly exhibited. The reaction of PSU-4-OH with allyl chloride was performed at 40°C to ensure quantitative etherification due to the lower electrophilicity compared to allyl bromide. Generally, allyl bromide was the preferred end-capper due to its lower volatility and higher reactivity at ambient temperature.

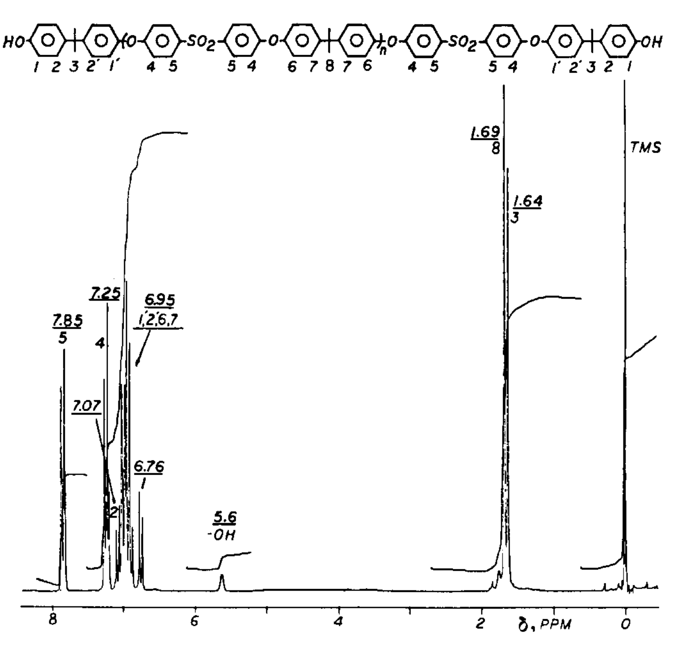


Figure 1 200 MHz ^{1}H n.m.r. spectrum of PSU-2-OH

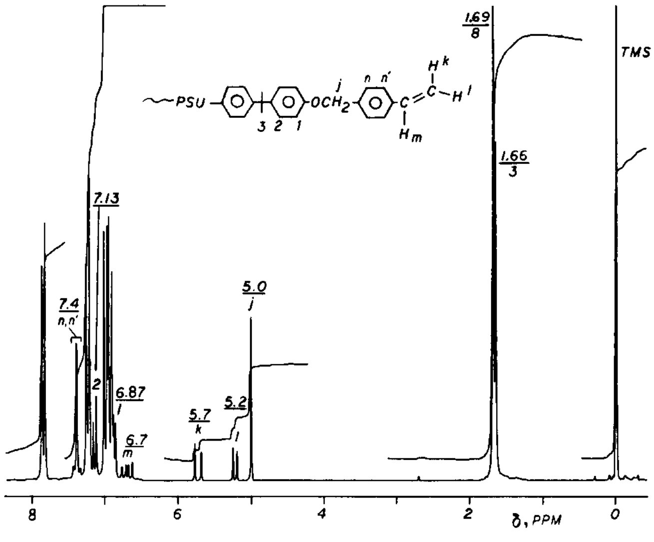


Figure 2 200 MHz ^{1}H n.m.r. spectrum of PSU-2-VB. Other resonances as labelled in *Figure 1*

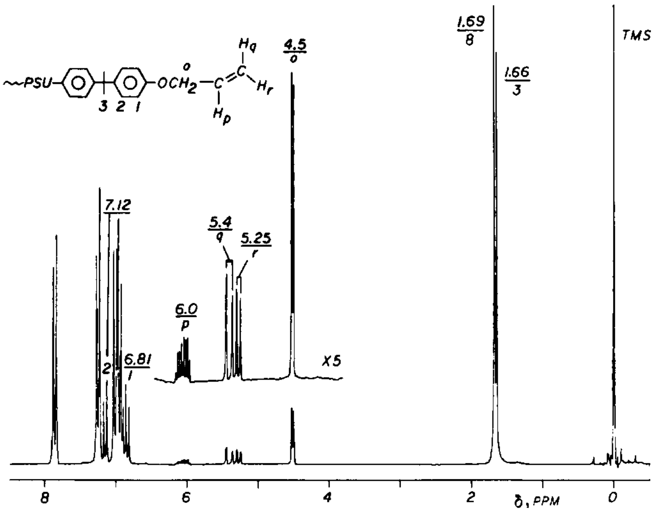


Figure 3 200 MHz ^{1}H n.m.r. spectrum of PSU-2-AE. Other resonances as labelled in *Figure 1*

As with PSU-VB[18], comparison of end group integrals with those of internal units for PSU-AE allowed estimation of its $\bar{M}_n$ by ^{1}H n.m.r. spectroscopy. The n.m.r. $\bar{M}_n$ listed in *Table 1* for PSU-AE were calculated by comparison of signal o integrals with those of signals 3 and 8 according to:

$$DP = \frac{A_{8+3}/6}{A_o/4} - 1$$

where *DP* corresponds to the repeat unit and

$$\bar{M}_n = DP[MW(\text{repeat})] + MW(\text{BPA-2H}) + MW(\text{allylether end groups})$$

Table 1 lists the molecular weight and thermal characterization data for the PSU-VB and PSU-AE used for the preparation of PSU–PDMS alternating block copolymers. Both vinyl functionalized PSUs of the same sample number were prepared from the same PSU-OH and show the expected agreement in the characterization data. Some small differences are probably the result of error in the analytical methods and/or small changes in molecular weight during the successive purifications. In any event, PTC etherification of PSU-OH with *p*-ClMS or allyl bromide (chloride) allowed the preparation of vinyl terminated PSUs with good functionality, making them suitable for alternating block copolymer synthesis. Excesses of the functionalizing reagents which helped to ensure quantitative etherification were easily removed via precipitation in methanol.

The α,ω-di(silane)PDMS obtained commercially were characterized as described previously[18]. *Table 2* lists the data, and a 200 MHz proton spectrum together with proton assignments is given in *Figure 4*. For lower molecular weight samples for which a reasonably accurate $\bar{M}_n$ by ^{1}H n.m.r. spectroscopy could be determined via comparison of end groups and internal integrals (signal c to signals a, b; *Figure 4*)[18], comparison of n.m.r. with v.p.o. $\bar{M}_n$ allowed a good check of functionality. For samples 1 and 2, good agreement between ^{1}H n.m.r. and v.p.o. $\bar{M}_n$ indicated their good functionality. For higher molecular weights, error in the integrals due to the very low intensity of signal c renders the ^{1}H n.m.r. method unreliable.

Alternating block copolymers of PSU–PDMS were prepared by Pt-catalysed hydrosilylation of either PSU-VB or PSU-AE with α,ω-di(silane)PDMS as depicted in *Scheme 1*. Use of PSU-VB has the advantage that, if desired, an excess of vinylbenzyl to ≡Si–H groups can be employed, as with the 'triblocks' discussed previously[18]; these excess styrene end groups can be later used to crosslink the block copolymer. Use of allylether groups, however, requires no inhibitor, which is necessary for vinylbenzyl to prevent thermal polymerization. They can be therefore used at higher temperatures without the threat of end group polymerization, although they may be susceptible to side reactions known for other allylic groups[7,25,26]. Additionally, as will be shown later, allylether groups showed a higher reactivity than vinylbenzyl under the outlined conditions, so that good reaction rates were obtained even at room temperature. Further, addition of ≡Si–H to allyl groups occurred only in an anti-Markovnikov manner[27] (Si addition to the terminal carbon), whereas addition of Si to either carbon occurred when vinylbenzyl was used.

The Pt-catalysed hydrosilylation reaction is known not to be free of side reactions[20–23] which consume ≡Si–H and thereby can decrease the functionality of the α,ω-di(silane)PDMS. Of course, for the preparation of high molecular weight block copolymers, it is necessary that an $\bar{F}_n = 2.0$ be maintained. Typically, however, the side reactions of ≡Si–H are much slower than the addition reaction[18,20]. Therefore, if the rate of the addition reaction is very fast compared to the side reactions, this method should be acceptable for block copolymer synthesis.

Table 3 lists the synthesis and characterization data for PSU–PDMS alternating block copolymers for the entire range of precursor molecular weights. Block copolymers were produced from both PSU-VB and PSU-AE, and representative ^{1}H n.m.r. spectra for these are presented in *Figures 5* and *6*, respectively, together with proton assignments. Similarly to the n.m.r. spectra of a model compound from hydrosilylation of *p*-ClMS with α,ω-di(silane)PDMS, and PSU–PDMS 'triblocks' previously produced[18], *Figure 5* shows the disappearance of signal c (PDMS ≡Si–H end groups) and the complete upfield shift of signal b (compare with *Figure 4*), as well as the resonances of the Si–C linkages formed: c″, d′ (anti-Markovnikov addition) and f′, g′ (Markovnikov). I.r.

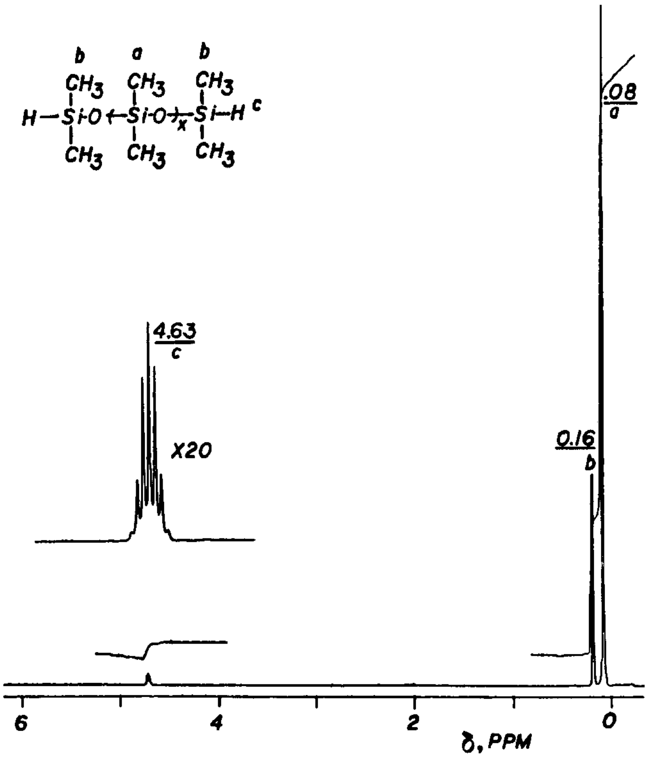


Figure 4 200 MHz ^{1}H n.m.r. spectrum of PDMS-1

Table 2 Characterization of α,ω-di(silane)PDMS

Sample	V.p.o. $\bar{M}_n$	G.p.c.[a] $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Thermal transition (°C, d.s.c.) T_g	T_c	T_{m_1}	T_{m_2}
1	540[b]	430	530	1.23	−146	—	—	—
2	1200[c]	1080	1800	1.67	−135	−101	−51[d]	−33
3	3400	3300	7400	2.24	−127	−90	−43	−25
4	3500	3800	8200	2.16	−128	−96	−47	−27[d]
5	5500	5500	12 800	2.33	−127	−91	−46	−28[d]
6	5600	5000	12 400	2.48	−126	−86	−42	−26[d]
7	11 000	11 400	29 300	2.57	−124	−83	−42[e]	−28[d]

[a] Column set 2

[b] $\bar{M}_n$ (n.m.r.) = 550

[c] $\bar{M}_n$ (n.m.r.) = 1370

[d] Major melting transition

[e] Bimodal

Table 3 Synthesis and characterization of alternating block copolymers of PSU and PDMS

							$(\text{PSU–PDMS})_n$							Thermal transitions (°C, d.s.c.)			
							G.p.c.[d]			$\bar{n}$ by		Memb. osmom.		PDMS			PSU
Sample	PSU no. ($\bar{M}_n$)/ PDMS no. ($\bar{M}_n$)[a]	PSU type[b]	PSU/ PDMS molar ratio[c]	ClBz at start (ml)	Temp (°C)	Time (h)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{n}$[e]	T_g	T_c	T_m	T_g
1	1(1200)/1(540)[f]	VB	1/1.05	2.0	100	17.0	18 000	127 000	7.0	10.7	55.7	—	—	—	—	—	54
2	2(2100)/1(540)	VB	1.1/1	3.5	100	19.0	46 000	137 000	3.0	14.7	34.0	41 000	15.5	—	—	—	108
3	3(3500)/1(540)[g]	AE	1.1/1	3.0	RT	13.0	25 000	63 000	2.5	5.1	7.2	—	—	—	—	—	134
4	4(3800)/1(540)	VB	1/1.05	2.5	100	14.0	39 000	139 000	3.6	6.6	12.1	—	—	—	—	—	139
5	6(6900)/1(540)	VB	1.05/1	2.5	100	12.0	39 000	80 000	2.1	3.7	3.7	—	—	—	—	—	146
6	4(3800)/2(1200)	VB	1/1	6.0	100	18.0	36 000	92 000	2.6	5.5	7.2	—	—	—	—	—	130
7	6(6900)/2(1200)	VB	1/1.05	5.5	100	12.5	51 000	127 000	2.5	4.6	5.6	42 000	5.2	—	—	—	158
8	3(3200)/3(3400)[h]	VB	1/1.05	8.5	100	18.0	25 000	70 000	2.8	3.2	4.5	—	—	−122	—	—	140
9	4(3800)/3(3400)[i]	VB	1/1.1	9.0	100	12.5	28 000	84 000	3.0	3.2	4.6	—	—	−126	—	—	140
10	4(4400)/4(3500)	AE	1/1.2	9.0	120	20.0	34 000	81 000	2.4	3.5	4.0	—	—	−123	—	—	142
11	5(5700)/3(3400)	AE	1/1.05	11.0	120	22.0	53 000	134 000	2.5	4.9	5.4	43 000	4.7	−128	—	—	156
12	6(6800)/3(3400)	AE	1/1.1	12.0	120	20.5	44 000	136 000	3.1	3.4	4.8	44 000	4.3	−135	−99[j]	−61[j]	161
13	4(4400)/6(5600)	AE	1/1.15	11.0	120	22.0	42 000	126 000	3.0	3.9	5.2	—	—	−120	−71	−41	145
14	5(5700)/6(5600)	AE	1/1.15	12.0	120	20.0	52 000	162 000	3.1	4.1	5.4	44 000	3.9	−126	−85	−49	152
15	6(6800)/6(5600)	AE	1/1.1	12.5	120	23.0	43 000	114 000	2.6	2.9	3.4	—	—	−127	−100	−49	159
16	4(4400)/7(11 000)	AE	1/1.3	12.0	120	18.5	47 000	132 000	2.8	2.7	3.2	—	—	−123	−91	−39[k]	137
17	5(5700)/7(11 000)[g]	AE	1/1.15	15.0	50	24.0	65 000	210 000	3.2	3.4	4.5	—	—	−126	−94	−44[l]	148
18	6(6800)/7(11 000)[g]	AE	1/1.1	16.0	50	17.5	57 000	180 000	3.2	2.7	3.6	—	—	−126	−95	−44[l]	160

[a] $\bar{M}_n$ by vapour pressure osmometry; catalyst SLM 86003 unless otherwise noted
[b] VB, α,ω-di(vinylbenzyl)PSU; AE, α,ω-di(allylether)PSU
[c] Based on v.p.o. $\bar{M}_n$
[d] Column set 2
[e] When compared to v.p.o. $\bar{M}_n$ of precursors
[f] Not purified by acetone/methanol precipitation
[g] Catalyst PC072'
[h] 5% hydroquinone as inhibitor
[i] Traces of unreacted vinylbenzyl groups
[j] Low in intensity
[k] Bimodal; value shown is at peak max.; also exhibits a shoulder at −42°C
[l] Bimodal; value shown is at peak max.; also exhibits a shoulder at −49°C

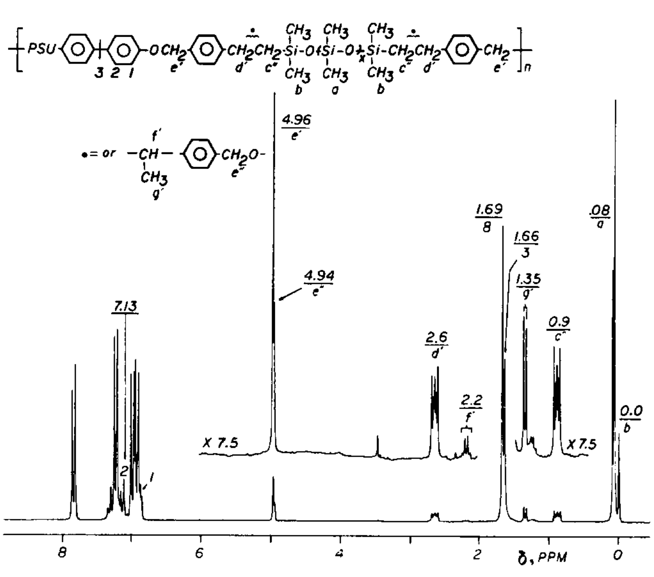


Figure 5 200 MHz ^{1}H n.m.r. spectrum of the alternating block copolymer of PSU-2-VB and PDMS-1 (sample 2, *Table 3*). Other resonances as labelled in *Figure 1*

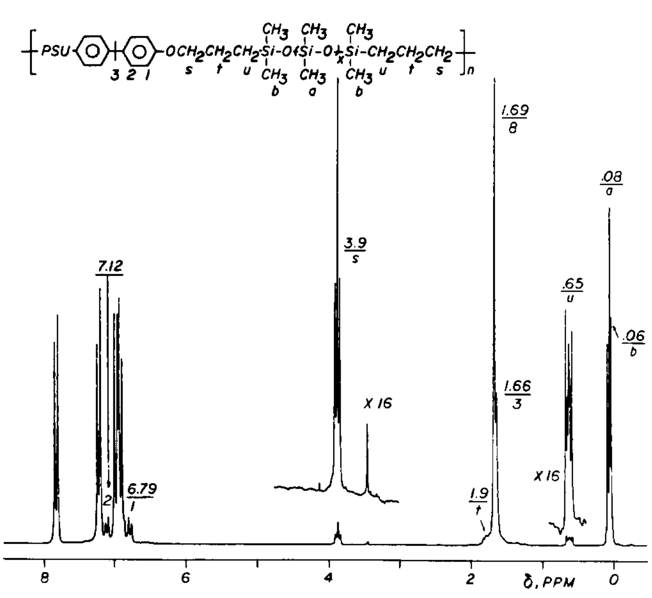


Figure 6 200 MHz ^{1}H n.m.r. spectrum of the alternating block copolymer of PSU-3-AE and PDMS-1 (sample 3, *Table 3*)

analysis also revealed no trace of the ≡Si–H absorption at ≈2130 cm^{-1}. Additionally, the signals of the PSU vinylbenzyl end groups (j, k, l, m; *Figure 2*) have now completely disappeared and only the signals e' and e'' (aliphatic benzyl ether protons from the reacted groups) remain in this region. In *Figure 6*, the complete disappearance of the ≡Si–H (signal c, *Figure 4*) and the complete upfield shift of signal b (compare with *Figure 4*) are observed, as in *Figure 5*, along with the absence of the 2130 cm^{-1} band in i.r. The change in signal b is somewhat different in this case due to the difference in the PSU end groups. Contrary to hydrosilylation of vinylbenzyl groups, ≡Si–H addition to allylether groups showed only anti-Markovnikov addition[27] (signals t, u, *Figure 6*). No evidence of Markovnikov addition was seen in the ^{1}H n.m.r. spectra of block copolymers produced from PSU-AE. The signal o (doublet, *Figure 3*) from the precursor PSU-AE is also completely absent and these protons now appear upfield in the block copolymer (signal s, triplet, *Figure 6*). The small signal at ≈3.5 ppm in both *Figures 5* and *6* was not assigned.

The block copolymerization was performed under similar conditions to those described for 'triblocks'[18], i.e. the reaction was performed initially in homogeneous solution by dilution with the necessary amounts of solvent, and then excess solvent was removed while maintaining homogeneity as the reaction progressed. The amount of chlorobenzene necessary to obtain a homogeneous solution for 1 g total of the precursors is given in *Table 3* for each block copolymerization. This amount increased with the molecular weight of the precursors. As reaction proceeded, less and less solvent was required to maintain homogeneity and therefore the excess could be removed. By this method, it was possible to concentrate the reaction mixture to 1 g of polymer in 2–3 ml of solvent, and still obtain an optically clear solution. Further concentration was limited by the solution's viscosity and the maintenance of adequate stirring.

This dilution–concentration method was chosen because it seems that homogeneity is necessary for attainment of high degrees of conversion. Although it was shown[9] that typically high concentrations are necessary for high degrees of conversion in Pt-catalysed hydrosilylation, the PSU–PDMS system did not attain homogeneity with reaction time in concentrated solution, unlike PS–PDMS[10], except when the precursor molecular weights were very low. This is likely to be due to an even higher incompatibility of PSU–PDMS than of PS–PDMS and may also be affected by the polydisperse character of the PSU (compared to the monodisperse nature of the PS in Reference 10). It was stated[10] for the PS–PDMS system that homogenization occurred because, as some block copolymer was formed, it acted as a compatibilizer for the homopolymers, thus furthering the reaction. Inoue *et al.*[28] postulated that the compatibilizing ability of a copolymer with regard to its corresponding homopolymers is prevalent when the molecular weight of the copolymer segment is equal to or higher than that of the corresponding homopolymer. It can therefore be expected that polydisperse precursors would behave differently from monodisperse ones in this type of two-phase immiscible system, especially since the incompatibility increases with increasing molecular weight of the precursors[18]. Since the PSU–PDMS system did not seem adaptable to the high concentration systems in References 10 or 12, the dilution–concentration method was developed. This method allowed compatibilization by initial dilution in a common solvent, as well as the final high concentrations believed necessary for high conversions[9].

To illustrate the preceding discussion, several reactions were performed in initially concentrated two-phase immiscible solutions (1 g polymer in 2 ml ClBz) and, despite long reaction times, the reaction mixtures never achieved homogeneity, and incomplete conversions were realized. *Figures 7* and *8* show ^{1}H n.m.r. evidence of this observation for block copolymers produced from both PSU-VB and PSU-AE, respectively. In *Figure 7*, a 1/1 mole/mole reaction of PSU-4-VB ($\bar{M}_n = 3800$ by v.p.o.) and PDMS-2 ($\bar{M}_n = 1200$ by v.p.o.) showed only 76% conversion of the PSU vinylbenzyl end groups (signals j, k, l) when performed in concentrated solution (*Figure 7a*), but complete conversion when the dilution–concentration method was used (*Figure 7b*). Similar results were obtained for block copolymers prepared from PSU-4-AE ($\bar{M}_n = 4400$ by v.p.o.) and PDMS-4 ($\bar{M}_n = 3500$ by v.p.o.), as shown in *Figure 8*. The initially concentrated reaction mixture never achieved homogeneity, even after several days of reaction, and showed a vinyl conversion of only 80% (*Figure 8a*, compare signals o and s). With initial dilution and solvent removal under similar conditions, the degree of vinyl conversion increased to 93% (*Figure 8b*), and the reaction mixture remained homogeneous even to high concentrations (1 g polymer in 2 ml solvent). Because of the inherent error in molecular weight determinations[18], it was usually necessary to vary the relative amounts of the precursors away from stoichiometry as determined by v.p.o. $\bar{M}_n$. Increasing the PDMS/PSU ratio by an additional 5 mol% in this system led to complete vinyl conversion (*Figure 8c*) and the highest degrees of chain extension as determined by g.p.c. The dilution–concentration method was therefore chosen because it allowed the highest degrees of conversion. Although it may also be feasible to use the incremental addition technique described elsewhere[5], this technique seemed impractical for the small quantities used here.

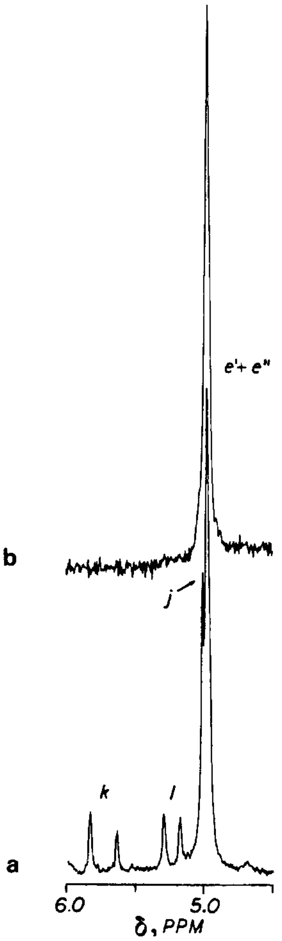


Figure 7 90 MHz ^{1}H n.m.r. spectra of alternating block copolymers of PSU-4-VB and PDMS-2: (a) 1/1 molar ratio PSU/PDMS, initial concentration 1 g polymer in 2 ml ClBz, no solvent removal; (b) 1/1 molar ratio PSU/PDMS, initial concentration 1 g polymer in 6 ml ClBz, solvent removal during reaction (sample 6, *Table 3*). Other reaction conditions as given in *Table 3*. Resonances as labelled in *Figures 2* and *5*

The use of *FT*n.m.r., in which a large number of scans are possible, and therefore large vertical scale expansions with good signal to noise ratio, allowed a reasonably accurate determination of the amount of unreacted versus reacted vinyl groups (as in *Figures 7* and *8*). *FT*n.m.r. was therefore used to vary the stoichiometry based on the measured amounts of unreacted vinyl groups which result from errors in molecular weight determinations and/or

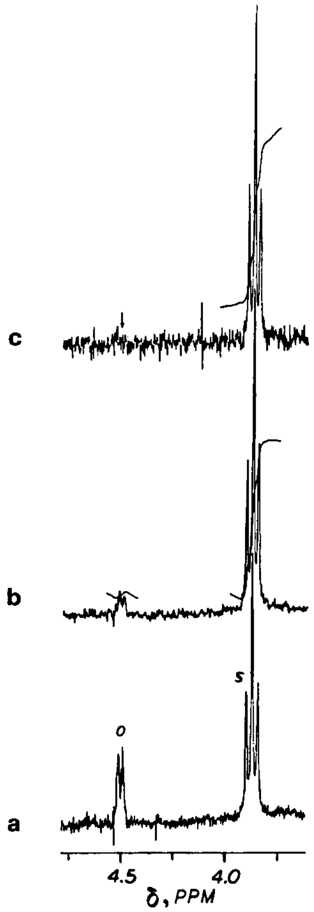


Figure 8 250 MHz ^1H n.m.r. spectra of alternating block copolymers of PSU-4-AE and PDMS-4: (a) 1/1.15 molar ratio PSU/PDMS, initial concentration 1 g polymer in 2 ml ClBz, no solvent removal; (b) 1/1.15 molar ratio PSU/PDMS, initial concentration 1 g polymer in 9 ml ClBz, solvent removal during reaction; (c) as (b) except molar ratio PSU/PDMS = 1/1.2 (sample 10, *Table 3*). Other reaction conditions as given in *Table 3*. Resonances as labelled in *Figures 3* and *6*

some consumption of ≡Si–H by side reactions. The ratios of the precursor polymers necessary for complete vinyl conversion for each block are listed in *Table 3*. Use of the dilution–concentration method to maximize conversion and *FT*n.m.r. to optimize the system stoichiometry resulted in complete vinyl conversions (within the detection limits of *FT*n.m.r. instruments) and the highest degrees of chain extension for all the blocks listed in *Table 3*.

Because the stoichiometry for the system was varied to obtain complete vinyl conversion, it can be speculated that there is an excess of ≡Si–H groups in these block copolymers. *FT*n.m.r. analysis, however, showed no evidence (within the detection limits of the instruments) of unreacted ≡Si–H, even with large numbers of scans and large vertical scale expansions. This signal, of course, is more difficult to see than the vinyl end groups of PSU because it is split into a heptet; further, excesses of ≡Si–H groups may be consumed by side reactions with reaction time. In any case, no evidence of unreacted ≡Si–H was found in any of the block copolymers listed in *Table 3*.

Table 3 lists the temperature employed in each block copolymerization. Based on other work[10,12], the hydrosilylation reaction was typically performed at high temperature (≈ 100–120°C). For reaction of PSU-VB with PDMS, higher temperatures proved to be necessary. In this case, the reaction proceeded well at 100°C and no polymerization of the vinylbenzyl groups was noted when inhibited with hydroquinone. For reaction with PSU-AE, although temperatures of 120°C were initially employed, good reaction rates were obtained even at room temperature. *Figure 9* compares the change in M_i (g.p.c. peak maximum) as a function of reaction time for the block copolymerization of PSU-3-VB, -AE with PDMS-1 under different conditions. At room temperature, with or without inhibitor, reaction of PSU-VB with PDMS proceeded slowly and low degrees of chain extension and incomplete conversion (61% by n.m.r.) were obtained. In this case, higher temperatures clearly seemed to be needed. On the other hand, reaction of PSU-AE with PDMS at room temperature was finished within an hour with both catalysts, showing complete conversion of allylether groups. At 120°C, this reaction was complete within 15 min and showed a somewhat higher degree of chain extension *versus* ambient reaction. When the ambient reaction was diluted three-fold, it proceeded more slowly, and although complete conversion was obtained within 2 h, the degree of chain extension was reduced compared with that obtained from concentrated solution.

The higher reactivity of the allylether chain ends than those of vinylbenzyl in this system proved to be critical in obtaining good degrees of chain extension when higher molecular weight precursors were employed. For low molecular weight pairings, hydrosilylation of the PSU-VB end groups at 100°C proved adequate to obtain complete conversions and good degrees of chain extension (e.g. samples 1–8, *Table 3*). As the molecular weight of the precursors was increased, however, conversions became incomplete and homogeneity of the reaction mixture could not always be maintained during solvent removal. Various attempts to produce block copolymer 8 (*Table 3*), for example, always showed some unreacted vinylbenzyl groups, even though the PDMS/PSU molar ratio was increased in an attempt to fully react the vinylbenzyl groups. The molar ratio given in *Table 3* gave the highest conversion; traces of vinylbenzyl groups were, however, still present in this block copolymer. The levels of incomplete conversion increased further with increasing precursor molecular weights when PSU-VB was used. Although this may not be a critical concern

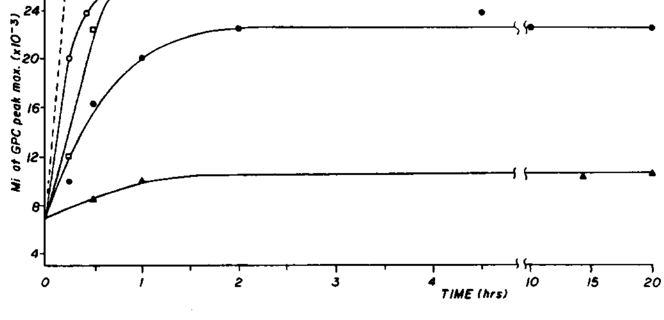


Figure 9 The effect of reaction time on the M_i at g.p.c. peak maximum (column set 1, u.v. detection) for alternating block copolymerizations of PSU-3 and PDMS-1: ■, PSU-3-AE, molar ratio PSU/PDMS = 1/1.1, $T = 120°C$, catalyst SLM 86003, $c = 1$ g polymer in 3 ml ClBz; □, as ■ except T = ambient; ○, as □ except catalyst PC072′; ●, as ○ except $c = 1$ g polymer in 9 ml ClBz; ▲, as ○ except with PSU-3-VB (molar ratio PSU/PDMS = 1/1)

where it is possible to use the remaining vinylbenzyl groups to thermally crosslink the block copolymer, it is unacceptable when high molecular thermoplastic elastomers are desired. The use of PSU-AE allowed good degrees of chain extension for all precursor molecular weight combinations tested, due to the higher reactivity of the allylether group in this system. In fact, even when the two highest molecular weight precursors were paired (PSU-6-AE and PDMS-7), complete conversion of the allylether groups and good degrees of chain extension could be obtained even at room temperature. Therefore, the use of allylether end groups was very much preferred for high molecular weight block copolymer synthesis in this system.

Although *Figure 9* indicated that reaction of PSU-3-AE and PDMS-1 at 120°C was faster and gave somewhat higher chain extension than at room temperature, the g.p.c. curves in *Figure 10* indicate that the *MWD* at 120°C changed with reaction time. *Figure 10a* shows a sample of PSU-3-AE and PDMS-1 prepared at room temperature after 28 h of reaction. The g.p.c. curve is the same as for a sample taken just after completion of this reaction (ca. 1 h). *Figure 10b,c,d* indicates, however, that at 120°C there were changes in *MWD* with reaction time. The reaction was complete in 15 min (*Figure 10b*), as determined by the absence of the PSU allylether groups in *FT*n.m.r. of this sample. With additional reaction time, however, changes in the high molecular weight end of the g.p.c. curves were readily noted (*Figure 10c,d*). The position of the peak maximum, though, remained constant throughout. Although these changes may be speculated to have been a result of some side reactions of excess PDMS $\equiv$Si–H in this case (the PSU/PDMS molar ratio here was shifted in favour of PDMS), all the blocks prepared at 100–120°C showed small humps at low elution volume even when vinyl groups were in excess. The changes in *MWD* then were likely to be the result of some side reactions of $\equiv$Si–H or the siloxane backbone caused by the Pt-catalyst[20–23] during the reaction at elevated temperature.

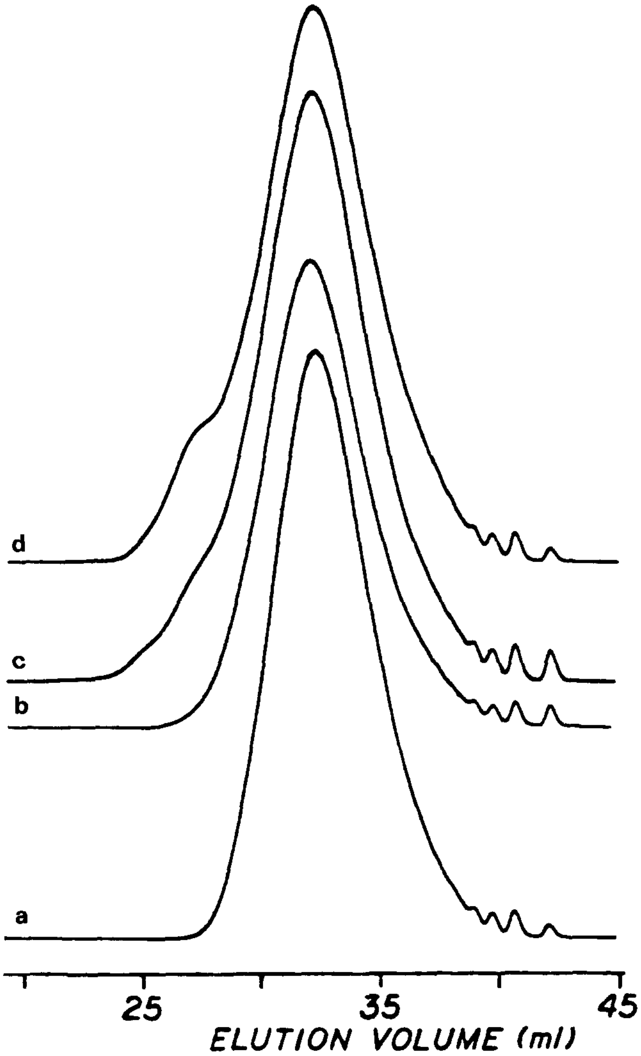


Figure 10 G.p.c. chromatograms (column set 1, u.v. detection) of: (a) block copolymer of PSU-3-AE and PDMS-1 (reaction conditions: molar ratio PSU/PDMS = 1/1.1, T = ambient, c = 1 g polymer in 3 ml ClBz; catalyst SLM 86003, time = 28 h); (b) block copolymer as in (a) except reaction T = 120°C, reaction time = 15 min; (c) as (b) except reaction time = 1.5 h; (d) as (b) except reaction time = 16.5 h

Although reaction of PSU-AE and PDMS proceeded quickly at room temperature and did not suffer from the changes in *MWD* mentioned above, solvent removal was difficult. For this reason, when solvent removal was required, elevated temperatures were needed. In addition, while reaction at 100–120°C allowed complete vinyl conversion in almost all cases (samples 1–16, *Table 3*), complete conversion could not be obtained for block copolymers of PSU-5,-6-AE and PDMS-7 at 120°C, even with substantial variations in stoichiometry. This was probably the result of side reactions or possibly deactivation of the catalyst[20–23,26,29]. Reaction at room temperature, however, did allow complete vinyl conversion, but the reaction was slower due to the difficulty in removing solvent. For this reason, the reaction in these cases was performed at 50°C. This temperature facilitated solvent removal and produced the same results as at room temperature. This reaction temperature then is considered optimum for the PSU-AE/PDMS system.

Figure 11 presents representative g.p.c. chromatograms of starting materials and the block copolymers formed from them. The as-prepared block copolymer shown in *Figure 11c* exhibited a small tail at high elution volume. This tail was composed of cyclics present in the PSU[30], which, of course, do not enter into the hydrosilylation reaction. Although these cyclics can be removed from PSU via extraction[11], they also can be easily removed after the block copolymer is formed by precipitation with a 75/25 v/v acetone/methanol mixture, leaving a pure block copolymer (*Figure 11d*). The removed fraction (*Figure 11e*), which in most cases amounted to only ≈ 5 wt% of the original block copolymer, was composed of the PSU cyclics plus some lower molecular weight block copolymer. Proton *FT*n.m.r. analysis revealed not only the presence of both precursor polymers in this fraction and the linkages between them, but also the lack of the original PSU vinyl and PDMS $\equiv$Si–H end groups. This may indicate that the lower molecular weight block copolymers in the removed fraction were cyclic in nature or had non-functional chain ends. All the block copolymers listed in *Table 3* (except sample 1) were purified of the low molecular weight tail by acetone/methanol precipitation. Block copolymer 1 was too soluble in acetone to allow this method to be used.

The degree of block copolymerization $\bar{n}$ in $(\text{PSU–PDMS})_n$ was determined for all block copolymers in *Table 3* by comparison of their g.p.c. molecular weights with the g.p.c. molecular weights of the precursors (given

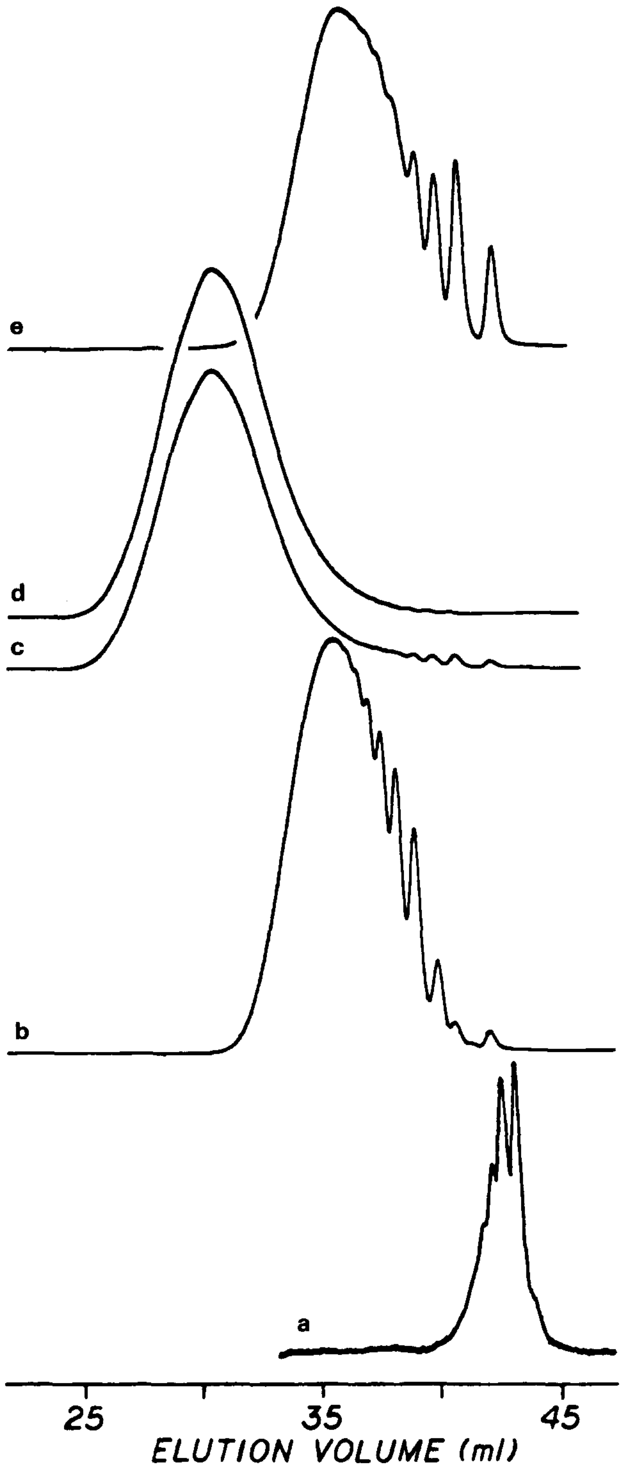


Figure 11 G.p.c. chromatograms of: (a) PDMS-1 (neat sample, THF, column set 1, r.i. detection – reverse polarity); (b) PSU-3-AE; (c) alternating block copolymer formed from PDMS-1 and PSU-3-AE, before purification; (d) block copolymer as in (c) purified by precipitation in acetone/methanol 75/25, v/v (sample 3, *Table 3*); (e) fraction removed from (c) by purification ((b)–(e) u.v. detection)

in *Tables 1* and *2*). Chain extensions of 3–5 by $\bar{M}_n$ and 3.5–5.5 by $\bar{M}_w$ were typical for the whole range of precursor molecular weights. Lower molecular weight combinations showed, as would be expected, even higher degrees of chain extension. The results are similar to those obtained by Chaumont *et al.*[10] for the PS–PDMS system, but show a large improvement in both block copolymer molecular weights and the molecular weights of the constituting precursors over the results of Gagnebien *et al.*[12] The polydispersity ($\bar{M}_w/\bar{M}_n$) of the block copolymers was always larger than the theoretical value of $\bar{M}_w/\bar{M}_n = 2$ for a step-growth polymerization. This was directly indicated in some cases by the small humps at low elution volumes in the g.p.c. curves, as in *Figure 10*. As stated earlier, this may have been a result of some side reactions[20–23], or possibly is inherent in the nature of Pt-catalysed hydrosilylation[26]. In any case, similar results were obtained for the PS–PDMS system[10].

Since g.p.c. is only a relative method, especially in the case of block copolymers, several block copolymers were characterized for their $\bar{M}_n$ by membrane osmometry. These results are included in *Table 3*. Comparison of the $\bar{M}_n$s of the block copolymers obtained from membrane osmometry with those of the precursors from v.p.o. allows a more quantitative assessment of the degrees of chain extension. As can be seen from *Table 3*, these values are in reasonably good agreement with those obtained from g.p.c. The values obtained also indicate that the hydrosilylation method is useful for block copolymer synthesis when the reaction is fast enough to allow high molecular weight block copolymer to be formed relatively free of competing side reactions. For PSU-AE, this method was applicable for the whole range of precursor molecular weights tested. Possible side reactions of the allylic groups[7,25,26] seemed to have little or no effect. For PSU-VB, while adequate for lower oligomer combinations, this method seemed unacceptable for higher precursor molecular weights. Due to the lower reactivity of the vinylbenzyl groups (compared to allylether) and the increasing dilution necessary as precursor molecular weight was increased, the reaction may have been slow enough to allow competing side reactions to become significant.

Table 3 lists the thermal characterization of these block copolymers by d.s.c., and some representative d.s.c. traces of starting materials and block copolymers are given in *Figure 12*. For block copolymers with the lowest molecular weight, PDMS-1, -2, no separate PDMS phase

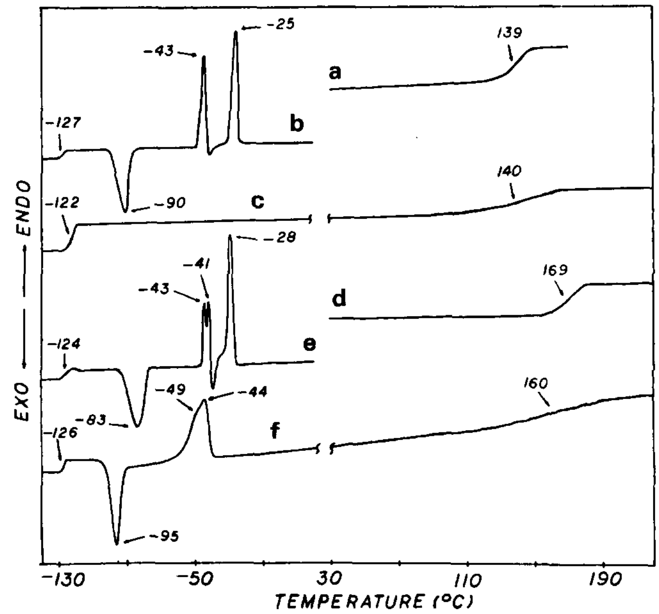


Figure 12 D.s.c. traces of: (a) PSU-3-VB; (b) PDMS-3; (c) block copolymer of PSU-3-VB and PDMS-3 (sample 8, *Table 3*); (d) PSU-6-AE; (e) PDMS-7; (f) block copolymer of PSU-6-AE and PDMS-7 (sample 18, *Table 3*)

was clearly observable in the d.s.c. (samples 1–7, *Table 3*). Only the PSU T_g was evidenced, due to the short length of the PDMS segment; however, some degree of PDMS phase separation was probably present, supported by the PSU T_g value and torsion pendulum measurements on similar 'triblocks'[19] and alternating blocks[5]. PDMS-3, of moderate molecular weight, (*Figure 12b*) showed good phase separation in all block copolymers prepared (samples 9–12), as seen by the sharp well defined T_g (see, for example, *Figure 12c*). Although PDMS-3 exhibited T_cs and T_ms (*Figure 12b*), T_c and T_m were typically absent from the block copolymers prepared from it (*Figure 12c*). Only block copolymer 12, with the highest molecular weight PSU, showed some crystallization and melting of the PDMS segment. As the molecular weight of the PDMS segment was further increased, the block copolymers (samples 13–18) always showed both T_c and T_m in addition to T_g. Although the homo-PDMSs normally exhibited two T_ms, the block copolymers usually showed only one broader melting peak in the region of T_m. For block copolymers 17 and 18, the bimodal nature of T_m, in PDMS-7 (*Figure 12e*) seemed to be carried over to the block copolymer as a shoulder on the one melting peak (*Figure 12f*). It was also noteworthy that the PSU T_gs in the block copolymers (*Figure 12c,f*) were more diffuse and extended over a broader temperature range than the rather sharp T_gs of the parent homopolymers (*Figure 12a,d*), as was observed and explained by others[31,32]. This was in contrast to the PDMS T_g which, when present in the block copolymers, was as sharp as for the homo-PDMS.

Generally, good phase separation between PSU and PDMS was obtained when the molecular weight of both blocks was >3000. For the PSU segment, the T_g was not only directly dependent on its molecular weight, i.e. continually increasing towards the high molecular weight value of $\approx 190°C$, but was also somewhat dependent on the PDMS segment that the PSU was paired with. This suggested an influence of the domain size/structure. A detailed investigation of this for PSU–PDMS alternating block copolymers was undertaken by others[32] and is not considered further here.

Mechanical properties and thermal stabilities of these PSU–PDMS block copolymers are expected to be equivalent to those reported earlier[5], the only structural difference lying in the nature of the linkages between blocks.

CONCLUSIONS

High molecular weight alternating block copolymers of PSU and PDMS were prepared by hydrosilylation of α,ω-di(vinyl)PSU with α,ω-di(silane)PDMS. Of the two α,ω-di(vinyl)PSUs prepared using PTC techniques, α,ω-di(allylether)PSU proved more suitable for alternating block copolymer synthesis. Block copolymers showing good phase separation into rubbery and glassy domains were obtained.

ACKNOWLEDGEMENTS

Generous financial support from the Sonderforschungsbereich 60 der Deutschen Forschungsgemeinschaft, NATO (travelling grant) and B. F. Goodrich are gratefully acknowledged.

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