# Thermally reactive oligomers of aromatic poly(ether sulphone) containing poly(dimethylsiloxane):
# 1. Synthesis and characterization*

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Thermally crosslinkable oligomers of aromatic poly(ether sulphone) (PSU) with incorporated poly(dimethylsiloxane) (PDMS) segments were produced via Pt-catalysed hydrosilylation of α,ω-di(silane)PDMS with α,ω-di(vinylbenzyl)PSU. A 2/1 molar ratio of PSU to PDMS was used to obtain statistically a 'triblock' copolymer with on average one PDMS segment incorporated between two PSU segments. Nuclear magnetic resonance analysis of prepared 'triblocks' revealed that the reaction could be performed without detectable side reactions of the hydrosilane end groups of the PDMS. Thermal characterization of the 'triblocks' showed the thermal transitions of both segments, both before and after curing, to be highly dependent on the molecular weight of the component segments, good phase separation being realized at relatively low molecular weights, ~3000 for both segments. Manipulation of the thermal transitions of both segments especially after cure was shown to be possible through proper choice of precursor molecular weights, or by blending of prepared 'triblocks' with varying amounts of homo-α,ω-di(vinylbenzyl)PSU. By these methods, it was possible to obtain cured PSU--PDMS-PSU 'triblocks' with PSU hard segment $T_g$ values near to 200°C and low-temperature PDMS $T_g$ values at about −120°C. Dynamic-mechanical/rheological studies were also performed on these 'triblocks', and this is the subject of the following paper.

**(Keywords: poly(ether sulphone); poly(dimethylsiloxane); synthesis; characterization)**

## INTRODUCTION

Functional polyaromatics which contain terminal or pendant groups that undergo thermally initiated crosslinking reactions without evolving volatile by-products are considered good candidates for matrix resins in high-performance composites. This is due to their good thermal stability and high glass transition temperatures. Aromatic poly(ether sulphone) (PSU) is one such polyaromatic which is tough, thermally stable and exhibits a glass transition temperature of ~180°C. Much work in the past has been performed which attached terminal or pendant ethynylphenyl (phenylacetylene-type) groups onto polysulphone[1,2]. In our laboratory, we prepared polysulphone oligomers containing terminal or pendant vinylbenzyl (styrene-type) groups[3,4]. This new class of thermally reactive oligomers exhibited a fast curing reaction when compared to its phenylacetylene counterpart, and proved to be a viable alternative in the reactive oligomer area.

Often, highly crosslinked networks tend to be brittle, so that we extended our work with α,ω-di(vinylbenzyl)PSU and sought to incorporate rubbery, thermally stable poly(dimethylsiloxane) (PDMS) segments into our PSU reactive oligomers. Because of the drastic incompatibility of these two polymers[5], phase separation into rubbery and glassy domains could be realized, which would give the desired properties of both polymers to the network. Ideally, the high $T_g$ and modulus of PSU would be maintained while the impact resistance of rubbery PDMS domains would be added. Incorporation of PDMS would not, however, jeopardize the thermal stability of the network, by virtue of its well known thermal resistance. Additionally, the very low glass transition temperature (~ −120°C) of PDMS would lend a very broad useful temperature range to the network.

In previous work[3,6–10], we have shown that phase transfer catalysis (PTC) can be exploited for the preparation of α,ω-difunctional telechelics from α,ω-di(hydroxyphenyl) polymers. It was shown that quantitative etherification of the hydroxyphenyl-terminated polymers could be realized with electrophilic monomers of the halobenzylic, haloallylic and bromoalkyl types using tetrabutylammonium hydrogen

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* Dedicated to Professor Dr Karl Hamann on the occasion of his 80th birthday.

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sulphate as phase transfer catalyst. This method readily yielded clean, bifunctional telechelics. In this work, this method was used to prepare α,ω-di(vinylbenzyl)PSU (the PSU reactive oligomers mentioned above)[3] by reaction of α,ω-di(hydroxyphenyl)PSU with *p*-chloromethylstyrene. These functionalized PSUs contain, as mentioned, terminal vinylbenzyl (styrene-type) groups which enable the oligomer to be thermally crosslinked.

By virtue of their end-standing vinyl functions, these styrene-terminated PSUs can be coupled with PDMS containing end-standing silane ($\equiv$Si–H) functions via hydrosilylation. This reaction, which involves the addition of $\equiv$Si–H across double bonds, is well known in the literature[11-14] and has been used to prepare block[5,15-18], graft[19-21] and network[22-26] polymers. Many different types of olefinic double bonds have been shown to be reactive towards hydrosilylation[11], and styrene has been shown[27,28] to have good reactivity and high yields in hydrosilylation reactions. The reaction is typically effected by the use of a platinum catalyst, and leads to Si–C linkages between antagonist functions which are known to be hydrolytically stable *versus* Si–O–C type linkages[15]. Although this reaction is not free of side reactions[25,26,29-31] which consume $\equiv$Si–H and thereby may limit its use in obtaining very high molecular weight block copolymers (stoichiometry considerations), it can be considered of practical use in cases where the side reactions are much slower than the addition reaction, as is often the case. In addition, it should be noted that the extreme incompatibility of these two polymers, although essential for the desired properties, also makes the coupling reaction particularly difficult because of phase separation even in solution[5]. This is especially true with Pt-catalysed hydrosilylation reactions in which high solution concentrations are typically required to obtain high conversions[32].

In our research, we exploited the hydrosilylation reaction to form linkages between α,ω-di(silane)PDMS and α,ω-di(vinylbenzyl)PSU. The work described here and elsewhere[33] concerns reaction between α,ω-di(vinylbenzyl)PSU and α,ω-di(silane)PDMS oligomers employing a 2/1 PSU to PDMS excess. This yields the reactive oligomers of PSU with incorporated PDMS blocks. Statistically, a 'triblock' copolymer is formed with, on average, one PDMS block incorporated between two PSU blocks, the chain end being of the reactive vinylbenzyl type. These thermally crosslinkable 'triblocks' were characterized by n.m.r., g.p.c., v.p.o., d.s.c. and torsion pendulum measurements. Further extensive rheological characterization of α,ω-di(vinylbenzyl)PSU and these 'triblocks' was performed and is the subject of the following paper. Additional work concerning the formation of alternating block copolymers from stoichiometric amounts of α,ω-di(vinylbenzyl)PSU or α,ω-di(allyl ether)PSU (produced via PTC etherification of α,ω-di(hydroxyphenyl)PSU with allyl bromide) and α,ω-di(silane)PDMS was also undertaken and will be presented in a subsequent publication[18].

## 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 no. 1) or Wacker Chemie, W. Germany (all others) and were used as received. *p*-Chloromethylstyrene (*p*-ClMS) was prepared and isolated according to Kondo *et al.*[34] Chlorobenzene (ClBz, Aldrich) for use in hydrosilylation reactions was dried with $P_2O_5$ 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 prior to use. The platinum catalyst was either $H_2PtCl_6 \cdot 6H_2O$ (Merck) used as a 0.05 M solution in propan-2-ol or an organic platinum compound obtained from Wacker Chemie (no. SLM-86003, data undisclosed). All other solvents and reagents (Aldrich) were reagent-grade materials and were used as received.

### *Techniques*

Number average molecular weights of the precursor oligomers were determined by $^1$H n.m.r., vapour-pressure osmometry (v.p.o.) and gel permeation chromatography (g.p.c.). Proton n.m.r. spectra were obtained from Varian XL-200 or Bruker WH-90 *FT*-n.m.r. instruments with $CDCl_3$ as solvent and TMS as internal standard. V.p.o. measurements were performed using Wescan 233 or Perkin–Elmer 115 instruments ($CHCl_3$ as solvent, 36°C). G.p.c. was performed with PL Gel columns of $10^5$, $10^4$, $10^3$, $5\times10^2$ and $10^2$ Å (column set no. 1) or $10^6$, $10^5$, $10^4$ and $10^3$ Å (column set no. 2) using THF (for PSU and blocks) or toluene (for PDMS) as the mobile phase at a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$. 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 achieved via Perkin–Elmer DSC-2 or DSC-7 instruments at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. Temperature calibration was performed with various thermal standards (e.g. Hg, Ga, In, Sn). Infra-red spectra were measured by a Perkin–Elmer 1330 instrument via thin films on KBr discs. Torsion pendulum measurements were performed on a Lonza apparatus on melt pressed samples of 25 mm length, 5.0 mm width and 0.7–1.0 mm thickness.

### *Synthesis of α,ω-di(hydroxyphenyl)PSU*

These oligomers with molecular weights in the range 1200–7000 were prepared in the conventional literature manner (samples 1–5) by condensing excess disodium salt of BPA with DCDPS in anhydrous DMSO, or by the *N,N'*-dimethylacetamide (DMAC)/$K_2CO_3$ method (sample 6) described by Viswanathan *et al.*[35] The excess of BPA to DCDPS was varied in order to obtain the desired molecular weights. Purification was performed by precipitation of the reaction mixture after filtration into acidified water followed by thorough drying. Two further purifications were undertaken by precipitation of chloroform solutions into slightly acidified (HCl) methanol.

### *Synthesis of α,ω-di(vinylbenzyl)PSU*

A typical synthesis is illustrated by the following example. Ten grams ($\bar{M}_n = 2000$ by v.p.o., $5.0\times10^{-3}$ moles, $1.0\times10^{-2}$ moles –OH groups) α,ω-di(hydroxylphenyl)PSU-2 were dissolved in 50 ml of ClBz. To this stirring solution, 3.3 g ($9.7\times10^{-3}$ moles) tetrabutylammonium hydrogen sulphate (TBAH) and 3.1 g ($2.0\times10^{-2}$ moles) of *p*-ClMS were added. The mixture was stirred for several minutes at room temperature, and then 4.0 g ($1.0 \times 10^{-1}$ moles) of NaOH in a 12.5 N aqueous solution were slowly added under vigorous stirring. During the NaOH addition, the colour changed from pale yellow to dark blue, but slowly changed to green and then again to yellow as the reaction proceeded. After approximately one hour, the colour had changed back to nearly its original shade, where it remained. As noted previously[3], n.m.r. analysis showed the reaction to be complete at this point, but the reaction was allowed to proceed for several more hours at room temperature in order to ensure complete conversion. After the reaction, the organic layer was separated from the aqueous, washed several times with dilute aqueous HCl, and then with distilled water. The organic phase was then diluted with chloroform, dried with sodium sulphate, and precipitated into slightly acidified (HCl) methanol. Two further purifications were performed by dissolution of the polymer in chloroform, filtration of the solution when necessary, and then precipitation in slightly acidified (HCl) methanol. The polymer was dried at room temperature under vacuum to constant weight. Recovered polymer yields were normally $>90\%$ except in the case of PSU-1 (81%), where lower molecular weight oligomers were lost during the repeated precipitations.

### *Synthesis of α,ω-di(chlorobenzyl)PDMS*

A typical synthesis is described as follows. Ten grams of α,ω-di(silane)PDMS-1 ($\bar{M}_n = 540$ by v.p.o., $1.85 \times 10^{-2}$ moles, $3.7 \times 10^{-2}$ moles ≡Si–H groups) were dissolved in 100 ml ClBz along with 7.0 g *p*-ClMS ($4.6 \times 10^{-2}$ moles) and 0.242 g ($2.2 \times 10^{-3}$ moles) hydroquinone (as inhibitor). The reaction mixture was purged well with nitrogen and then 0.7 ml of the hexachloroplatinic acid solution was added. The solution was further purged with nitrogen and then heated to 80°C under brisk stirring. The reaction was allowed to proceed for 2 h. After cooling, ClBz was removed via a rotary evaporator under reduced pressure. The remaining fluid was diluted with petroleum ether (30–60°C) and washed several times with distilled water in order to remove platinic acid residues and hydroquinone. It was then washed several times with DMSO to remove the excess *p*-ClMS, and then again with water. The petroleum ether solution was then dried with sodium sulphate, and petroleum ether was stripped away in a rotary evaporator. The product was a pale yellow viscous fluid, obtained in 81% yield (theor. $\bar{M}_n = 845$, v.p.o. $\bar{M}_n = 900$, *n.m.r.* $\bar{M}_n = 860$).

### *Synthesis of PSU with incorporated PDMS segments*

*Method A.* One gram total of α,ω-di(vinylbenzyl)PSU and α,ω-di(silane)PDMS in a 2/1 PSU to PDMS mole/mole ratio (based on their v.p.o. $\bar{M}_n$) along with a small amount of hydroquinone (10 mol% of vinyl groups as inhibitor) was dissolved in 3 ml of ClBz. The solution, which was often inhomogeneous owing to oligomer incompatibility, was purged well with nitrogen and then one drop (~0.02 ml) of the chloroplatinic acid solution was added. The solution was further purged with nitrogen and then quickly heated to 80–100°C under stirring. Often, the reaction mixture became homogeneous with reaction as the temperature was raised (clearing occurred normally in the 60–70°C range). In some cases, however, the reaction mixture did not clear even after long reaction times. Normally, the reaction was allowed to proceed at 80–100°C for several hours under nitrogen. After cooling, the reaction mixture was diluted with chloroform, and then precipitated into methanol. A further purification was performed by dissolution of the polymer in chloroform, filtration of the solution, and precipitation into slightly acidified (HCl) methanol. The polymer was dried under vacuum at room temperature.

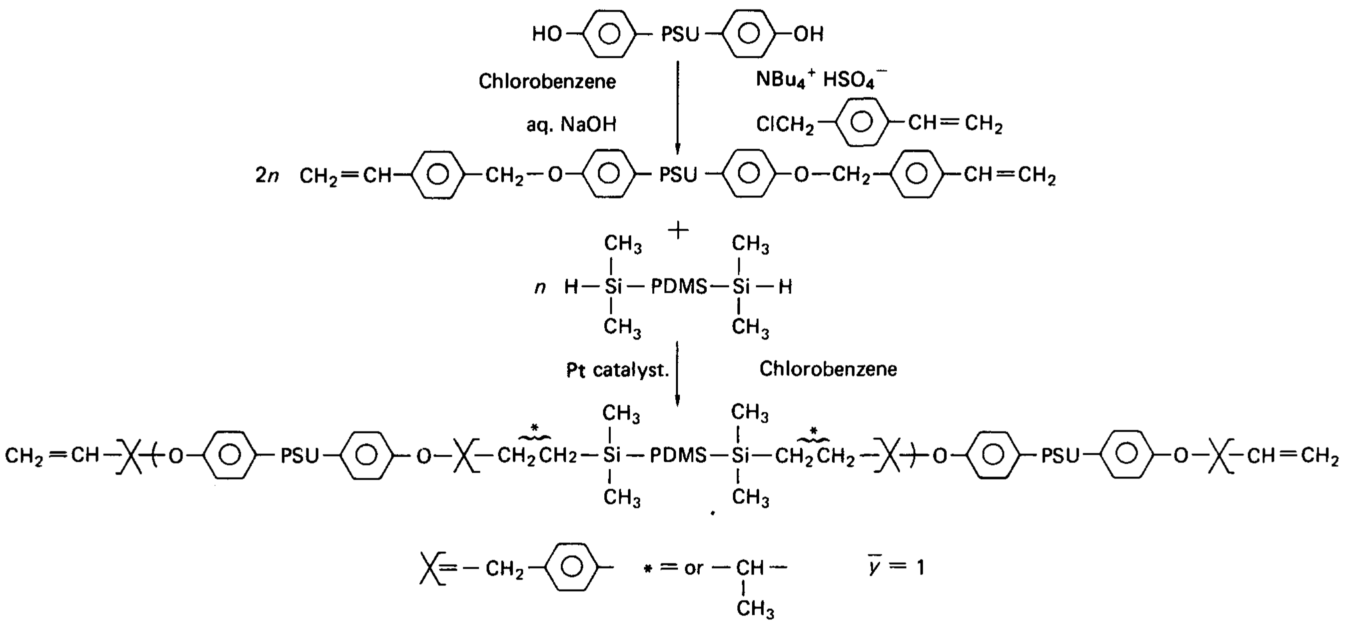
*Method B.* One gram total of the parent oligomers and hydroquinone (as in method A) were dissolved in 2 ml of ClBz. The reaction mixture was heated to 100°C. Often the reaction mixture was inhomogeneous at the start, and remained so even at 100°C, so that just enough ClBz was added to obtain an optically clear solution. After further purging with nitrogen, one drop (~0.02 ml) of the Wacker catalyst solution was added under vigorous stirring. The reaction mixture was then sparged vigorously with nitrogen at such a rate as to remove the excess solvent as quickly as possible while maintaining homogeneity. The solution was concentrated to 1 g of polymer in 1.5–2.0 ml ClBz, the point at which easy stirring started to become hampered by the solution's viscosity. The flow of nitrogen was stopped at this point, the reaction vessel sealed and the reaction allowed to proceed for several hours at 100°C. Purification and drying of the polymer was performed as in method A.

## RESULTS AND DISCUSSION

The reaction pathway for the synthesis of 'triblock' copolymers of PSU and PDMS is outlined in *Scheme 1*. The conventional synthesis of α,ω-di(hydroxyphenyl)PSU when performed properly is well known[36] to give only phenol- (hydroxyphenyl-) terminated telechelics when BPA is used in excess *versus* DCDPS. These phenol-terminated telechelics were subjected to phase transfer catalysed Williamson etherification with *p*-ClMS in the presence of TBAH as phase transfer catalyst. This method has been shown previously by us[3] to yield quantitative etherification of the PSU phenol chain ends and gives α,ω-di(vinylbenzyl)PSU. In previous work[3,4], we used a commercial mixture of ClMS (60% *meta*, 40% *para*). For this work, however, we used only the *para* isomer in order to avoid differences in isomeric reactivity in both the curing and hydrosilylation reactions.

Typical 200 MHz proton n.m.r. spectra for α,ω-di(hydroxyphenyl)- and α,ω-di(vinylbenzyl)PSU are presented in *Figures 1* and *2*, respectively, together with proton assignments. These spectra provide evidence of the complete etherification of α,ω-di(hydroxyphenyl)PSU with *p*-ClMS as was previously shown[3]. In addition to the complete disappearance of the –OH signal (*Figure 1*) evidenced in *Figure 2*, as well as in the i.r. spectra (not shown here, but given in ref. 3), of the etherified polymer, the quantitative downfield shifts of signals 1, 2 and 3 belonging to terminal BPA units are clearly seen after etherification. Contrary to what was noted before[3], the signal 3 does not shift to the downfield side of signal 8 (1.69 ppm), but does exhibit a downfield shift from 1.64 to 1.66 ppm after etherification. Also evidenced in *Figure 2* are the signals of the terminal vinylbenzyl ether (*Figure* 2, signals j, k, l, m, n, n') groups added via etherification.

*Table 1* presents the molecular weight and thermal characterization of a series of α,ω-di(vinylbenzyl)PSU



Scheme 1

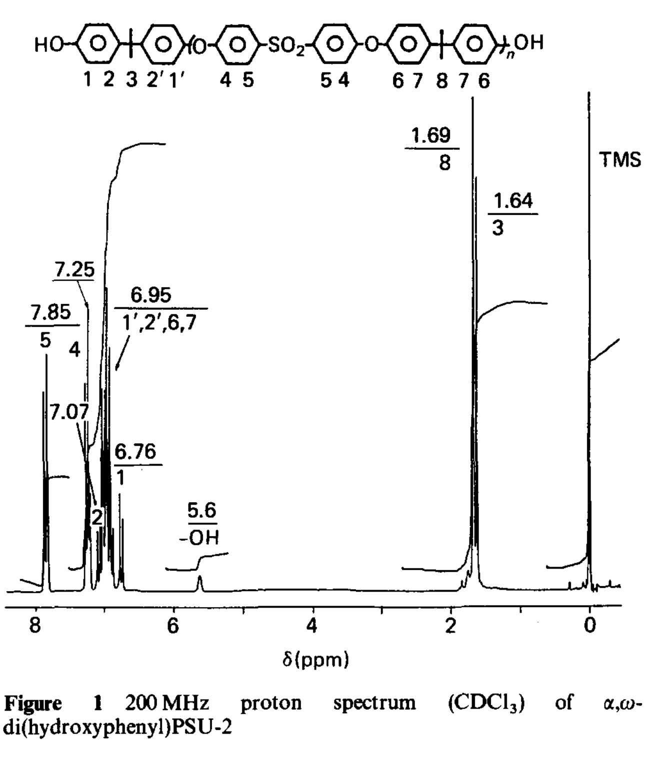


**Figure 1** 200 MHz proton spectrum ($CDCl_3$) of α,ω-di(hydroxyphenyl)PSU-2

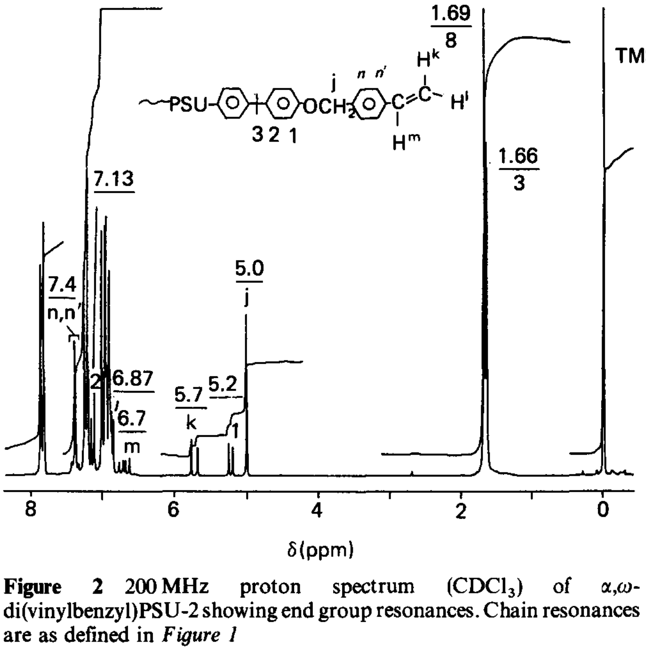


**Figure 2** 200 MHz proton spectrum ($CDCl_3$) of α,ω-di(vinylbenzyl)PSU-2 showing end group resonances. Chain resonances are as defined in *Figure 1*

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

| | $\bar{M}_n$ | | | G.p.c. | | | Thermal transitions (°C/K) | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Theor.[a] | V.p.o. | N.m.r. | $\bar{M}_n$ | $\bar{M}_w$ | *PD* | $T_g^i$ | $T_g^f$ | $T_g^f - T_g^i$ |
| 1 | 830 | 1200 | 1300 | 1250 | 1750 | 1.4 | 75/348 | 213/486 | 138 |
| 2 | 1500 | 2100 | 2500 | 2700 | 3500 | 1.3 | 113/386 | 201/474 | 88 |
| 3 | 3100 | 3200 | 3900 | 4400 | 8100 | 1.8 | 139/412 | 190/463 | 51 |
| 4 | 4100 | 3800 | 5200 | 5500 | 11000 | 2.0 | 147/420 | 190/463 | 43 |
| 5 | 6200 | 5600 | 7500 | 7400 | 17000 | 2.3 | 162/435 | 187/460 | 25 |
| 6 | 8200 | 6900 | 10200 | 10000 | 21000 | 2.1 | 167/440 | 187/460 | 20 |

[a] Based on mole ratio of BPA to DCDPS and including end groups

oligomers. The agreement between the v.p.o. $\bar{M}_n$ and that expected from theoretical calculations is generally good, indicating good functionality. PSU samples 1 and 2 show values for $\bar{M}_n$ that are higher than theoretical because unreacted BPA, which is expected to be in significant amounts in the unpurified α,ω-di(hydroxyphenyl)PSU (and is part of the theoretical calculation), is lost by precipitation of α,ω-di(hydroxyphenyl)PSU with methanol. Additionally, small amounts of lower molecular weight species present in both hydroxy-terminated and functionalized PSU are lost by the repeated precipitations in methanol. For the lower molecular weight oligomers (nos. 1 and 2), however, the agreement between v.p.o. $\bar{M}_n$ and n.m.r. $\bar{M}_n$ (determined from the end group vs. internal resonances) is good, indicating their good functionality. The n.m.r. $\bar{M}_n$ was determined via the relationships:

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

where *DP* corresponds to the repeat unit. Thus

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

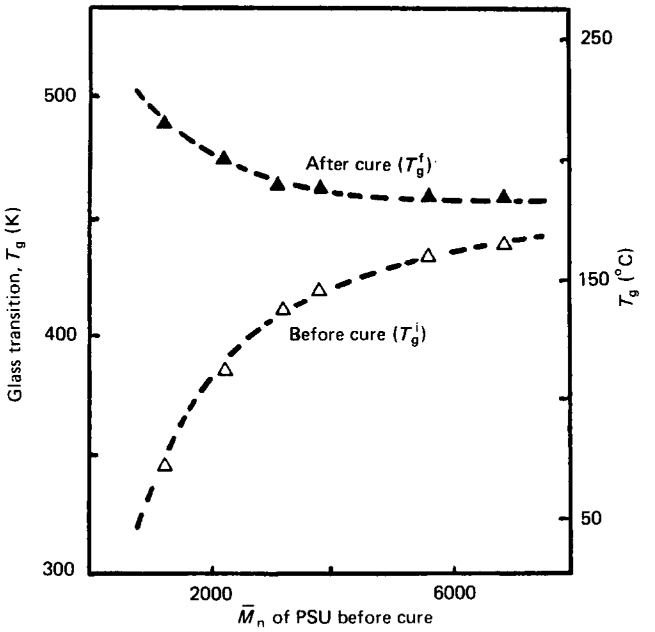


**Figure 3** Dependence of the glass transition temperature ($T_g$) of α,ω-di(vinylbenzyl)PSU before and after cure on pre-cure oligomer molecular weight

For higher molecular weights, error in the n.m.r. integrals for the end groups due to their low concentration, as well as the presence of small amounts of low molecular weight cyclics[37] which contain no end groups, skew the values increasingly higher. G.p.c. values are based on polystyrene calibration, and thus, although only qualitative, they do show the same molecular weight trend as indicated by v.p.o. and n.m.r. results. Initial $T_g$ values also show the expected increasing trend with increasing molecular weight. This is evidenced in *Figure 3*. As was also expected from previous results[3], the $T_g$ after curing shows a decreasing trend with increasing molecular weight. This is, of course, due to the crosslink density. With a low initial molecular weight, the crosslink density of the formed network is high and the $T_g$ is in excess of 200°C. With increasing oligomer molecular weight, the network crosslink density is lowered and the final $T_g$ approaches that of conventional, uncrosslinked, high molecular weight PSU (*Figure 3*). Typical d.s.c. traces are presented in *Figures 8b–d*. The thermal values in *Table 1* are also listed in kelvin for referencing with our succeeding article.

The α,ω-di(silane)PDMSs obtained commercially were characterized by v.p.o., g.p.c., n.m.r. and d.s.c. measurements. Results are presented in *Table 2*. The g.p.c. measurements of $\bar{M}_n$, while only qualitative, show good agreement with those obtained from v.p.o. D.s.c. analysis of these oligomers which are polydisperse show, in addition to $T_g$, crystallization ($T_c$) and two melting transitions ($T_{m1}$, $T_{m2}$) for all samples except no. 1. These data are in good general agreement with those of Clarson *et al.*[38] obtained for monodisperse samples. A typical d.s.c. trace is presented in *Figure 8a*.

A 200 MHz proton n.m.r. spectrum for α,ω-di(silane)PDMS is presented in *Figure 4*. This spectrum indicates the resonances of internal $-CH_3$ protons (signal a, 0.08 ppm), which appear generally as a singlet; those of terminal $-CH_3$ protons (signal b, 0.16 ppm), which appear as a doublet due to coupling with the ≡Si–H proton, and are shifted downfield *versus* internal protons; and those of the terminal ≡Si–H protons (signal c, 4.63 ppm) which appear as a septet due to coupling with the six terminal $-CH_3$ protons. Comparison of the integrals of ≡Si–H protons to $CH_3$ protons, at least for low molecular weights where the integral error is low, allows the $\bar{M}_n$ to be determined via the equation:

$$DP=X=[(A_{a+b}/6)/(A_c/2)]-2$$

and

$$\bar{M}_n=DP[MW(\text{repeat})]+MW(\text{end groups})$$

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

| Sample | V.p.o. $\bar{M}_n$ | G.p.c. $\bar{M}_n$ | G.p.c. $\bar{M}_w$ | G.p.c. *PD* | Thermal transitions (°C) $T_g$ | $T_c$ | $T_{m1}$ | $T_{m2}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 540[a] | 430 | 530 | 1.23 | −146 | – | – | – |
| 2 | 1200[b] | 1080 | 1800 | 1.67 | −135 | −101 | −51[c] | −33 |
| 3 | 3400 | 3300 | 7400 | 2.24 | −127 | −90 | −43 | −25 |
| 4 | 3500 | 3800 | 8200 | 2.16 | −128 | −96 | −47 | −27[c] |
| 5 | 5500 | 5500 | 12800 | 2.33 | −127 | −91 | −46 | −28[c] |
| 6 | 5600 | 5000 | 12400 | 2.48 | −126 | −86 | −42 | −26[c] |
| 7 | 11000 | 11400 | 29300 | 2.57 | −124 | −83 | −42[d] | −28[c] |

[a] $\bar{M}_n$ (n.m.r.) = 550. [b] $\bar{M}_n$ (n.m.r.) = 1370. [c] Indicates major melting transition. [d] Bimodal

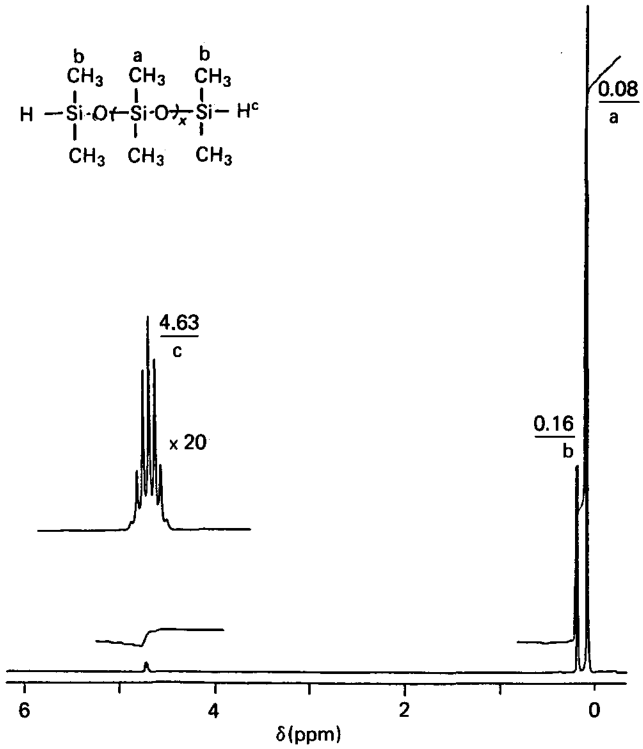


**Figure 4** 200 MHz proton spectrum ($CDCl_3$) of α,ω-di(silane)PDMS-1

The $\bar{M}_n$ of sample 1 determined by n.m.r. shows excellent agreement with that obtained from v.p.o. (*Table 2*), indicating good functionality. Sample 2 also shows good agreement between v.p.o. and n.m.r. results. The higher molecular weight samples, however, do not allow a n.m.r. $\bar{M}_n$ to be determined due to the extremely low intensity of the Si–H integral compared with that of the $CH_3$ protons.

As a model for the reaction between α,ω-di(vinylbenzyl)PSU and α,ω-di(silane)PDMS and additionally to synthesize an α,ω-dielectrophilic PDMS, we reacted PDMS-1 with *p*-ClMS in the presence of a platinum catalyst to yield α,ω-di(chlorobenzyl)PDMS. Hydroquinone was added to prevent the polymerization of *p*-ClMS. The 200 MHz proton spectrum is presented in *Figure 5*. There are several important features to note in this spectrum. First, there are no traces of unreacted Si–H or double bonds from unreacted *p*-ClMS remaining in the product, indicating quantitative reaction and product purity, respectively. Even large vertical scale expansions revealed no evidence of these. Secondly, the signal b due to terminal $-CH_3$ protons of PDMS, which originally appeared downfield from internal $-CH_3$ protons (see *Figure 4*), is now completely shifted upfield to 0.0 ppm after reaction, and is now a singlet, again indicating complete conversion of ≡Si–H bonds to Si–C linkages. The complete disappearance of the ≡Si–H bond ($\sim 2130\,cm^{-1}$) in the i.r. spectra was also noted. Thirdly, the signals of the Si–C linkages formed appear at 0.9 ppm (signal c′) and 2.6 ppm (signal d) due to the terminal or anti-Markovnikov addition to the double bond ($\sim 70\%$) and at 1.35 ppm (signal g, doublet) and 2.2 ppm (signal f, quartet) due to Markovnikov addition. The Markovnikov convention for the ionic addition of hydrogen halides (H–X) to double bonds is applied here replacing Si for X, although, of course, the polarity of the H–Si bond is opposite to that found in H–X. The signals for the formed Si–C linkages (signals c′, d, f and g, four protons) also show the expected integral values when equated to the aromatic (signals h, h′, i and i′, four protons) and $CH_2Cl$ (signal e, two protons) signals of the end groups. These signals, when compared with those of the $CH_3$ protons of the PDMS chain, allow the $\bar{M}_n$ to be calculated via the equations:

$$DP = X = \frac{A_{a+b}/6}{A_e/4} - 2 = \frac{A_{a+b}/6}{A_{c'+d+f+g}/8} - 2 = \frac{A_{a+b}/6}{A_{h+h'+i+i'}/8} - 2$$

and

$$\bar{M}_n = DP[MW(\text{repeat})] + MW(\text{end groups})$$

For low molecular weight samples, this method can be considered accurate, and indeed for PDMS-1 where an $\bar{M}_n$ of 850 is expected after reaction, a value of 860 by n.m.r. was obtained. When this value is compared with the v.p.o. result of 900, evidence of good functionality is shown.

All the above evidence indicates that quantitative functionalization of α,ω-di(silane)PDMS with *p*-ClMS can be obtained to yield α,ω-di(chlorobenzyl)PDMS. This polymer with chlorobenzyl chain ends is an α,ω-dielectrophile that can be subjected to Williamson phase transfer catalysed etherification with α,ω-di(hydroxyphenyl) polymers (eq. PSU) to provide an alternative route to block copolymers. This method is currently under investigation by us and results will be published later.

For the synthesis of reactive oligomers of polysulphone with incorporated PDMS segments, it was generally sought to maintain as high a crosslink density as possible, as well as the desired properties of both blocks. To this end, it was desired to keep the molecular weight of both blocks low enough to minimize the distance between crosslinks, yet high enough so good phase separation could be attained. For our purposes, we chose a 2/1 excess of α,ω-di(vinylbenzyl)PSU to α,ω-di(silane)PDMS. Statistically, a 'triblock' copolymer (i.e. $\bar{y} = 1$ in *Scheme 1*) with on average one PDMS block incorporated between

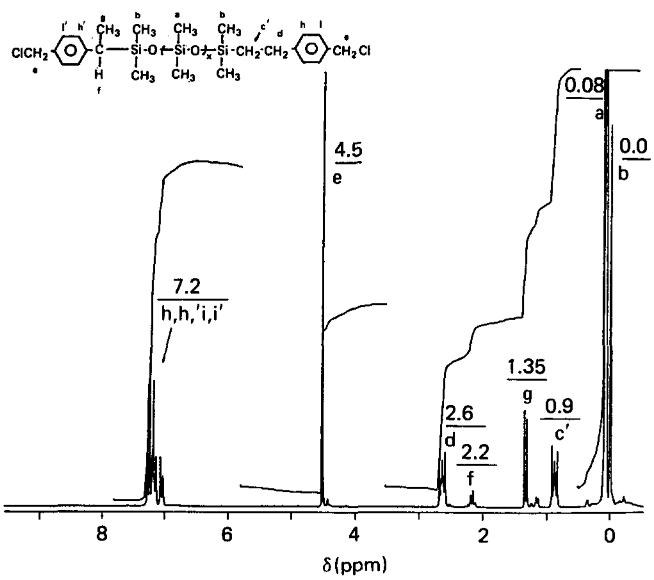


**Figure 5** 200 MHz proton spectrum ($CDCl_3$) of α,ω-di(chlorobenzyl)PDMS-1

two PSU blocks. Based on the statistical nature of the 'step' reaction, other species are also expected to be present, including higher blocks ($y=2$ or larger), unreacted PSU ($y=0$), and possibly also some cyclics. The excess of PSU to PDMS ensures, neglecting any side reactions, the complete conversion of ≡Si–H and thus only styrene-type chain ends. Of course, side reactions are known to be possible[25,26,29–31], and indeed in a blank reaction performed with PDMS-1 as described in the earlier subsection 'Synthesis of PSU with incorporated PDMS segments', however without PSU, a significant decrease in ≡Si–H was noted by n.m.r., as well as changes in molecular weight distribution by g.p.c. after 20 h of reaction at 100°C. Typically, however, these side reactions are much slower than the addition reaction. This fact was noted by Macosko and Benjamin[25], who found, in their network forming system, that in the limit of complete conversion of ≡Si–H to products 5–10% of the ≡Si–H was consumed by side reactions. This is in a system in which the mobility becomes very seriously hampered with conversion due to network formation. In our system, with the good reactivity of styrene towards hydrosilylation, the 2/1 excess of styrene to ≡Si–H, and the good mobility of the end groups in solution, the side reactions are expected to be much lower.

Another possible side reaction in this system is the premature polymerization of the styrene end goups of the PSU. Styrene, of course, polymerizes readily and must be inhibited with free radical inhibitors. During the hydrosilylation reactions, the polymerization of the PSU styrene ends was inhibited by hydroquinone. To ensure that the PSU end groups were not consumed by polymerization during the hydrosilylation reaction, a blank reaction was performed with PSU-1 under similar conditions as described in the earlier subsection mentioned in the previous paragraph, however without PDMS. Even after several hours at 100°C in the presence of hydroquinone, n.m.r. analysis revealed no change in the concentration of double bonds and g.p.c. analysis showed no difference in molecular weight or molecular weight distribution.

Two methods were used for the preparation of 'triblocks' listed in *Table 3*. Method A was first used and proved adequate when the molecular weight of one or both blocks was low (samples 1–7, *Table 3*). In these cases, the reaction mixture was optically homogeneous at the start or became homogeneous as the temperature was raised (and/or the reaction proceeded). With higher molecular weight pairings, however, the reaction mixture was inhomogeneous at the start and remained inhomogeneous even at 100°C, and even after long reaction times, when method A was used. The conversion of vinyl groups as measured by n.m.r. (discussed subsequently) showed conclusively that when the reaction mixture remained inhomogeneous, incomplete conversion resulted. In order to ensure complete conversion for higher molecular weights, it was realized that the reaction should be performed homogeneously. This would require dilution of the reaction mixture; however, Chaumont *et al.*[32] have shown that typically very high concentrations are necessary to obtain high conversion in Pt-catalysed hydrosilylation reactions. These two requirements are, of course, in direct opposition to one another. Dilution of the reaction mixture would also tend to favour cyclic formation. Our solution to the problem, as described in

**Table 3** Reaction conditions and characterization of PSU–PDMS 'triblocks'

| | | | | | Thermal characterization | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Before cure ($T^i$) | | | | After cure ($T^f$) | | | | |
| | | | | | PDMS (°C) | | | PSU (°C/K) | PDMS (°C) | | | PSU (°C/K) | PSU Δ |
| Sample | PSU no. ($\bar{M}_n$)/PDMS no. ($\bar{M}_n$) | Group | ClBz (ml) at start | Vinyl conv. by n.m.r.[c] | $T_g$ | $T_c$ | $T_m$ | $T_g$ | $T_g$ | $T_c$ | $T_m$ | $T_g$ | $T_g^f - T_g^i$ (°C) |
| 1 | 1(1200)/1( 540) | A, B | 3 | 0.58 | – | – | – | 60/333 | – | – | – | 102/375 | 42 |
| 2 | 1(1200)/2(1200) | B | 3 | 0.55 | – | – | – | 49/322 | – | – | – | 93/366 | 44 |
| 3 | 1(1200)/4(3500) | B, D | 3 | 0.52 | −122 | – | – | 44/317 | −123 | – | – | 82/355 | 38 |
| 4 | 1(1200)/5(5500) | B | 3 | 0.56 | −123 | −78 | −43 | 38/311 | −123 | −76 | −43 | 70/343 | 32 |
| 5 | 2(2100)/1( 540) | A | 3 | 0.55 | – | – | – | 104/377 | – | – | – | 134/407 | 30 |
| 6 | 3(3200)/1( 540) | A | 3 | 0.55 | – | – | – | 127/400 | – | – | – | 153/426 | 26 |
| 7 | 4(3800)/1( 540) | A, C | 3 | 0.51 | – | – | – | 136/409 | – | – | – | 156/429 | 20 |
| 8 | 4(3800)/1( 540) | A, C | 3 | 0.57 | – | – | – | 139/412 | – | – | – | 162/435 | 23 |
| 9 | 4(3800)/2(1200) | C | 5 | 0.53 | – | – | – | 136/409 | – | – | – | 166/439 | 30 |
| 10 | 4(3800)/3(3400) | C, D | 8 | 0.52 | −126 | – | – | 150/423 | −126 | −94 | −56 | 180/453 | 30 |
| 11 | 3(3200)/3(3400) | D | 7 | 0.50 | −126 | – | – | 137/410 | −122 | −82 | −47 | 178/451 | 41 |
| 12 | 2(2100)/3(3400) | D | 6 | 0.49 | −124 | – | – | 97/370 | −122 | – | – | 128/401 | 31 |

[a] Samples 1–7 prepared by method A; 8–12 by method B
[b] For 1 g total of polymer
[c] Expected conversion of vinyl groups = 0.50
[d] No transition could be seen in d.s.c.

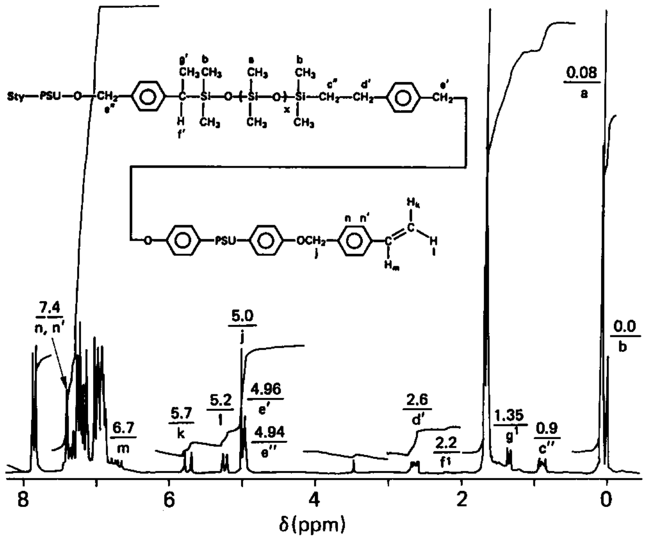


Figure 6 200 MHz proton spectrum ($CDCl_3$) of 'triblock' no. 1 prepared from PSU-1 ($\bar{M}_n = 1200$) and PDMS-1 ($\bar{M}_n = 540$)

method B, was to start the reaction homogeneously with the minimum amount of solvent necessary (as indicated in *Table 3*), and then concentrate the reaction mixture by removing the solvent quickly as the reaction proceeded. This is possible because, as block copolymer is formed, less and less solvent is required to maintain homogeneity, and therefore the excess can be removed. In this way, it was possible to concentrate the reaction mixture to ~2 ml or less per gram of polymer and still maintain homogeneity. By this method, the expected degrees of conversion were attained. Method B, therefore, was the preferred method. The catalyst was changed along with the method because it was noted that reactions with chloroplatinic acid sometimes darkened with reaction time, especially if oxygen was not strictly excluded from the system, and because alcohol as catalyst solvent is the source of a possible side reaction[20,32]. The Wacker catalyst solution avoided both these problems.

A typical 200 MHz proton spectrum of a 'triblock' copolymer is presented in *Figure 6*. Comparison of this spectrum with *Figures 2*, *4* and *5* reveals several important facts. First, the quantitative conversion of ≡Si–H is demonstrated, as with the model reaction, by the complete disappearance of signal c (*Figure 4*) from the 'triblock' spectrum. The complete absence of the ≡Si–H band (~2130 cm$^{-1}$) in the i.r. spectra of the 'triblocks' was also noted. Secondly, the signal b (0.16 ppm) due to terminal $-CH_3$ protons of PDMS (see *Figure 4*) is now completely shifted upfield to 0.0 ppm (*Figure 6*), also supporting the complete conversion of ≡Si–H (as in *Figure 5*). Thirdly, similar to the model compound, the Si–C linkages formed are indicated by the signals c″ and d″ (anti-Markovnikov, ~70%), and f′ and g′ (Markovnikov). Fourthly, the signal of the benzyl ether protons, formerly only j (5.0 ppm, *Figure 2*), now appears as three signals, j, e′ and e″ due to attachment to unreacted styrene groups, anti-Markovnikov addition products, and Markovnikov addition products, respectively. Comparison of integral values for signals c″, d″, e′, e″, f′, g′, j, k and l should yield specific relationships between these signals considering the 2/1 ratio of vinyl to ≡Si–H groups, e.g. $(c''+d'+f'+g')/(e'+e''+j)=1$, $(k+l)/(e'+e''+j)=0.5$, $(k+l)/(c''+d'+f'+g')=0.5$, etc. For reaction between lower molecular weight oligomers, all these integrals could be measured reasonably accurately and good agreement with the aforementioned relationships was obtained within experimental error. With higher molecular weight pairings, the resonances of the ≡Si–H linkages (especially signals f′ and g′) became difficult to measure accurately due to the proximity to, and low intensity compared with, main chain resonances. In these cases, only the relationship $(k+l)/(e'+e''+j)=0.5$ was compared. *Table 3* lists the values obtained from this relationship for all the 'triblocks' prepared. Within the experimental error inherent in the n.m.r. method and the v.p.o. determined precursor molecular weights, the agreement with the expected value of 0.50 is very good. This further indicates complete conversion of ≡Si–H to ≡Si–C linkages. Side reactions of ≡Si–H, if present in this case, apparently do not contribute significantly, and therefore do not detract from the practical utility of this method.

Typical g.p.c. chromatograms for the prepared 'triblocks' are presented in *Figures 7b* and *c*. The changes in elution volume with reaction *versus* the starting PSU (*Figure 7a*) are readily seen for these triblocks, as well as the expected presence of some unreacted PSU homopolymer due to the statistical nature of the reaction. The relative intensity in the u.v. curves is unfortunately highly skewed to the unreacted PSU in these curves because the PDMS segments do not absorb in the u.v. Refractive index detection is equally faulty because the refractive index increment of PDMS in THF is very small and negative, while that of PSU is positive. In order to have an idea of the magnitude of this effect in the u.v., the 'triblock' shown in *Figure 7c* was purified by extraction of the unreacted PSU with a 80/20 v/v DMF/methanol solution. The g.p.c. trace of the purified 'triblock' is presented in *Figure 7d* and shows that the sample is essentially free of unreacted PSU. The extracted portion amounted to only about 10 wt% of the original 'triblock' and contained only a small portion of block copolymer. G.p.c. molecular weight determination of the original 'triblock' (*Figure 7c*) yielded an $\bar{M}_n = 4300$, $\bar{M}_w = 15000$, $PD = 3.5$, compared to the purified sample (*Figure 7d*) with $\bar{M}_n = 15000$, $\bar{M}_w = 24000$, $PD = 1.6$, showing the large influence of the small unreacted PSU portion on the g.p.c. determined molecular weights. Therefore, g.p.c. analysis for these 'triblocks' was used only in a relative manner, as it was realized that the molecular weights obtained were always skewed low.

V.p.o. molecular weight determinations were also performed for the prepared 'triblocks'. If conversion is complete, no side reactions are present, and only linear polymer is formed, then the expected v.p.o. $\bar{M}_n$ of the 'triblocks' would be simply the additive $\bar{M}_n$ values of the two PSU blocks plus that of the middle PDMS block. Generally, agreement of the obtained values with those expected was satisfactory (e.g. 'triblock' no. 1, v.p.o. $\bar{M}_n$ expected = 2940, obtained = 2900; 'triblock' no. 5, expected = 4740, obtained = 4250). In some cases, however, agreement was rather poor. This occurred when the 'triblocks' were formed from higher molecular weight starting oligomers (samples 10 and 11). In the worst case, for 'triblock' no. 10, a v.p.o. $\bar{M}_n$ of 6600 was obtained when 11000 was expected. This result is puzzling considering the n.m.r. results, and it was noted that these v.p.o. determinations showed poor reproducibility and

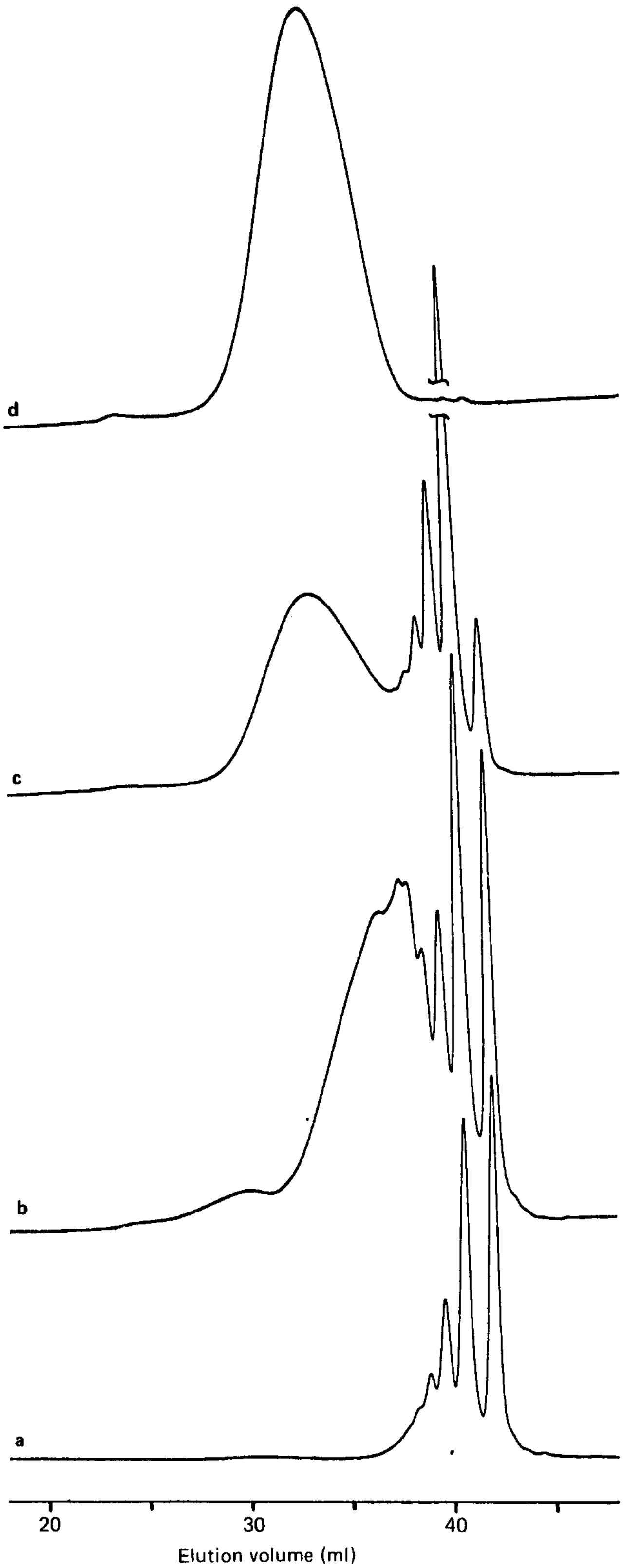


**Figure 7** G.p.c. chromatograms (column set no. 1, u.v. detection) of: (a) $\alpha,\omega$-di(vinylbenzyl)PSU-1; (b) 'triblock' no. 1 from *Table 3*; (c) 'triblock' no. 4 from *Table 3*; (c) 'triblock' as in (c) purified by extraction with an 80/20 v/v DMF/methanol solution

rather large experimental scatter even though samples were dried for long periods. Further, g.p.c. measurements indicated higher molecular weight for these samples than that obtained from v.p.o.

Although n.m.r. and g.p.c. data indicated that the discrepancy in the v.p.o. results was in some way associated with the v.p.o. method for these samples, it was also realized that these samples were prepared from initially more dilute reaction conditions which tend to favour cyclic formation. If cyclics are formed in significant amounts during the hydrosilylation reaction, these would have a very significant impact on the $\bar{M}_n$ obtained. It was therefore attempted to assess the amount of cyclics formed by extracting them from cured samples. Several 'triblocks' (nos. 8, 9, 10 and 12) and two homo-PSUs (nos. 2 and 4) were thermally cured and then the soluble fractions were removed via extraction with $CHCl_3$. For the homo-PSUs, the soluble fraction amounted to 3 wt% (no. 2) and 6 wt% (no. 4) of the cured samples. G.p.c. and n.m.r. analysis showed that this fraction was composed partly of cyclics and partly of material of the same order of molecular weight as the uncured material. N.m.r. analysis revealed no traces of unreacted double bonds. For the 'triblocks' the extracted portion amounted in each case to ~20 wt% of the cured sample. G.p.c. analysis showed that the molecular weight of this fraction was of the same order as the uncured 'triblock' and contained again some cyclic PSU. 90 MHz *FT*-n.m.r. analysis again revealed no traces of unreacted double bonds or $\equiv$Si–H (even with a large number of scans and large vertical scale expansions), but indicated the presence of PSU and PDMS, as well as the Si–C linkages between them. Comparison of the integrals of PSU and PDMS resonances for this fraction and the original 'triblock' showed that only part of the extracted portion could be PSU–PDMS cyclics. At best estimate for cured 'triblock' no. 10, cyclic PSU–PDMS made up about half of the soluble fraction, or about 10 wt% of the uncured 'triblock'. These cyclics, then, explain at least in part the lower-then-expected v.p.o. $\bar{M}_n$ values, the rest being likely a result of problems with v.p.o. measurements of these samples. Further improvements in reaction conditions should minimize the amount of cyclics formed.

*Table 3* further presents the thermal characterization of the prepared 'triblocks' by d.s.c. (see also *Figure 8*). The data are split into four groups, A–D, as listed in *Table 3*. Group A (samples 1, 5–8) presents a PSU series of different molecular weights with the lowest molecular weight PDMS (no. 1). Because the PDMS segment is very short (average length seven repeat units), phase separation for PDMS is poor, and therefore the PDMS serves to lower the $T_g$ of the PSU and the resulting network. This is illustrated in *Figure 9* (curves 1). No separate $T_g$ for the PDMS was observed in d.s.c.; however, torsion pendulum measurements of cured 'triblock' no. 8 revealed a small gradual step change in $G'$ in the temperature range −120 to −75°C, and the corresponding small loss peak in $\tan\delta$ centred at ~ −95°C, indicating a small amount of phase separation even for this low PDMS molecular weight (*Figure* 10 (curves 2)). For the reader's convenience, in *Figure 9* and subsequent figures the 'triblocks' are identified by their component v.p.o. $\bar{M}_n$ values for ready molecular weight referencing.

Group B (samples 1–4, *Table 3*) represents a series of different PDMS molecular weights with the lowest molecular weight PSU (no. 1). Although the $T_g$ of the PSU segment can always be observed both before and after cure, due to the low PSU molecular weight, phase separation is poor, and therefore not only is the PSU $T_g^i$

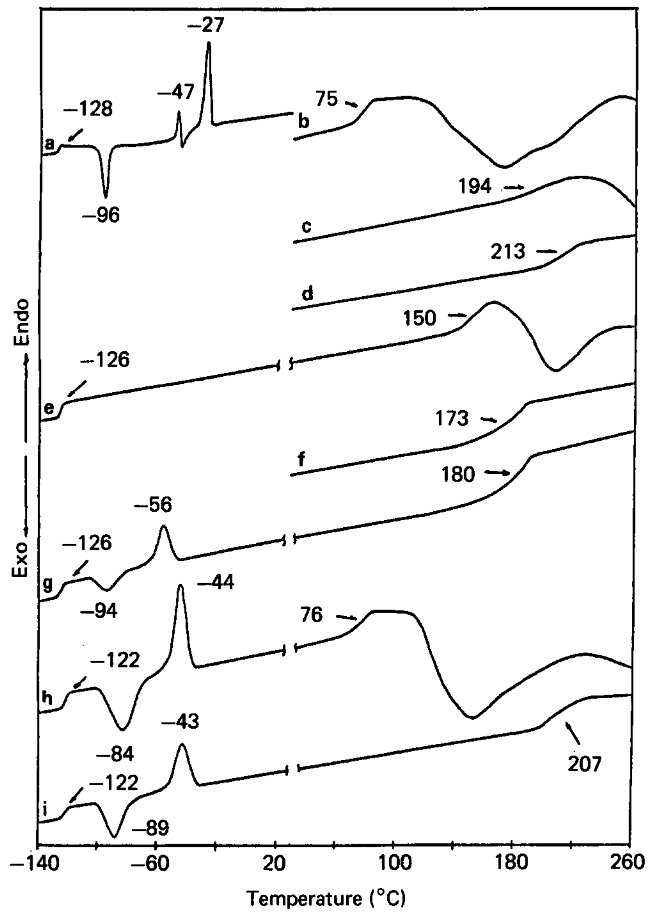


**Figure 8** D.s.c. traces of: (a) α,ω-di(silane)PDMS-4; (b) α,ω-di(vinylbenzyl)PSU-1 (first heating); (c) PSU-1 as in (b) (second heating); (d) PSU-1 as in (c) (final heating, after curing at 260°C for 1 h); (e) 'triblock' no. 10 (first heating); (f) 'triblock' no. 10 (second heating); (g) 'triblock' no. 10 (final heating, after curing at 260°C for 1.5 h); (h) blend of purified 'triblock' no. 4 with PSU-1, 50/50 w/w (first heating); (i) blend as in (h) (final heating, after curing 3 h)

somewhat lowered, but the PSU $T_g^f$ is also drastically reduced with incorporation of PDMS. The deterioration of the PSU $T_g$ is more pronounced with PDMS molecular weight as shown in *Figure 11* (curves 1), a result of the poor phase separation and increasing distance between crosslinks. Samples 3 and 4 from this group show clearly a separate PDMS phase due to the higher PDMS molecular weight. Sample 4 even exhibits $T_c$ and one $T_m$.

Group C like group B represents a series of different molecular weight PDMS; however, in this case the PSU block is higher molecular weight PSU no. 4. The effect of the PDMS segment length on the PSU $T_g$ before and after cure is illustrated in *Figure 11* (curves 2). Incorporation of a short PDMS segment causes $T_g^i$ and $T_g^f$ to drop, but as the PDMS molecular weight is raised, phase separation improves and the PSU $T_g$ values approach those of the parent homopolymer. 'Triblocks' nos. 8 and 9 show no d.s.c. transition for the PDMS segment due to its low molecular weight, but 'triblock' no. 10 does exhibit a sharp well defined PDMS $T_g$ both before and after curing due to the higher PDMS molecular weight. In fact after curing, this PDMS segment even shows $T_c$ and $T_m$. Torsion pendulum measurements on cured samples from this series are illustrated in *Figure 10*. As with 'triblock' no. 8, no. 9 exhibits a gradual step change in $G'$ and the corresponding tan $\delta$ peak in the range −135 to −85°C, although no transition was seen in d.s.c. 'Triblock' no. 10 shows a gradual but somewhat large drop in $G'$ from the PDMS $T_g$ at −126°C to the PDMS melting point at ~ −45°C along with the corresponding changes in tan $\delta$, and then a long 'rubbery' plateau up to near to $T_g$ of the PSU.

Based on the previous results, it was realized that good PDMS phase separation was obtained with PDMS $\bar{M}_n \sim 3400$. The samples (3, 10–12) in group D, therefore, were prepared from this molecular weight PDMS with different molecular weight PSU. The thermal data indicate improved PSU phase separation with molecular weight as expected (see also *Figure 9* (curves 2)). They also indicate that for this molecular weight PDMS, a PSU $\bar{M}_n$ of only ~3000 is necessary for good phase separation. Indeed, for 'triblocks' nos. 10 and 11, PSU $T_g$ values before cure are essentially equivalent to those of the corresponding homopolymers, and post-cure $T_g$ values approach those of the PSU networks without PDMS. For the PDMS segment, a well defined $T_g$ is always seen before and after cure. D.s.c. traces for 'triblock' no. 10 are given in *Figures 8e–g*.

Torsion pendulum measurements for two 'triblocks' in group D (nos. 10 and 12) are presented in *Figure 12* along with the corresponding PSU homopolymers. The two homopolymers, as expected, show a very high modulus up until their $T_g$. The 'triblocks', on the other hand, show a large drop in $G'$ in the PDMS transition region and then a 'rubbery' plateau up until the PSU $T_g$. 'Triblock' no. 12, which exhibits only $T_g$ for PDMS, shows most of this drop at the PDMS $T_g$ and thereby a longer low-temperature plateau. 'Triblock' no. 10, however, exhibits a longer high-temperature plateau and a higher plateau modulus due to the higher PSU molecular weight. The crystallization of the PDMS that occurs in this sample is somewhat undesirable for low-temperature network properties because of its stiffening effect. It may be possible, therefore, to avoid this through incorporation of a small percentage of ethyl or phenyl groups in place of the methyl groups of PDMS.

In summary, the thermal data indicate that, for the range of PSU molecular weights tested, good phase

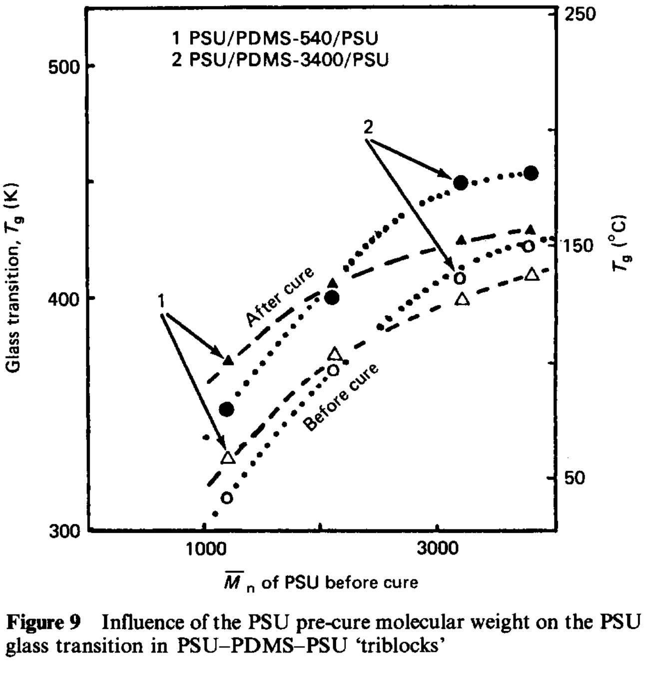


**Figure 9** Influence of the PSU pre-cure molecular weight on the PSU glass transition in PSU–PDMS–PSU 'triblocks'

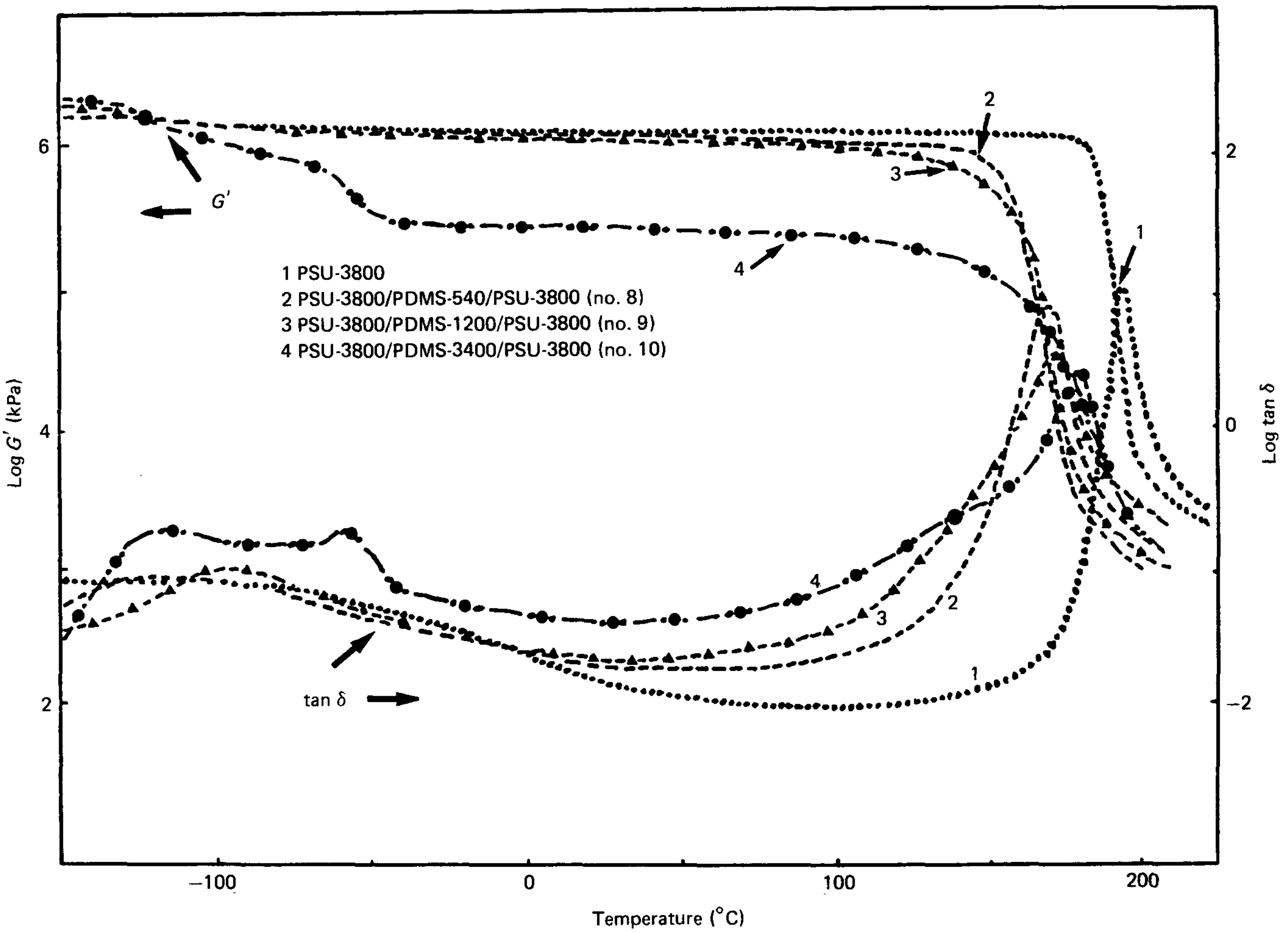


**Figure 10** Torsion pendulum measurements on cured samples of: α,ω-di(vinylbenzyl)PSU-4 ($\bar{M}_n = 3800$) and 'triblocks' formed from it with different molecular weight PDMS (as indicated)

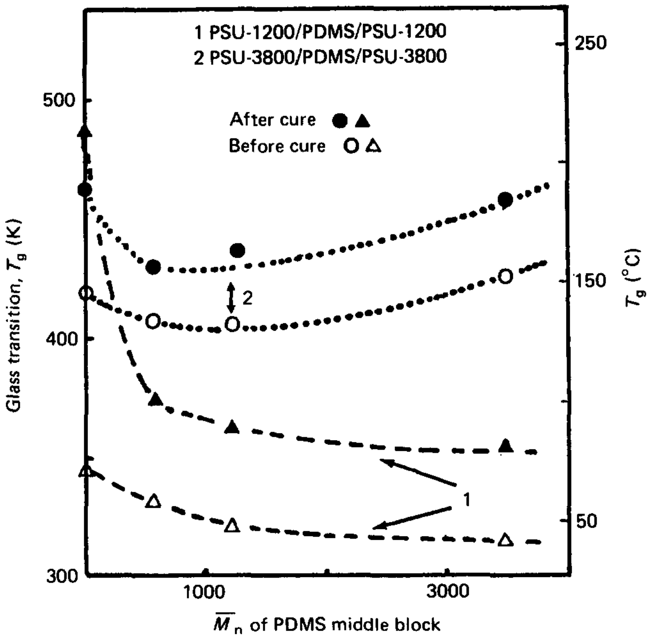


**Figure 11** Influence of the PDMS molecular weight on the PSU $T_g$ in PSU–PDMS–PSU 'triblocks' (as indicated)

separation for PDMS is obtained somewhere in the range $\bar{M}_n = 1200–3400$. Below this point partial phase separation can be observed. For samples with good PDMS phase separation, a PSU molecular weight of only 3000 is necessary to maintain a high hard segment $T_g$.

As noted earlier, the triblocks contain some unreacted PSU due to the statistical nature of the 'step' reaction as shown by g.p.c. in *Figure 7*. In order to assess the effect of this component on the overall PSU $T_g$ especially after curing, two samples (nos. 3 and 4, *Table 3*) were purified of unreacted PSU by extraction with an 80/20 v/v DMF/methanol solution. These samples were chosen because the higher molecular weight of PDMS and the low molecular weight of PSU allow good separation between block and unreacted PSU components to be realized. A block copolymer essentially free of unreacted PSU was obtained as shown in *Figure 7d* (compare with *Figure 7c*). The weight percentage of PDMS in the purified samples was estimated by g.p.c., n.m.r. and v.p.o. measurements, knowing the molecular weights of the block components. The purified blocks were then blended (via dissolution and precipitation) with various amounts of PSU-1 in order to determine how much PDMS could be incorporated into the network to still obtain a high hard segment $T_g$. *Figure 13* illustrates the dependence of the PSU $T_g$, determined by d.s.c. both before and after curing, on the PDMS (or PSU) content of blends of PSU-1 and purified 'triblock' no. 4. As seen in *Figure 13*, the presence of unreacted PSU in the original 'triblock' has

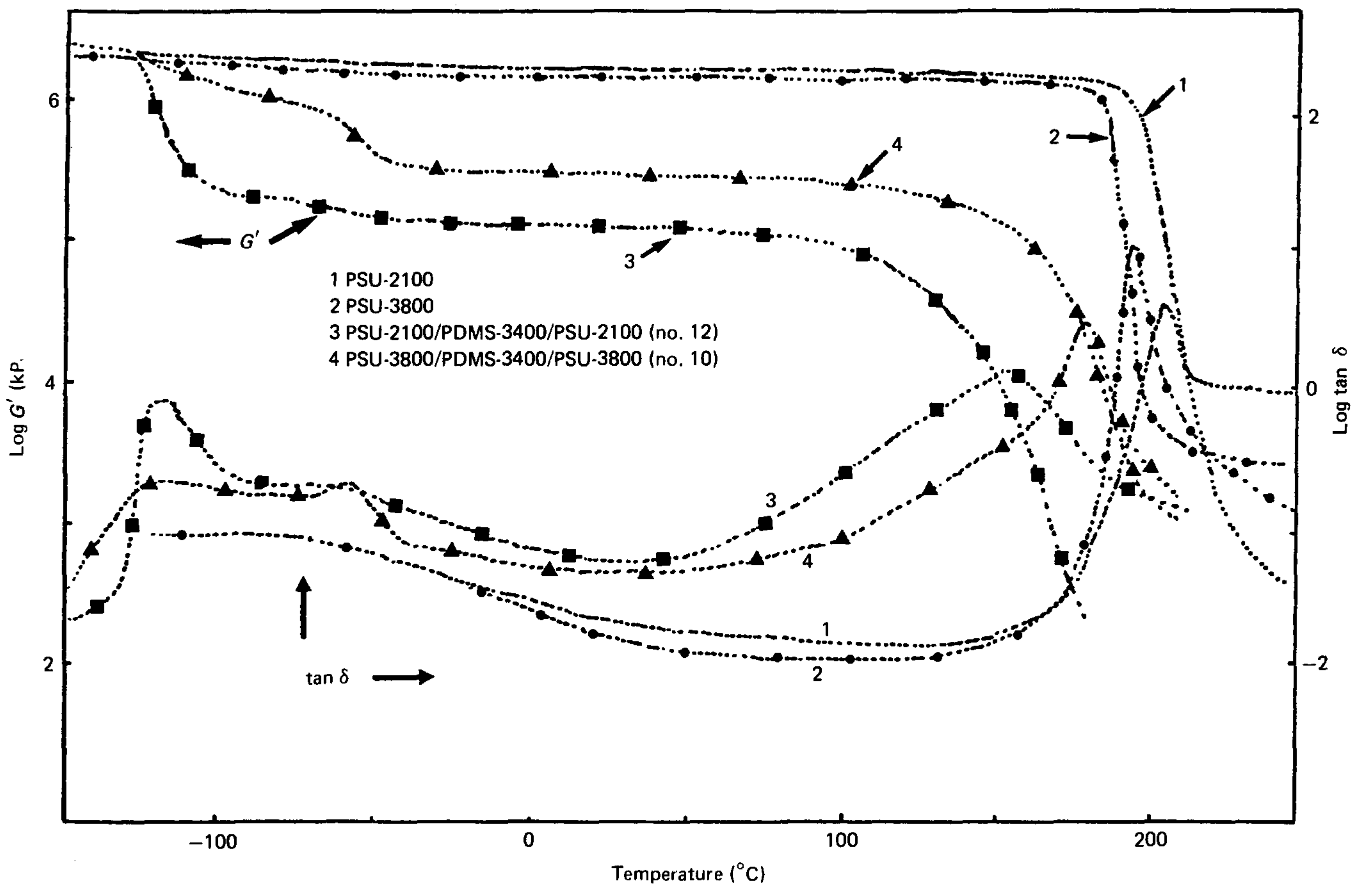


**Figure 12** Torsion pendulum measurements on cured samples of: α,ω-di(vinylbenzyl)PSU-2 ($\bar{M}_n = 2100$) and -4($\bar{M}_n = 3800$), and their respective triblocks with PDMS-3 ($\bar{M}_n = 3400$)

some positive effect on the hard segment $T_g$ before and after curing by comparison with the purified sample; however, even without 'free' PSU, the PSU component of the purified block exhibits its own phase, although small and diffuse as noted from d.s.c. Blending of purified 'triblock' no. 4 with PSU-1 allows as much as 40 wt% of PDMS to be incorporated into the network while a PSU $T_g$ of ~200°C is maintained (for purified 'triblock' no. 3, 35 wt% PDMS). Apparently, the added PSU homopolymer enhances phase separation because of its incompatibility with PDMS and therefore a discrete PSU phase is formed. Only one transition for PSU was noted in all cases by d.s.c. It was also noted that although the as-prepared and purified 'triblocks' nos. 3 and 4 yielded clear films from solution, films of the blends showed certain degrees of translucence or opacity due to the phase separation into relatively large domains. Of course, the ultimate properties of the networks are also a function of the system morphology but this is beyond the scope of the present study. D.s.c. traces of a 50/50 w/w blend of PSU-1 and purified 'triblock' no. 4 (~38% PDMS) are presented in *Figures 8h* and *i*.

It is noted that blending of these triblocks with homo-α,ω-di(vinylbenzyl)PSU is somewhat similar to changing the initial ratio of PSU to PDMS. A 2/1 ratio was chosen by us; however, of course other ratios could also be used. A higher PSU to PDMS ratio would mean a lower molecular weight block and more unreacted PSU; a lower ratio would mean a higher molecular weight block and less unreacted PSU with the corresponding differences in crosslink density. This, then, presents another possibility for network property manipulation.

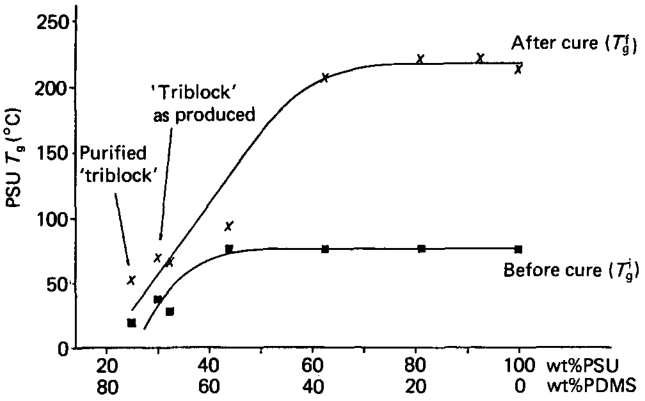


**Figure 13** Dependence of the PSU glass transition *versus* weight percentage of PSU (or PDMS) for blends of PSU-1 and purified 'triblock' no. 4

## CONCLUSIONS

Thermally reactive oligomers of PSU with incorporated PDMS segments were prepared via Pt-catalysed hydrosilylation reaction of α,ω-di(vinylbenzyl)PSU with α,ω-di(silane)PDMS in a 2/1 PSU to PDMS ratio. The reaction was performed without detectable side reactions of the PDMS ≡Si–H end functions and yielded oligomers with thermally reactive styrene-type end groups. Thermal characterization of the produced 'triblocks' revealed the thermal transitions to be highly dependent on the molecular weight of the composing segments. Tailoring of the thermal transitions, and thereby the properties of the networks, was shown to be possible through proper choice of the molecular weights of both segments, their ratios, or by blending of 'triblocks' with homo-α,ω-di(vinylbenzyl)PSU.

## ACKNOWLEDGEMENT

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