

Synthesis and Characterization of Polysulfone–Poly(alkylene oxide) Block Copolymers Containing Poly(dimethylsiloxane)

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SYNOPSIS

Block copolymers of polysulfone–poly(alkylene oxide)–poly(dimethylsiloxane) have been prepared by the addition of preformed α,ω -bis(hydrogensilyl) poly(dimethylsiloxane) oligomers to allyl end-capped poly(alkylene oxide)–polysulfone. The hydrosilylation reaction, catalyzed by platinum, was employed for incorporation of the siloxane chain into the copolymers in a 1 : 1 or 1 : 2 molar ratio of Si–H-terminated polydimethylsiloxane to allyl end-capped polysulfone. The products were characterized by IR, $^1\text{H-NMR}$, and gel permeation chromatography. The thermal stability was determined by thermogravimetric analysis. Differential scanning calorimetry was used to investigate microphase separation in the block copolymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Considerable emphasis has been placed on the synthesis of block copolymers composed of rigid and flexible segments because substantial physical property changes can be obtained by altering their composition and/or the size of segments.^{1,2} Siloxane incorporation into the conventional polymers main-chain is used to transfer their specific characteristics because of their unique combination of properties, including low temperature, flexibility, hydrophobicity, gas permeability, and physiological inertness.^{3,4} One class of block copolymers extensively discussed in the literature is the polysulfone (PSF) containing poly(dimethylsiloxane) (PDMS) as flexible segments, which exhibit properties ranging from thermoelastomers to thermoplastics.^{5–7} They have been receiving attention for membrane application^{8–10} or as impact modifier additives for polysulfone homopolymers.¹¹ Such polysulfone–poly(dimethylsiloxane) (PSF–PDMS) has been previously described in the literature and may be achieved by different synthesis approaches, by copolymer condensation reaction of preformed hydroxy-terminated

polysulfone oligomers and bis silylamine-terminated PDMS,^{5,7–9} or by addition reaction of hydrosilane ($\equiv\text{Si-H}$) to vinyl end groups of aromatic polyether-sulfone oligomers.^{12,13} Another synthetic route for PSF–PDMS was presented in our previous paper¹⁴ based on condensation reaction of chlorine-terminated polysulfone and Si–H-terminated siloxane oligomers in the presence of amine as acid acceptor. Consequently, the resulting PSF–PDMS system contains Si–C linkages.

Modified polysulfone macromers with allyl end-capped poly(alkylene oxide) (PSF–PAO) have been obtained via a classical polycondensation reaction from chlorine-terminated PSF with α,ω -allylhydroxy poly(ethylene oxide) (PEO) and poly(ethylene oxide–propylene oxide) (PEO–PPO) copolymers, respectively.¹⁵

The aim of the present work was to prepare polysulfone (PSF–PAO–PDMS) containing Si–C linkages based on $(\text{CH}_2)_3\text{PAO}$ intersegments by hydrosilylation of the modified polysulfone with α,ω -hydrogensilyl-terminated PDMS using a Pt catalyst (Schemes 1–3).

The block copolymers were characterized by molecular weight gel permeation chromatography (GPC), reduced viscosity (RV), silicone content, and glass transition temperature (T_g). Thermogra-

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vimetric analysis (TGA) data were used to compare their thermal stability. Their structures were confirmed by IR and $^1\text{H-NMR}$ spectra.

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M-80 Carl Zeiss, Jena Spectrophotometer using KBr discs. $^1\text{H-NMR}$ spectra were run on a Jeol 60 MHz NMR Spectrometer at 50°C in CDCl_3 with TMS as an internal reference. The RVs of oligomers and block copolymer solutions (0.2% w/v) in dichloroethane at 25°C were determined using an Ubbelohde Suspended Level Viscometer. Viscosimetric analysis was used to obtain viscometry average molecular weights (\bar{M}_v). Number-average molecular weight (\bar{M}_n), weight-average molecular weight (\bar{M}_w), and molecular weight distributions were determined using a modular Gilson HPLC system controlled by GME-712 Software (UV detector; Gilson Medical Electronics Inc. Middleton, WI). Tetrahydrofuran at a flow rate of 1 ml/min and two Zorbax PSM-S (DuPont) bimodal columns were used to perform separation. These columns provide a linear calibration for polystyrene standards (DuPont and Pierce). Personal software was used to convert GME chromatograms into molecular weight averages.

The melting and softening points were measured with a Gallenkamp hot-block melting-point apparatus. Differential scanning calorimetry (DSC) curves of block copolymers over a temperature range of 20°C – 220°C were recorded on a Mettler DSC-12 E using 5 to 7 mg of each sample with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. For a temperature range of -130°C to -40°C , we used a Perkin-Elmer 7 Thermal Analysis System with $20^\circ\text{C}/\text{min}$ heating rate. The T_g was taken as the midpoint between the intersection of the baseline traces and departure from baseline upon heating through the transition

region on the second run. TGA curves were obtained in air with an F. Paulik Derivatograph at a heating rate of $12^\circ\text{C}/\text{min}$.

Materials

4,4'-Dichlordiphenylsulfon (Fluka) was recrystallized from toluene. 2,2-Bis(4-hydroxyphenyl)propan (Bisphenol A) (Fluka) was used as received. 1-methyl-2-pyrrolidone (NMP; Aldrich) was vacuum-distilled over phosphorus pentoxide. Chlorobenzene (PhCl) and dichloroethane (Aldrich) were dried on 4A molecular sieves and vacuum-distilled. Octamethylcyclotetrasiloxane 98% (D_4) (Fluka) was vacuum-redistilled. 1,1,3,3-Tetramethyldisiloxane 97% (Aldrich) was used as received. Styrene divinylbenzene sulfonic acid copolymer (Vionit CS 34 C) was dried in vacuum at 90°C for 3% w/v water content. The platinum catalyst was $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Merck).

Synthesis of the α,ω -Si-H-terminated PDMS (I)

α,ω -Hydrogensilyl-terminated PDMS (I) from predicted molecular weight was prepared by equilibration of D_4 and functionalized Si-H 1,1,3,3-tetramethyldisiloxane, as end-capped in the presence of Vionit CS 34 C, by the preparative method described in literature.^{16,17} Si-H terminated PDMS was characterized by $^1\text{H-NMR}$ and IR spectroscopy. The \bar{M}_n were determined by Si-H reactive endgroup analysis.¹⁸ \bar{M}_w , \bar{M}_n , and molecular weight distribution were determined by GPC (Table I).

Chlorine-Terminated Polysulfone

Chlorine-terminated PSF oligomers were synthesized from 4,4'-dichlordiphenylsulfon and 2,2-bis(4-hydroxy phenyl)propan (Bisphenol A) via polycondensation reaction in NMP and PhCl, promoted by the action of K_2CO_3 .^{19,20}

Table I Characteristics of α,ω -SiH-terminated PDMS

Sample Code	H Content (%)	\bar{M}_n^a	\bar{M}_v^b	\bar{M}_w^c	\bar{M}_n^c	\bar{M}_w/\bar{M}_n	η (cSt)	T_g
I-1	0.017	11700	22700	40800	14500	2.81	487	-118
I-2	0.010	19200	29140	55600	23100	2.40	1618	-120

^a \bar{M}_n based on end groups data.

^b \bar{M}_v based on viscosimetry data.

^c GPC data.

Table II Characteristics of PSF-PAO

Sample ^a Code	PSF (\bar{M}_n)/PAO (\bar{M}_n) ^b	\bar{M}_v ^c	\bar{M}_w ^d	\bar{M}_n ^d	\bar{M}_w/\bar{M}_n	RV ^e
V-1	1 (38000) : 1 (1000) ^f	7825	—	—	—	0.09
VI-1	1 (5100) : 2 (2850)	3180	7400	2300	3.22	0.10
VI-2	1 (20400) : 2 (2850)	10500	21300	7200	2.96	0.15
VI-3	1 (31400) : 2 (2850)	12100	24570	7800	3.15	0.16
VI-4	1 (37000) : 2 (2850)	18245	27810	10300	2.70	0.18
VI-5	1 (38000) : 1 (2850)	14290	29640	9500	3.12	0.21

^a From Scheme 2.^b \bar{M}_n (PSF) based on viscosimetry data. \bar{M}_n (PAO) based on allyl end-groups analysis.^c \bar{M}_v based on viscosimetry data in dichloroethane solution.^d Based on GPC data.^e 0.2 g/dL solution in dichloroethane.^f PAO-polyethylene oxide.

α,ω -Diallyl poly(alkylene oxide) polysulfone (V, VI)

α,ω -diallyl (ethylene oxide) polysulfone (V) and α,ω -diallyl poly(ethylene oxide-propylene oxide) polysulfone (VI) were prepared in a two-step synthesis by the condensation reaction of various-molecular-weight chlorine terminated polysulfone (II) and allyl-PAO-OH as described in a previous paper.¹⁵

The characteristics of modified polysulfone are listed in Table II.

Synthesis of PSF-PAO-PDMS Block Copolymers (VII, VIII)

A series of PSF-PAO-PDMS (VII, VIII) block copolymers were synthesized by hydrosilylation reaction of allyl-terminated PSF-PAO with Si-H-terminated PDMS in PhCl, catalyzed by $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 2% w/v solution in isopropanol.

The method is outlined as follows: 2.81 g (0.089 mmol) PSF-PAO (VI) and 50 mL dry PhCl were

charged in a 250-mL reaction flask fitted with stirrer, thermometer, Dean-Stark trap, condenser, and nitrogen inlet. The system was slowly heated to 130–140°C to remove the water-chlorobenzene azeotrope (20% v) and continuously purged with dry nitrogen. After cooling to about 90°C, 0.1 mL solution 2% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in anhydrous isopropanol was added. The system was reheated to 130°C and 3 g (0.245 mmol) PDMS was added drop by drop and stirred for 24 h.

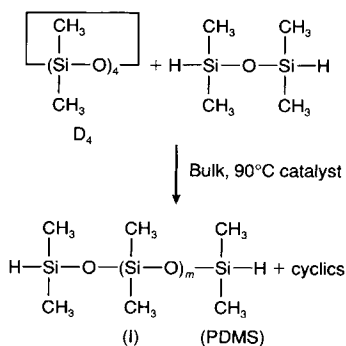
The complete conversion of Si-H groups to Si-C linkages is controlled by the IR spectra of the reaction mixture. After cooling, the reaction mixture was coagulated in excess methanol (ca. 700 mL). The precipitate was filtered, washed with water and hot methanol, and purified of unreacted PSF with 20/80 (v/v) MeOH/DMF.

The unreacted silicone was rigorously extracted with petroleum ether (30–60°C) in a Soxhlet Extractor. Finally, the product was dried in a vacuum oven at 50°C for 20 h.

Table III Block Copolymers PSF-PAO-PDMS

Sample Code	PSF-PAO Code	PSF (mmole $\times 10^{-1}$)	PDMS (mmole $\times 10^{-1}$)	\bar{M}_w ^a	\bar{M}_n ^a	\bar{M}_w/\bar{M}_n	\bar{N}_A/\bar{N}_B ^b	PDMS ^c (%)	RV ^d
VII-1	V-1	1.50	2.50	5300	1300	4.08	43/14	15.46	0.09
VIII-1	VI-1	0.98	1.03	9600	5100	1.88	38/14	12.20	0.12
VIII-2	VI-2	0.53	1.05	19100	6400	2.98	61/13	17.22	0.21
VIII-3	VI-3	0.84	2.10	22400	7000	3.20	62/43	34.50	0.24
VIII-4 ^e	VI-5	0.50	0.63	26200	11500	2.28	57/45	35.90	0.15
VIII-5	VI-5	0.85	2.00	36000	10800	3.33	—	41.50	0.22

^a GPC data.^b Ratio of average number (\bar{N}) of PSF (A) and PDMS (B) blocks ¹H-NMR determined.^c PDMS content, determined from ¹H-NMR spectra.^d 0.2 g/dL solution in dichloroethane at 25°C.^e PDMS ($\bar{M}_n = 19200$).



Scheme 1

The resulting product is a fluffy, white-yellow, soluble polymer in several organic solvents. The polymers display a good hydrolytic stability.

The characteristics of synthesized block copolymers are listed in Table III. Films cast from 10% (w/v) methylene chloride or chloroform solution were transparent, colorless, and flexible.

RESULTS AND DISCUSSION

The precursor oligomers, hydrosilyl-terminated PDMS, were prepared as shown in Scheme 1.

The lengths of siloxane segments (D_n) in PDMS were determined by $^1\text{H-NMR}$ spectroscopy and

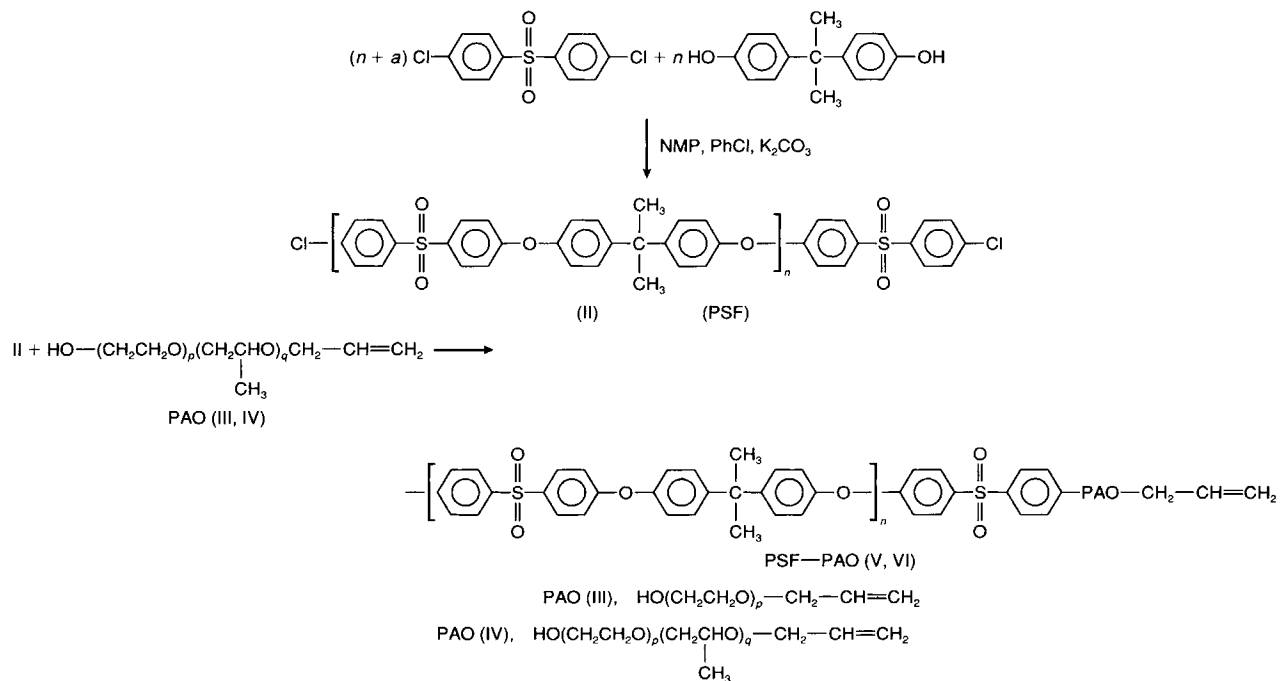
maintained constant for all synthesized block copolymers.

Modified polysulfone PSF-PAO was prepared from chlorine-terminated PSF with various \bar{M}_n (5,000–38,000) with α,ω -allyl, hydroxy end-capped PEO or PEO-PPO in a one-step reaction (Scheme 2).

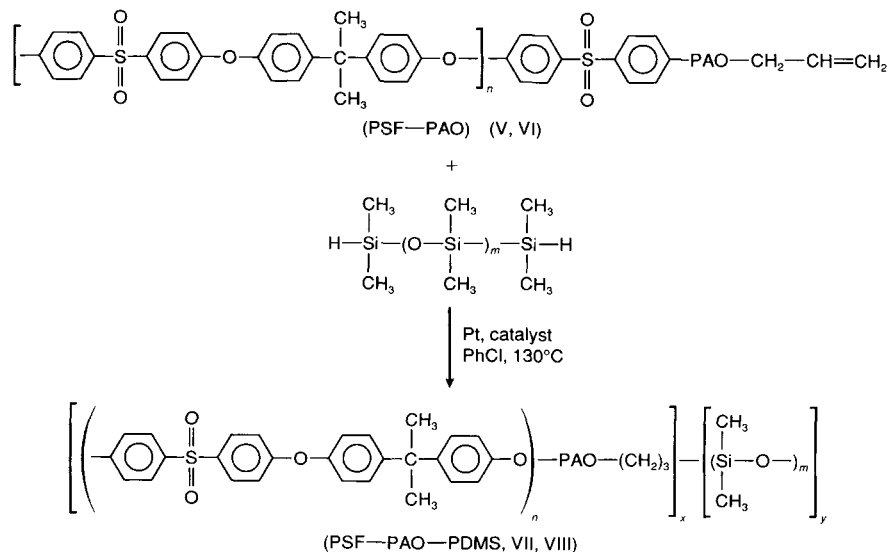
The synthesis of PSF-PAO-PDMS block copolymers was carried out in a 1 : 1 or 1 : 2 molar ratio solution of allyl end-capped PSF-PAO and Si-H-terminated PDMS by hydrosilylation. This produced a linear $(\text{AB})_n$ structure containing hydrolytically stable Si—C linkages with PAO intersegments, as shown in Scheme 3.

The IR spectra of PSF-PAO-PDMS block copolymers demonstrated the conversion of Si-H end groups to Si-C linkages by the complete disappearance of the 2140 cm^{-1} absorption band characteristic of the Si-H-terminated PDMS and the appearance of a large absorption band at $1000\text{--}1100\text{ cm}^{-1}$ for the Si-O-Si linkages which is not present in the spectra of PSF-PAO [Fig. 1(a,b)].

$^1\text{H-NMR}$ was used to determine the composition and the relative block size of the block copolymers from the ratio of the peak intensities of PDMS methyl proton resonance at $\delta = 0.1\text{ ppm}$, propylene oxide proton at $\delta = 1.15\text{ ppm}$, and ethylene oxide proton at $\delta = 3.8\text{ ppm}$ from the PAO segment and the aromatic proton of PSF at $\delta = 7.4\text{ ppm}$ (Fig. 2).



Scheme 2



Scheme 3

The proton signal $-\text{CH}_2-$ from $\text{Si}-(\text{CH}_2)_3$ linkage at $\delta = 0.35$ ppm observed in the $^1\text{H-NMR}$ spectrum is in accordance with a structure containing Si-C linkage between the PSF and PDMS blocks. The expected $(\text{AB})_n$ structure was also confirmed from $^1\text{H-NMR}$ spectra. The relative lengths of the blocks in the formed block copolymers were determined from the average number \bar{N}_A of PDMS and \bar{N}_B of PSF blocks.

The molecular weights of the precursor oligomers and block copolymers were determined using GPC

analysis. The block copolymers PSF-PAO-PDMS have a molecular weight distribution similar to its starting PSF-PAO (Fig. 3).

Matzner and colleagues,²¹ Auman and coworkers,²² and Collyer and colleagues⁹ reported microphase separation in PSF-PDMS block copolymers by observation of two T_g for each phase, for PDMS, and for PSF, respectively.

Evidence for the PSF-PAO-PDMS block copolymer formation was obtained from DSC analysis used to compare the T_g on the starting material

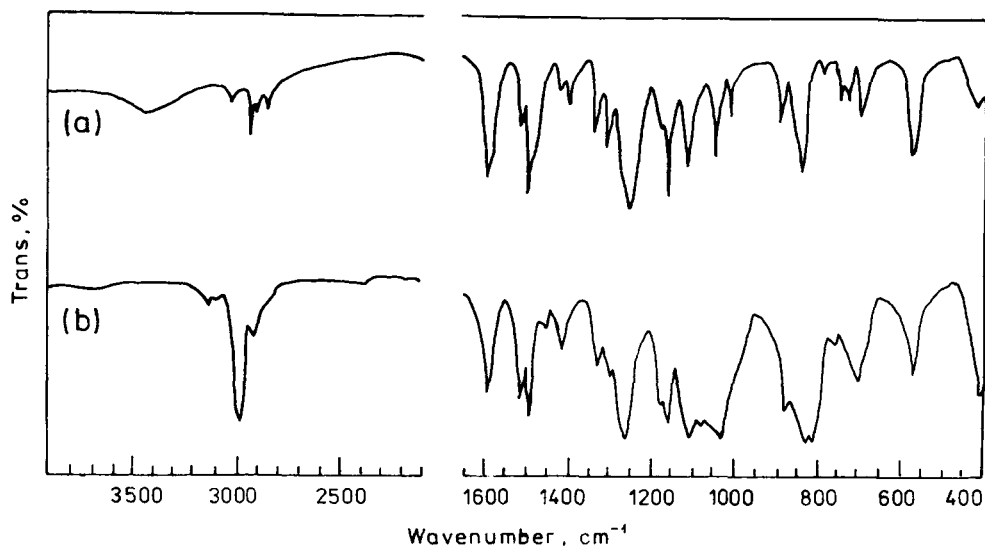


Figure 1 IR spectra of PSF-PAO (VI-5 (a)) and PSF-PAO-PDMS block copolymer (VIII-5 (b)).

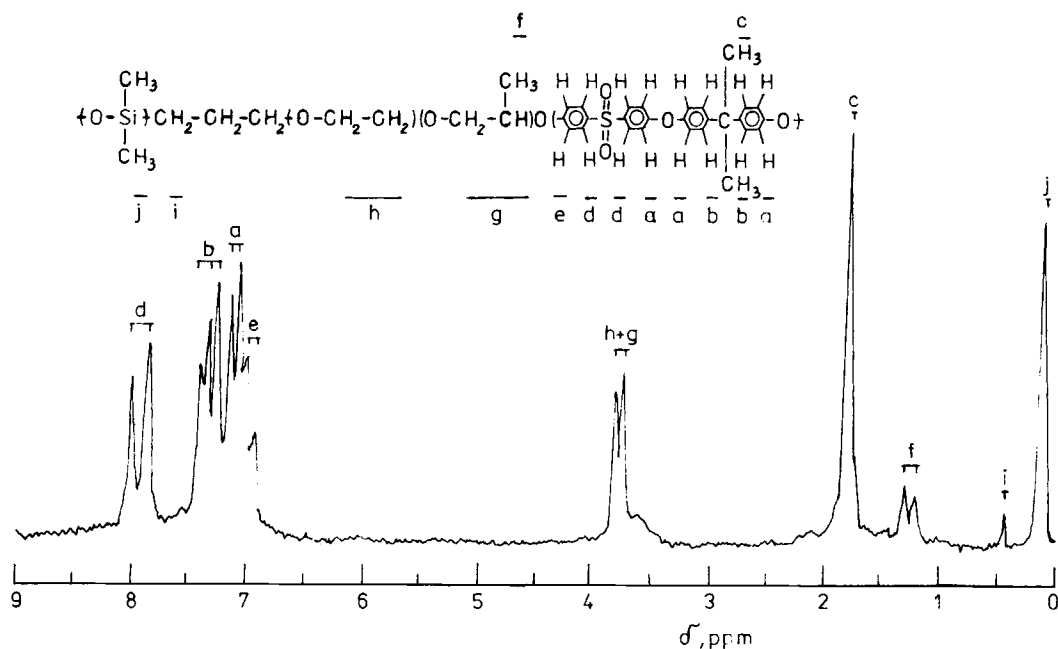


Figure 2 $^1\text{H-NMR}$ spectra of PSF-PAO-PDMS (VIII-5).

(PSF-PAO) and the block copolymers containing PDMS segments over a temperature range -125 – 50°C and from 20°C to 220°C at first and second heating runs (Figs. 4 and 5, respectively.) As a result of the DSC curves, the block copolymers showed

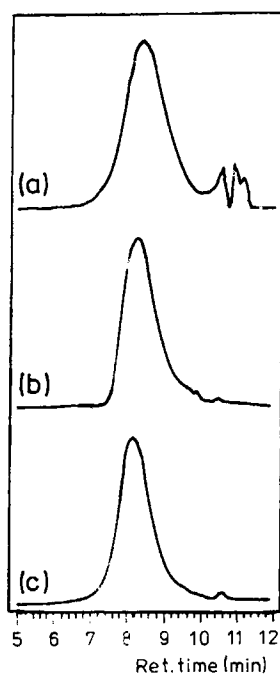


Figure 3 HPLC data-based UV-detector traces for (a) HPDMS (I-1), (b) PSF-PAO (VI-2) and (c) PSF-PAO-PDMS (VIII-5).

two T_g which indicated a microphase separation. The first observed T_g in the negative temperature range (-98°C), attributed to PDMS precursor oligomers, was at a higher temperature as indicated in the literature^{9,21,22} (Fig. 4) and also as compared to that determined for Si-H terminal siloxane (Table I). This might be correlated with the presence of the polyalkylene oxide intersegment in the structure of block copolymers. The second T_g observed for all samples (VII.1–VIII.5) are in the temperature range 90 – 160°C , 20 – 30 degrees higher than those for the starting PSF-PAO due to the same influence of polyalkylene oxide. The T_g s were determined from original DSC curves and are listed in Table IV.

The thermal stability of the PSF-PAO-PDMS block copolymer was studied by TGA and differential thermal analysis. The samples were heated at a constant temperature rate of $12^\circ\text{C}/\text{min}$ in air. The initial decomposition temperature and the temperature % weight loss were determined from original thermograms and tabulated in Table IV. The comparison of the T_{10} values (342 – 415°C) for the modified polysulfone (V.1–VI.5) with that of PSF-PAO-PDMS (VII.1–VIII.5) (389 – 477°C) indicated that the thermal stability of block copolymers increased due to incorporation of siloxane units.

CONCLUSIONS

PSF-PAO-PDMS block copolymers were prepared by hydrosilylation reaction of allyl end-capped PSF-

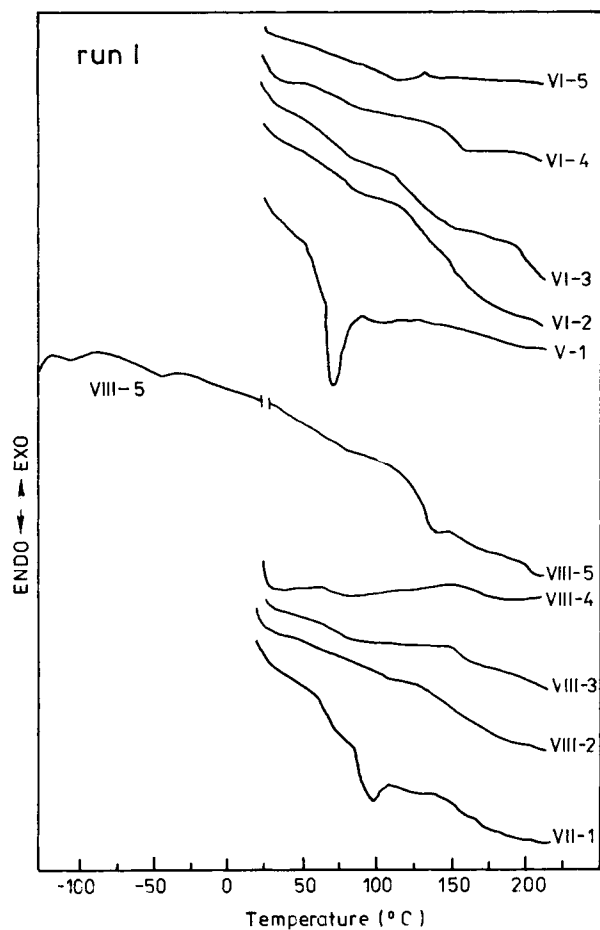


Figure 4 DSC traces of PSF-PAO copolymers (V-1, VI-2,3,4,5) and PSF-PAO-PDMS block copolymers (VII-1, VIII-2,3,4,5) (run I).

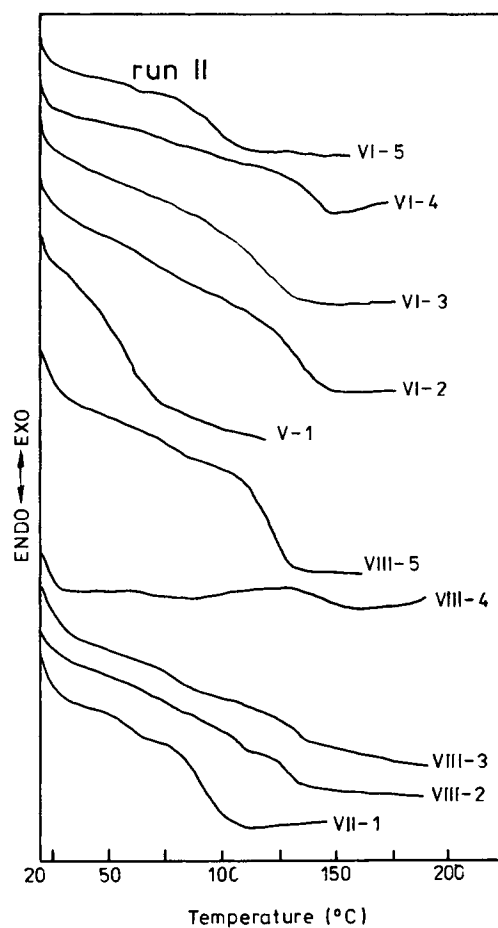


Figure 5 DSC traces of PSF-PAO (V-1, VI-2,3,4,5) and PSF-PAO-PDMS (VII-1, VIII-2,3,4,5) (run II).

Table IV Thermal Characteristics and T_g of PSF-PAO and PSF-PAO-PDMS Block Copolymers

Sample Code	IDT (°C)	TGA Temperature (°C) for Various % to Decompose				T_g^a
		10	20	30	50	
V-1	50 ^b	342	392	426	512	60
VI-1	312	400	490	509	535	92
VI-2	348	360	396	493	505	138
VI-3	351	373	404	435	492	117
VI-4	305	415	470	487	524	130
VI-5	340	402	464	485	508	152
VII-1	80 ^b	416	484	509	525	88
VIII-1	348	477	503	516	551	-98,123
VIII-2	316	394	430	457	510	-98,160
VIII-3	301	389	428	450	539	136
VIII-4	361	472	498	511	521	130
VIII-5	355	472	498	511	541	145

^a T_g from the DSC data (run I).

^b PAO-PEO.

PAO with Si-H-terminated PDMS in PhCl catalyzed by $H_2PtCl_6 \cdot 6H_2O$ solution in isopropanol and were characterized by GPC, 1H -NMR, and IR analysis.

The block copolymers were found to display microphase separation.

The TGA data indicate a better thermal stability for the synthesized block copolymers.

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