Polymer Bulletin 37, 329–336 (1996)

Polymer Bulletin

Synthesis of polysulfone block copolymers containing polydimethylsiloxane

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Received: 8 December 1995/Revised version: 6 May 1996/Accepted: 7 May 1996

Abstract

The synthesis of polysulfone-polydimethylsiloxane (PSU-PDMS)linear block copolymers has been carried out in solution by condensation of chloro-terminated bisphenol A, diphenylsulfone and α, ω-di (hydrogensilyl) -polydimethylsiloxane with Si-C bond. ^{1}H-NMR spectra of the block copolymers allow the estimation of siloxane and polysulfone ratio. The molecular weight of the polysulfone and polysiloxane oligomers and the block copolymers was determined by GPC. Thermogravimetric analysis indicates a thermal stability of block copolymers up to 400 °C and allows estimation of the process activation energy. Microphase separation of the block copolymers was observed by differential scanning calorimetry (DSC).

Introduction

The incorporation of polyorganosiloxanes as "soft" segments into high performance polymeric materials such as polysulfone has been of great interest over the past several years and has been used to prepare block, graft or perfect alternating copolymers for special technical applications (1-3). The organosiloxane block copolymers containing a Si-C or Si-O-C link between two distinctly different segments, offers an opportunity for improving their properties. The siloxane block displays a unique combination of characteristics which includes high flexibility of the siloxanic backbone, low glass transition temperature, thermal stability, a wide temperature range, and hydrophobicity (4,5). In addition, polysiloxanes may lead to surface modifications, due to their surface energy lower than of most other materials. Therefore, they tend to separe on the surface, even if they represent a component of a microphase separated system (3). Block copolymers containing high molecular weight segments of polysulfone and polydimethylsiloxane with a Si-O-C bond between two different polymer segments, have been synthesized by Noshay (6-11,14,15) by the condensation reaction of preformed dihydroxy-terminated polysulfone oligomers and bis-silylamine terminated polydimethylsiloxane. As an alternative route, Percec (12) and Nagase (13,16) propose the hydrosilylation reaction to incorporate polysiloxane block into aromatic polyethersulfone with vinyl endgroup oligomers, including a hydrolitically stable Si-C bond between the segments.

The paper deals with synthesis of polysulfone-polydimethylsiloxane block copolymers by the condensation reaction of α,ω-di(hydrogensilyl)-polydimethylsiloxane (HPDMS) oligomers with a α,ω-di(chloro)polysulfone (PSU) oligomers in the presence of urea. The obtained block copolymers with an AB structure were characterized by IR, ^{1}H-NMR, GPC, thermal stability and DSC.

Experimental

Materials

Dichlorodimethylsilane and chlorodimethylsilane, 99% purity, (Fluka). 4,4'-dichlorodiphenylsulfone and 2,2-bis(4-hydroxyphenyl)propane (Union Carbide Corporation) were used as received. Chlorobenzene was dried on molecular sives and freshly distilled. Other solvents and reagents were high grade commercial products used without further purification.

Analysis

IR absorption spectra were obtained on a Perkin Elmer 577 spectrophotometer on KBr discs. ^{1}H-NMR analyses were performed on a Jeol-C-60 HL spectrometer using a $CDCl_3$ solution. Viscosimetric analysis in $C_2H_4Cl_2$ solution was used to obtein viscosimetry average molecular weights ($\bar{M}_n$). Reduced viscosity was determined on an Ubbelohde viscosimeter in $C_2H_4Cl_2$ at 25 °C. M_n, M_w and molecular weight distributions (M_w/M_n) were determined using a Molecular Gilson HPLC system controlled by the GME-712 Software, UV-detector. THF at flow rate of 1 mL/min and two Zorbax PSM-S bimodal columns calibrated for polystyrene standard were used to perform separation. Differential scanning calorimetry (DSC) curves were recorded on a Perkin Elmer 7 Thermal Analysis System for a temperature range of -130 °C to 220 °C using 5 to 7 mg of each sample, at a heating rate of 20 °C/min, under nitrogen. DTA and DTG curves were registered on a MOM Paulik-Paulik-Erdey derivatograph (12 °C/min. heating rate) within a 20-600°C temperature range, in air.

Synthesis of α,ω-di(hydrogensilyl)-polydimethylsiloxane (HPDMS)

A difunctional Si-H terminated polysiloxane oligomer HPDMS was obtained by the "equilibration reaction" of octamethylcyclotetrasiloxane (D_4) and functionalized Si-H 1,1,3,3-tetramethyldisiloxane (TMDS) as endcapper, in the presence of a 2-3% dried copolymer styrenedivinylbenzene sulfonic acid (Vionit CS-34 C) with an water content of 3% w/v, as cationic polymerization catalyst under stirring for $2^1/_2$ hours at 90 °C (17). Using various D_4/TMDS molar ratios for different molecular weights Si-H terminated polydimethylsiloxanes were obtained. The average molecular weights ($\bar{M}_n$), ($\bar{M}_v$) and ($\bar{M}_w$) were determined by Si-H endgroup analyses (18) and by GPC data (Table 1).

Table 1. α,ω-di(hydrogensilyl)-polydimethylsiloxane characteristics

Sample	D_4/TMDS	$\bar{M}_n$ ^{a}	$\bar{M}_v$ ^{b}	$\bar{M}_n$ ^{c}	$\bar{M}_w$ ^{c}	M_w/ $\bar{M}_n$	$H_{content}$ %
HPDMS-1	11.5/1	3250	2300	1807	2443	1.35	0.0615
HPDMS-2	22.5/1	6500	5432	3762	5977	1.58	0.0303
HPDMS-3	26.7/1	7900	6800	-	-	-	0.0253
HPDMS-4	33.6/1	9800	10269	19038	28483	1.49	0.0203
HPDMS-5	40.5/1	12000	22717	14500	40800	2.81	0.0171

a - $\bar{M}_n$ based on end groups data

b - $\bar{M}_v$ based on viscosimetry from relations $\lg \eta_{cst/25\,C} = 1,00 + 0,0123\, M^{0,5}$

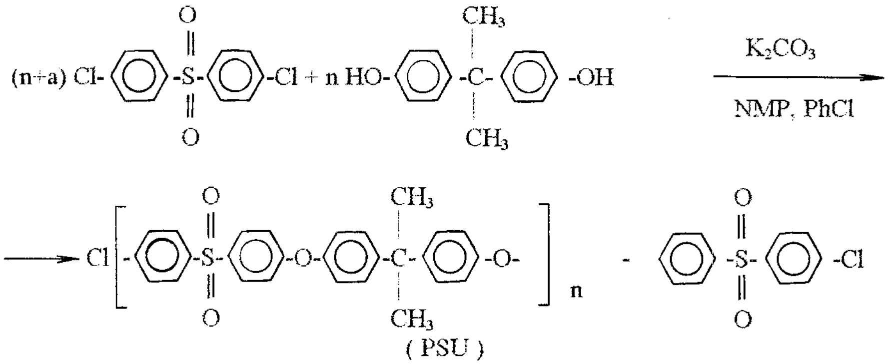
c - GPC data

Synthesis of chlorine terminated polysulfone oligomers (PSU)

Chlorine terminated PSU oligomers were synthesized by condensation of 2,2-bis (4-hydroxyphenyl)propane (bisphenol A) with a calculated excess of bis(4,4′-chlorophenyl) sulfone (DCDPS) according to the literature procedure (19,20) as shown in Scheme I.

A 26% excess of K_2CO_3 (with respect to bisphenol A) was employed as a base, to generate "in situ" the phenolate salt. In a flask fitted with a Dean-Stark trap, condenser, N_2 inlet and stirrer, 22.831 g (0.1 mole) bisphenol A, 34.749 g (0.12 mole) DCDPS, 17.413 g (0.1 mole) anhydrous well powdered potassium carbonate and 26% excess, 150 cc N-methylpyrolidone and 75 cc chlorobenzene are charged.

The reaction mixture is heated under stirring with a constant purge of N_2 at 160 °C until water and chlorobenzene are removed from the system. The temperature was raised to 180°C and kept at that value for 6 hours.



Scheme I

The mixture was then cooled and filtered to remove the salt. Further on, the dark solution was coagulated in a highspeed blender containing seven volumes of methanol. The product was filtered, washed with water and methanol and dried in vacuum at 80 °C for 16 hours. The synthesized chloroterminated PSU oligomers were characterized by halogen endgroup analysis and reduced viscosity (Table 2).

Table 2. α,ω-dichloro-PSU characteristics

Sample	$\bar{M}_n$[a]	$\bar{M}_n$[b]	Cl % exp	Cl % calc	RV[c]	m.p. (°C)
PSU-1	5100	5174	1.48	1,37	0.094	195-200
PSU-2	16000	16217	0.46	0,44	0.244	245-249
PSU-3	36700	36572	0.28	0.20	0.408	252-258

a - $\bar{M}_n$ based on viscosimetry and osmometry data

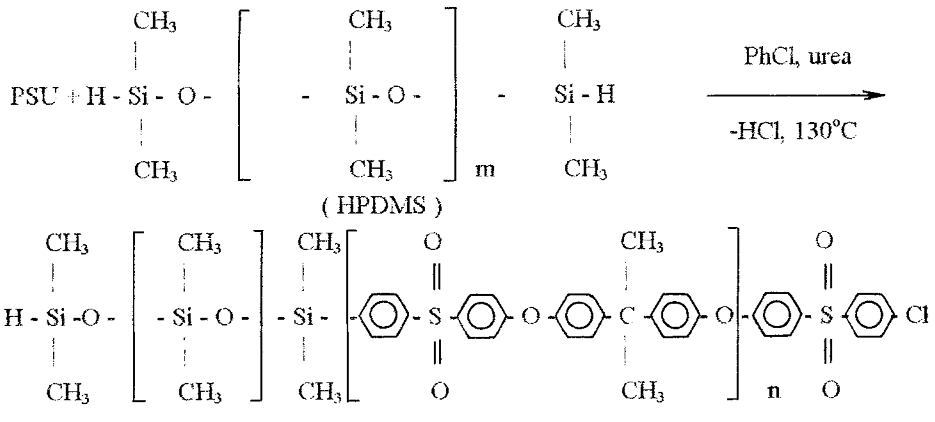
b - $\bar{M}_n$ calculated from the chlorine content

c - 0,2 g/dL solution in DMF

Synthesis of block copolymers

Polysulfone/polydimethylsiloxane block copolymers were synthesized by reacting the oligomers in a chlorobenzene solution at 130 °C. The polysulfone was dehydrated by azeotropic distillation before addition of the siloxane oligomer. The details of typical synthesis are given below : In a 250 mL three-neck round bottom flask, equipped with a mechanical stirrer, nitrogen inlet, Dean-Stark trap and condenser 5 g (0.31 mmole)

PSU(M=16000), 50 cc chlorobenzene and 0.1 g (1.66 mmole) urea are charged. 20% of chlorobenzene was distilled out to remove the azeotrop chlorobenzene-water after which the trap was replaced by a drop funnel, 3 g (0.46 mmole) HPDMS (M=6500) being added dropwise. The reaction solution was heated at 130-135 °C and maintained under stirring for 24 h. After cooling, the solution was coagulated in methanol excess. The filtered product was washed with water and methanol to remove the urea chlorohydrate. The polymer was then reprecipitated by dissolving it into a minimal amount of dichloroethane, followed by pouring into methanol and filtration. The unincorporated siloxane was removed using an extensive extraction with petroleum ether in a Soxhlet extractor. After drying overnight in vacuum at 50 °C the resulting product (5.7 g, 82%) was a white fluffy polymer with reduced viscosity 0.36 (0.2 g/dL in $C_2H_4Cl_2$ at 25 °C).



PSU-PDMS (I-IX) Scheme II

Results and discussion

The Si-H terminated PDMS of controlled molecular weight and possessing a narrow molecular weight distribution were prepared from D_4 and Si-H functionalized disiloxane (TMDS) by cationic polymerization, in the presence of acid catalyst (VIONIT CS-34 C). The molecular weight of the polysiloxane is controlled by the D_4/TMDS ratio. The molecular weight and molecular weight distribution M_w/M_n and Si-H end group analysis were presented in Table 1.

The synthesis of polysulfone oligomers outlined in Scheme I involves the condensation reaction of Bisphenol A with bis (4,4′- chlorophenyl)sulfone (DCDPS). A calculated excess of sulfone monomers was used to obtain the chloro-terminated PSU oligomers. The characteristics of the synthesized polysulfone were presented in Table 2.

In order to incorporate the polysiloxane segments into polysulfone, a condensation reaction of chloro-termined PSU-oligomers and Si-H functionalized PDMS in 1:1 molar ratio was performed , in the presence of urea as an HCl acceptor,(Scheme 2).

The average molecular weights of the HPDMS and polysulfone oligomers were both varied. The characteristics of the synthesized PSU-PDMS block copolymers are presented in Table 3.

Table 3. Characteristics of PSU-PDMS Block copolymers

Sample code	Block size PSU	PDMS	Siloxane %	$\bar{M}_\eta$[a]	$\bar{M}_w$ (GPC)	M_n (GPC)	M_w/M_n	RV[b]
I	5100	3250	12	7600	18000	4900	3.67	0.18
II	5100	7900	19	9350	22500	7600	2.96	0.33
III	5100	12000	17	1200	30250	10250	2.95	0.22
IV	16000	3250	11.5	9100	43250	8100	5.33	0.34
V	16000	6500	17.5	0900	79100	5900	13.40	0.21
VI	16000	9800	19	2200	45700	10300	4.43	0.36
VII	37000	3250	8.5	8600	35000	5800	5.03	0.36
VIII	37000	6500	7	0200	36700	8600	4.26	0.33
IX	37000	9800	18	0850	49700	9100	5.46	0.20

a - $\bar{M}\eta$ calculated from $\eta = 3{,}685.\ 10^{-4}\ M^{0{,}656}$ in $C_2H_4Cl_2$

b - 0,2 g/dL solution in $C_2H_4Cl_2$

The IR spectra of PSU-PDMS block copolymers evidenced a complete conversion of the Si-C linkages between the siloxane and polysulfone segments, by the disapperance of the Si-H absorbtion bands at 2120 cm^{-1} and the presence of a characteristic Si-phenyl band at 1430 cm^{-1} and a large band at 1100-1000 cm^{-1} for the Si-O-Si, which are not present in the IR spectra of PSU oligomers (Fig. 1).

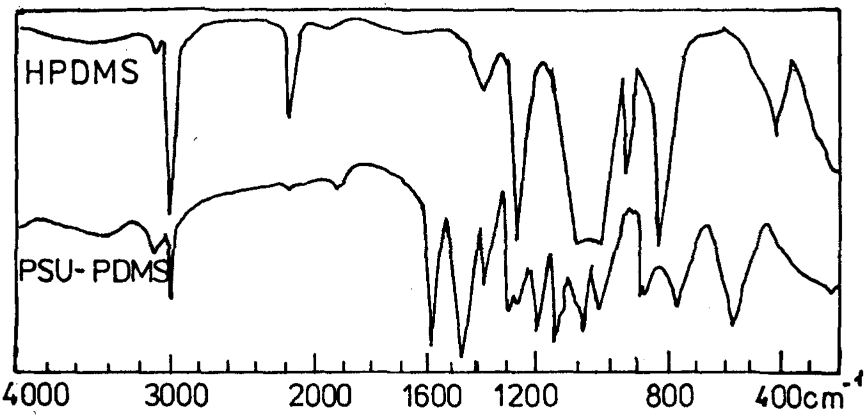


Figure 1. IR spectra of PSU - PDMS block copolymer and HPDMS

The molecular weight and molecular weight distribution of PSU-PDMS block copolymers were investigated by GPC. Molecular weight distribution were found to be monomodal and not bimodal as might be expected for a mixture of two oligomers.

The composition and siloxane content were determined from ^{1}H-NMR spectra from the ratio of relative areas of the methyl proton resonance of siloxane and aromatic proton resonance of PSU (Fig. 2).

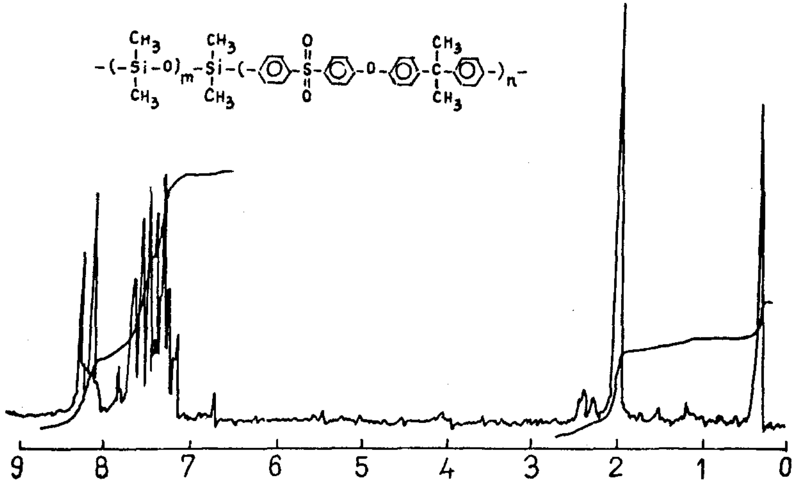


Figure 2. ^{1}H - NMR spectra of PSU - PDMS block copolymer.

Differential scanning calorimetry (DSC) was used to analyse microphase separation in the PSU-PDMS block copolymers. The results summarized in Table 4 provided some evidence for the formation of block copolymers. All the PSU-PDMS block copolymers showed a T_g at -122°C and evidenced of crystalization temperature T_c in the -98 °C, range which coresponds to that of the PDMS. A detectable T_g in the 143-168 °C range could be observed for the PSU phase only for the copolymers containing higher molecular weight PDMS-blocks (M_n =6500-12000) indicating better microphase separatioon with increasing PDMS content.

Table 4. Results of DSC analysis of PSU - PDMS during the second heating cycle.

Sample	PDMS			PSU
	T_g	T_c	T_m	T_g
I	- 122	- 94	-	-
II	- 122	- 96	-	143
III	- 122	- 96	-	143
IV	- 123	- 98	-	-
V	-	-	-	-
VI	- 123	- 97	- 50	149
VII	- 123	- 98	-	-
VIII	-	-	-	-
IX	- 123	- 98	-	168

The thermal stability of PSU - PDMS was studied by thermogravimetric analysis (TGA - DTA). The temperatures of % weight losses were determined from the original termogram as listed in Table 5.

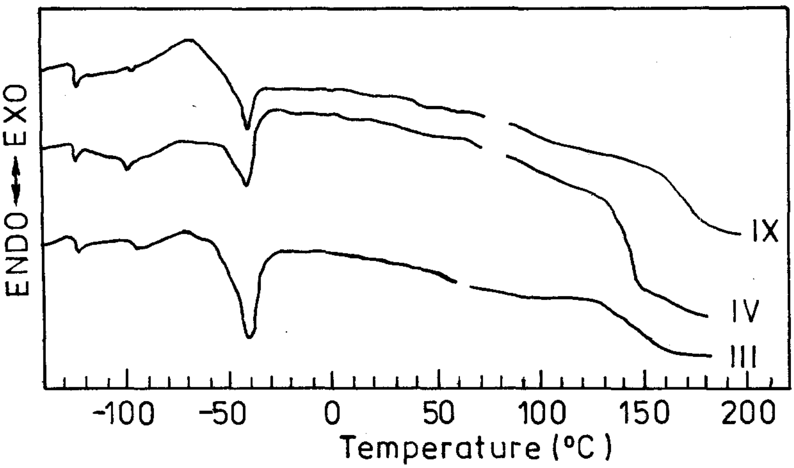


Figure 3. DSC traces of PSU-PDMS (III, IV, IX) run II

Table 5. TGA analysis of PSU - PDMS block copolymers.

Sample	Temperature (°C) for Various % to Decompose					E Kcal/mol	n
	5	10	20	30	50		
I	408	450	487	502	530	31.87 ± 0.32	0.4
II	394	452	490	502	536	34.46 ± 0.38	0.3
III	102	328	490	510	531	41.14 ± 0.37	0.4
IV	373	452	491	512	580	15.12 ± 0.06	0.5
V	147	366	438	469	523	18.57 ± 0.06	0.5
VI	412	441	482	511	573	24.86 ± 0.41	0.7
VII	154	223	447	482	546	21.92 ± 0.08	0.3
VIII	471	494	507	516	588	31.94 ± 0.41	0.5
IX	450	484	507	517	568	39.54 ± 0.31	1.2

The date of thermogravimetric analysis of PSU-PDMS block copolymers show an intermediate thermal stability between the values recorded with polysulfone and polydimethylsiloxane homopolymers (Fig. 4).

The thermal decomposition kinetics of the thermogravimetric weight loss data allows estimation of the activation energy E, as well as the reaction order *n* of the process from the Arrhenius relation, by Coats-Redfern method.

For PSU-PDMS (VI) block copolymers, for example, E=24.86 Kcal/mol and n= 0.7 between 407-528 °C, were obtained values lower than the kinetic data for the corresponding polysulfone: E=30.46 Kcal/mol and 0.4 respectively. The lower E value shows that the siloxane block influences the thermal process.

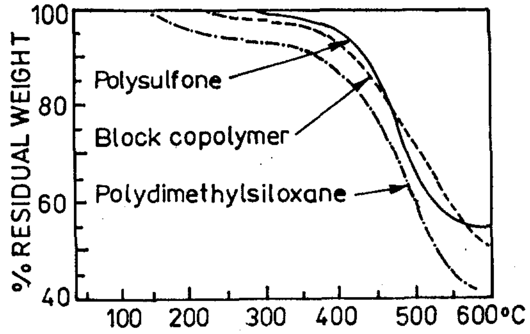


Figure 4. TGA of PSU-PDMS block copolymers and homopolymers (at 12 °C/min - in air).

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