# Polysulfone-Polydimethylsiloxane Block Copolymers Containing Si-O-C Bonds

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# POLYSULFONE-POLYDIMETHYLSILOXANE BLOCK COPOLYMERS CONTAINING Si-O-C BONDS

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## ABSTRACT

Polysulfone-polydimethylsiloxane block copolymers containing Si-O-C bonds were synthesized through the condensation reactions of α,ω-di(hydrogensilyl)polydimethyl-siloxane and α,ω-di(chlorosilyl) polydimethylsiloxane oligomers with hydroxy-terminated poly-sulfone, in solution.

The synthesized compounds were characterized using IR, ^{1}H-NMR and ^{13}C-NMR spectrometry, GPC and DSC analysis. All data agree with the proposed structures.

## INTRODUCTION

Various methods have been previously employed in order to synthesize multiphase perfectly alternating polysulfone-polydimethylsiloxane (PSF-PDMS) block copolymers [1-2].

The silylamine or hydride functionalized polydimethylsiloxane oligomers and polyethersulfone, with mutually reactive end groups by condensation or hydro-

silylation reactions, are usually used to prepare the desired copolymers heaving Si-O-C [3-7] and Si-C [8-10] intersegment linkages, respectively. Our recent reports [10] have described the synthesis of PSF-PDMS block copolymers with alternating $(AB)_n$ structure and $Si-(CH_2)_3-$ linkages via platinum catalyzed hydrosilylation reaction and by condensation of chloro-terminated polysulfone and $\alpha,\omega$-di(hydrogensilyl)-PDMS [11].

The poor hydrolytic stability of the Si-O-C bond was not evidenced for (PSF-PDMS) block copolymers of higher molecular weight segments [3, 6]. This was attributed to the random occurrence of Si-O-C linkages along the polymer backbone and the shielding of these linkages by hydrophobic PDMS segments [12]. The aim of this work was to find a new synthetic route to prepare strictly controlled alternating PSF-PDMS block copolymers with Si-O-C intersegment linkages, potentially improved hydrolytic and thermostability based on condensation reactions of hydroxy-telechelic polysulfone with more available difunctional silylchloride- and silylhydridedimethylsiloxane oligomers.

The obtained PSF-PDMS block copolymers with Si-O-C linkages are soluble in 1,2-dichlorobenzene, chloroform, THF. They were characterized by molecular weight (GPC), reduced viscosity (RV), IR, $^1$H-NMR, $^{13}$C-NMR, TGA and DSC analysis.


# EXPERIMENTAL


### Measurements

Number-average molecular weights (Mn), weight-average molecular weights (M$_W$) and molecular weight distributions were determined using a Gilson HPLC system (UV-detector; Gilson Medical Electronics Inc. Middleton, WI). THF at 1 ml/min flow rate and two Zorbax PSM-S (DuPont) bimodal columns calibrated for polystyrene standards were used to perform separation.

The reduced viscosities (RV) for precursors PSF oligomers and block co-pol-mers were determined in dichloroethane 0.2 g/dL solution at 25°C on an Ubbelohde viscometer. IR absorption spectra were obtained on a Perkin-Elmer 577 Spectrometer using KBr pellets. $^1$H-NMR and $^{13}$C-NMR were performed on a AC-80-Bruker Spectrometer with TMS as internal standard.

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 samples, at a heating rate of 20°/min under N$_2$. DTA and DTG

analysis were registered on a MOM Paulik-Paulik-Erdey derivatograph within a 20-600°C temperature range, in air, with 12°/min heating rate.

**Materials**

4,4'-Dichlorodiphenyl sulfone (Aldrich) was recrystallized from toluene. 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A, Fluka), was used as received. Dichloroethane and chlorobenzene (PhCl, Aldrich) were purified by fractional distillation under reduced pressure and dried over a type 4A molecular sieve. 1-Methyl-2-pyrrolidone (NMP, Aldrich) was vacuum distilled over phosphorus pentoxide. Dichlorodimethylsilane 99% purity (Fluka) was used as received. Octamethyl-cyclotetrasiloxane ($D_4$) and 1,1,3,3-tetramethyldisiloxane 97% purity was vacuum redistilled. Styrene divinilbenzene sulfonic acid copolymer (VIONIT CS-34C) was dried in vacuum at 90°C for 3% w/v water content. Piperydine was vacuum distilled over NaOH pellets and dibutyltin dilaurate was used as received.

**Synthesis of α,ω-Di(hydrosilyl)polydimethylsiloxane (HPDMS)**

Si-H ended polydimethylsiloxane oligomers (HPDMS) of desirable molecular weights were obtained by the "equilibration" reaction of organocyclo-siloxanes ($D_4$) with 1,1,3,3-tetramethyldisiloxane (TMDS) using VIONIT CS-34C (2-3%) H-form catalyst with water content of 3% w/v [13]. The HPDMS were characterized by molecular weights (viscosimetric, GPC and Si-H end groups analysis) as presented in Table 1.

**Synthesis of α,ω-Di(chlorosilyl)polydimethylsiloxane (ClPDMS)**

Dichlorosilyl ended polydimethylsiloxane (ClPDMS) oligomers were synthesized by the equilibration reactions of octamethylcyclotetrasiloxane ($D_4$) with 1,1,3,3-tetramethyl-1,3-dichlorodisiloxane (ClTMDS), as end capped, in the presence of a 2-3% dried copolymer styrene divinylbenzene sulfonic acid (VIONIT CS-34C), as catalyst under stirring for $2^{1/2}$ hours at 90°C. The products were characterized by molecular weights and end groups analysis (Table 1). Mn were determined by Si-Cl reactive end groups analysis [14] and GPC.

**Synthesis of α,ω-Hydroxy-terminated Polysulfone (PSF)**

Hydroxy-terminated polysulfone (PSF) oligomers were synthesized from the polycondensation of 4,4'-dichlorodiphenylsulfone and 2,2-bis(4-hydroxyphenyl) propane (Bisphenol A) in excess in anhydrous NMP promoted by the action of $K_2CO_3$ [15]. Their characteristics are listed in Table 2.

TABLE 1.  Characteristics of X-terminated PDMS (X = H, Cl)

| Sample code | X Content, % | | $Mn^a$ | $Mn^b$ | $Mn^c$ | $Mw^c$ | Mw/Mn | $\eta^{25}$ (cSt) |
|---|---|---|---|---|---|---|---|---|
| | H | Cl | | | | | | |
| PDMS-H | 0.067 | - | 3000 | 1245 | 1800 | 3440 | 1.91 | 21 |
| PDMS-Cl | | 1.865 | 3800 | 5900 | 3100 | 5200 | 1.67 | 64 |

a - Mn based on end groups data (Si-H and SiCl endgroups were determined by analytical quantitative methods [14] )

b - Mn based on viscosimetry data

c - GPC data

TABLE 2.  Characteristics of PSF

| Sample | $Mn^a$ | $Mn^b$ | $Mw^b$ | Mw/Mn | $RV^c$ | m.p.$^d$ (°C) |
|---|---|---|---|---|---|---|
| PSF-1 | 5000 | 3000 | 13300 | 4.43 | 0.014 | 149-160 |
| PSF-2 | 7600 | 4800 | 15400 | 3.19 | 0.118 | 165-170 |
| PSF-3 | 10700 | 2700 | 13000 | 4.81 | 0.163 | 180-200 |
| PSF-4 | 14650 | 5700 | 24100 | 4.22 | 0.217 | 191-210 |
| PSF-5 | 18700 | 6800 | 61200 | 9.0 | 0.259 | 214-220 |

a- Mn based on viscosimetry data was calculated using the following expression:
$[\eta]= 3.685 \times 10^{-4} \times M^{0.656}$, in solvent $C_2H_4Cl_2$.

b- Mn, Mw were determined  using GPC data in THF.

c- 0.2 g/dL solution in DMF

d- m.p. were measured with a Gallenkamp hot block melting-point apparatus.

## Synthesis of Polydimethylsiloxane-Polysulfone Block Copolymers (PSF-PDMS)

The PSF-PDMS block copolymers were synthesized from the conden-sation reactions of hydroxy-terminated PSF oligomers with hydrogen or chloro-terminated PDMS in dry 1,2-dichlorobenzene, catalyzed by dibutyltin dilaurate (1b) or piperidine (1a) (Scheme 1). The polysulfone was dehydrated by azeotropic

(a)

CH$_3$ CH$_3$
Cl—Si—O—Si—Cl    (ClPDMS)
CH$_3$ CH$_3$ $_n$

CH$_3$
HO—⟨⟩—C—⟨⟩—O—⟨⟩—SO$_2$—⟨⟩—O—⟨⟩—C—⟨⟩—H    (PSF)
CH$_3$   $_m$

(ClPDMS) + (PSF)  $\xrightarrow[\text{Bz-Cl, -HCl}]{\text{Piperidine}}$

CH$_3$ CH$_3$                              CH$_3$                      CH$_3$
→Cl—Si—O—Si—O—⟨⟩—C—⟨⟩—O—⟨⟩—SO$_2$—⟨⟩—O—⟨⟩—C—⟨⟩—O—H
CH$_3$ CH$_3$ $_n$    CH$_3$                      CH$_3$        $_m$ $_\alpha$
( PSF - PDMS )

(b)

CH$_3$ CH$_3$
H—Si—O—Si—H    (HPDMS)
CH$_3$ CH$_3$ $_n$

( HPDMS ) + ( PSF )  $\xrightarrow[\text{Bz-Cl}]{\text{Dibuthyltin dilaurate}}$

CH$_3$ CH$_3$                              CH$_3$                      CH$_3$
→ Cl—Si—O—Si—O—⟨⟩—C—⟨⟩—O—⟨⟩—SO$_2$—⟨⟩—O—⟨⟩—C—⟨⟩—O—H
CH$_3$ CH$_3$ $_n$    CH$_3$                      CH$_3$        $_m$ $_\alpha$
( PSF - PDMS )
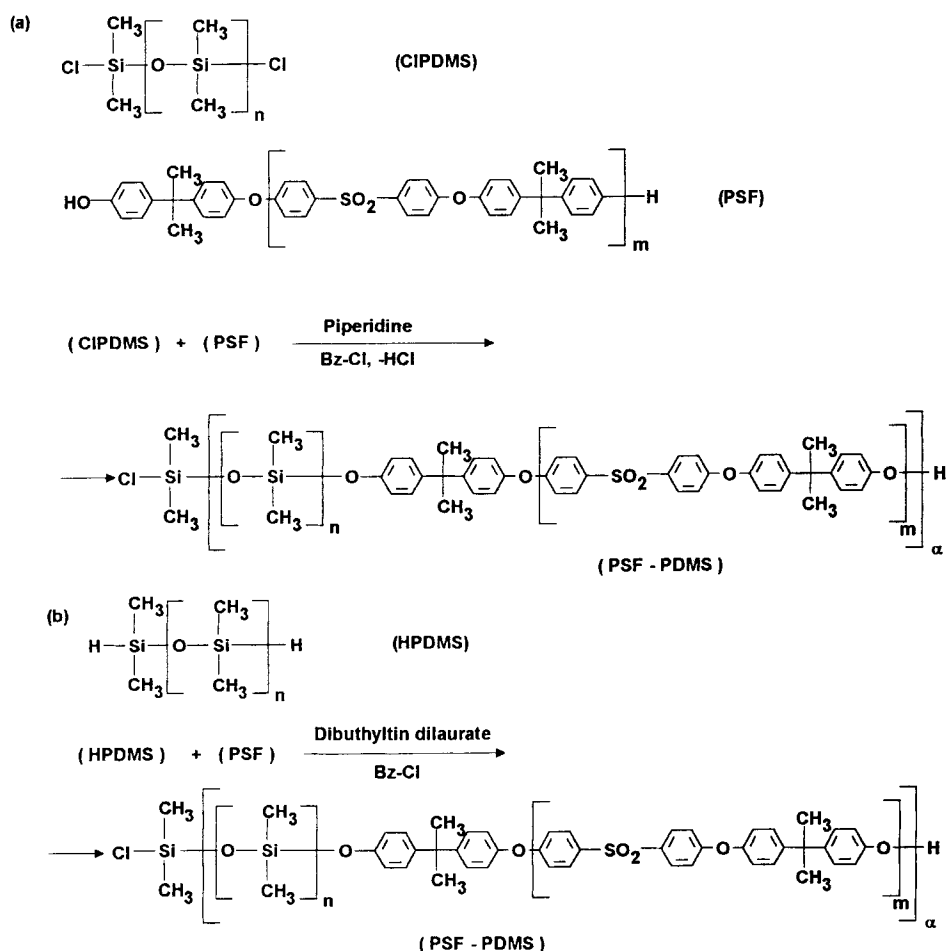
Reaction Scheme (1)

distillation before addition of the siloxane oligomers. The method is outlined as follows: a) 4g (0.37 mmole) of hydroxy-terminated PSF oligomer were charged along with 50 cm$^3$ of dry PhCl to a 250 ml reaction flask fitted with a dry nitrogen inlet, a mechanical stirrer, a thermometer, an addition funnel and Dean-Stark trap. The content of the reaction flask was heated, with stirring, until dissolution of the PSF was complete and a slow reflux was established. 10 cm$^3$ PhCl were then distilled off to complete dehydration of the system, and the temperature was adjusted to 90°C. 2 ml piperydine were added to the reaction flask. The system was then heated to 130°C, and 1.5g (0.39 mmole) of dichloro-terminated polydimethyl-

siloxane ( Mn = 3800) were added through the addition funnel in steadly decreasing increments over 150 min. in order to approach the stoichiometric end point gradually. After addition of the PDMS oligomer was complete the mixture was heated for a further 2 hours. The mixture was filtered to remove the piperydine clorohydrate. The olvent was then removed by heating the reaction mixture under vacuum to yield crude copolymer. The block copolymer was purified by removing of the unincorporated siloxane using an extensive extraction with petroleum ether in a Soxhlet extractor. The resulting product is a fluffy white-yellow polymer, soluble in several organic solvents. The characteristics of the synthesized block copolymers are listed in Table 3. b) The $\alpha,\omega$-di(Hydrogensilyl)polydimethysiloxane (HPDMS) was used in the condensation reactions with hydroxy-terminated PSF oligomers in presence of dibuthyltin dilaurate, as catalyst.

Into a 250 ml round bottom flask, equipped with a thermometer, nitrogen gas inlet, mechanical stirrer and dropping funnel, were placed 3.6g (0.72 mmole) of hydroxy-terminated PSF (Mn = 5000) and 50 mL chlorobenzene (PhCl). The mixture was heated and 10 ml PhCl - $H_2O$ azeotrope was distilled.

The temperature of the system was adjusted to 90-100°C and 1g dibuthyltin dilaurate was added. Then, the system was heated at 130°C, and stirred for 24 hours. The complete conversion of Si-H groups to Si-O-C linkages is controlled by the IR spectra of the reaction mixture. Then, the solvent was removed by heating the reaction mixture under vacuum to yield copolymer. The unreacted silicone was rigorously extracted with petroleum ether (30-60°C) in a Soxhlet extractor. Finally, the product is a soluble polymer in the several organic solvents. The characteristics of the synthesized block copolymers are listed in Table 3.

## RESULTS AND DISCUSSION

Two condensation reactions were developed for synthesis of PSF-PDMS block copolymers concerning the different end groups of the PDMS oligomers, as shown in Scheme 1a and 1b. The hydroxy-telechelic polysulfone oligomers can be reacted either with Si-Cl ended PDMS in a 1:1 molar ratio, in solution in presence of piperydine as HCl acceptor, either by Si-H ended PDMS catalyzed by dibuthyltin dilaurate. Similar (AB)$_n$ structures of PSF-PDMS block copolymers with perfectly alternating and well-defined polysulfone and siloxane blocks were obtained in both reactions.

The molecular weight of the siloxane precursors chlorosilyl- and hydrogensilyl-ended PDMS were controlled by the $D_4$/TMDS and $D_4$/ClTMDS ratio,

TABLE 3. The Characteristics of the Synthesized Block Copolymers

| Sample | Block size | | Siloxane [a] | PSU [a] | Mw | Mn | Mw/Mn | RV [b] | Tg [e] | |
| | PSF | PDMS | % (mole) | % (mole) | (GPC) | (GPC) | | | PSF-PDMS | PSF |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5000 | 3000[c] | 36.48 | 63.55 | 15600 | 5400 | 2.89 | 0.1359 | -123, 164 | 164 |
| 2 | 7600 | 3000 | 11.82 | 88.16 | 10500 | 3600 | 2.92 | 0.0909 | -123, 170 | 168 |
| 3 | 10700 | 3000 | 6.26 | 93.73 | 13500 | 3300 | 4.09 | 0.0882 | -123, 173 | 170 |
| 4 | 14650 | 3000 | 5.62 | 94.36 | 20900 | 10200 | 2.05 | 0.1158 | -123, 176 | 173 |
| 5 | 18700 | 3000 | 24.96 | 75.02 | - | - | - | 0.1144 | -123, 175 | 180 |
| 6 | 5000 | 3800[d] | 44.38 | 55.64 | 14000 | 3600 | 3.89 | 0.1366 | -122, 165 | 164 |
| 7 | 7600 | 3800 | 18.32 | 81.66 | 15000 | 4900 | 3.06 | 0.1827 | -122, 148 | 168 |
| 8 | 10700 | 3800 | 38.03 | 61.95 | - | - | - | 0.1167 | -122, 152 | 170 |
| 9 | 14650 | 3800 | 28.44 | 71.54 | 16200 | 5200 | 3.12 | 0.1917 | -122, 168 | 173 |
| 10 | 18700 | 3800 | 13.03 | 86.95 | 47400 | 6000 | 7.9 | 0.4251 | -122, 182 | 180 |

a - from $^1$H - NMR spectra;
b - 0.2 g/dL solution in dichloroethane at 25°C;
c - PDMS, H - reactive end groups;
d - PDMS, Cl - reactive end groups;
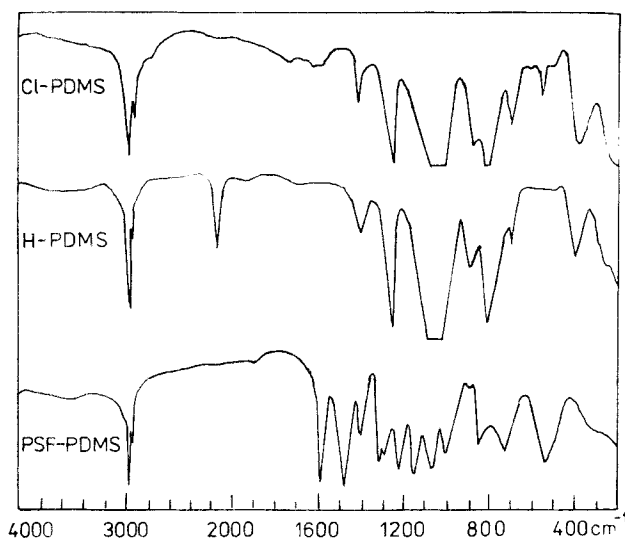e - Tg from DSC data (run II).

**Figure 1.**    IR  spectra  of  Cl-PDMS  oligomers  and  PSF-PDMS  block copolymers.

respectively . The average molecular weight Mn of the siloxane oligomers was determined by GPC and end groups analysis and are presented in Table 1. Homologous series of hydroxy-telechelic polysulfone oligomers with different molecular weights (Mn= 5000-20000) were prepared from 4,4'-dichloro-diphenylsulfone with a calculated excess of 2,2-bis(4-hydroxyphenyl)propane. The characteristics were presented in Table 2. The characteristics of synthesized PSF-PDMS block copolymers are presented in  Table 3.  The products of both reactions were established by a variety of techniques to be $(AB)_n$ block copolymers with Si-O-C linkages along the polymer backbone and not a simple physical blend.

The IR spectra of PSF-PDMS block copolymers showed a complete con-version of the Si-H and Si-Cl end groups to Si-O-C linkages between the siloxane and polysulfone segments by the disappearance of the characteristic absorption bands for Si-H at 2120 cm$^{-1}$, respectively for Si-Cl at 585 cm$^{-1}$ and 520 cm$^{-1}$ and the presence of a characteristic band for Si-O-C at 965 cm$^{-1}$ and a large band at 1100-1000 cm$^{-1}$ for the Si-O-Si linkages, which are not present in the IR spectra of PSF oligomers (Figure 1).

Compositional and structural composition information on the PSF-PDMS block copolymers was obtained using the ^{1}H-NMR and ^{13}C-NMR analysis. By [1]H-
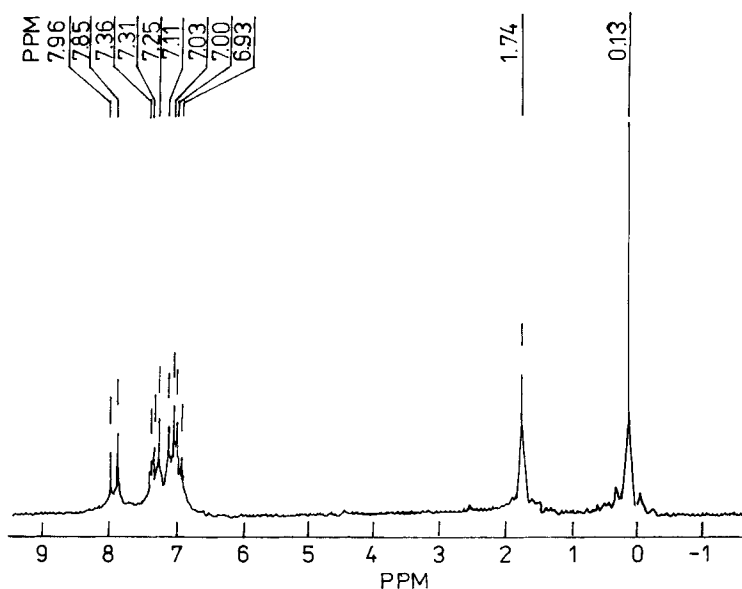
**Figure 2.**     ¹H-NMR spectra of PSF-PDMS block copolymer.

NMR analysis was determined the composition and the relative block size of the block copolymers from the ratio of the peak intensities of PDMS methyl proton resonance at 0.13 ppm and the aromatic protons of the PSF at 7.95-6.93 ppm (Figure 2). The expected $(AB)_n$ structure was also confirmed. The ¹³C-NMR spectrum of PSF-PDMS block copolymers is shown in the Figure 3. This spectrum has been used to identify the peaks of the methyl Si-methylcarbon atoms and the Si-O-phenyl carbon atoms. The carbon atoms of the Si-O-Ph at the end of the block copolymer resonate apart from internal blocks. The molecular weights of the pre-cursors oligomers and block copolymers PSF-PDMS were determined using GPC analysis. Molecular weight distribution was found to be monomodal and not bimodal as might be expected for a mixture of two oligomers (Figure 4).

Differential scanning calorimetry (DSC) was used to investigate the micro-phase separation in the block copolymers. The PSF-PDMS block copolymers appear to display a two-phase morphology (Figure 5). This is to be expected as the tendency for microphase separation in a block copolymer which is directly pro-portional to the difference in the solubility parameters of the blocks PSF/PDMS ($\delta$ = 21.7 and 14.7). The PSF-PDMS block copolymers showed one $T_g$ at -123 °C which is identical to that of the PDMS precursor oligomers and the second $T_g$ is
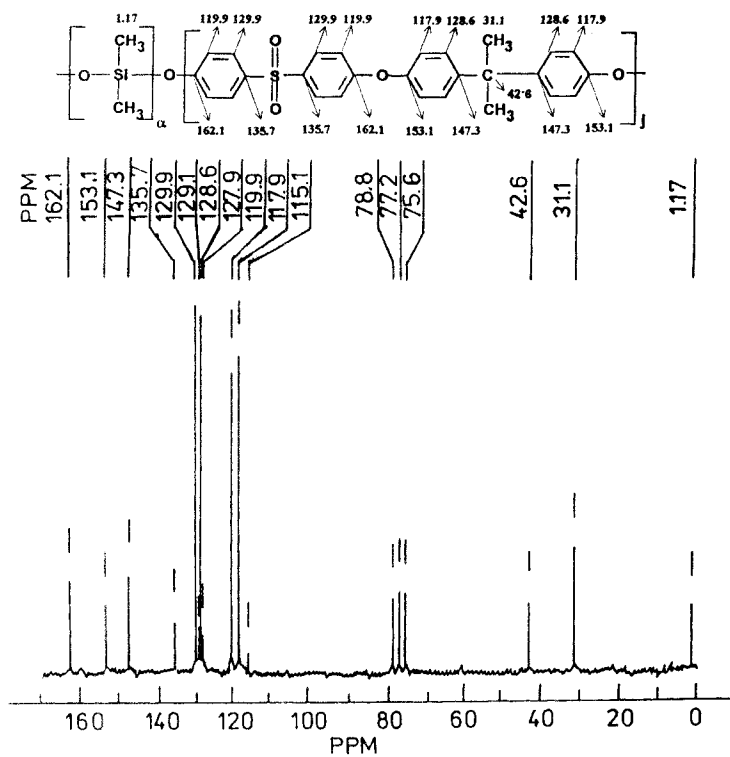
**Figure 3.** $^{13}$C-NMR spectra of PSF-PDMS in CDCl$_3$.
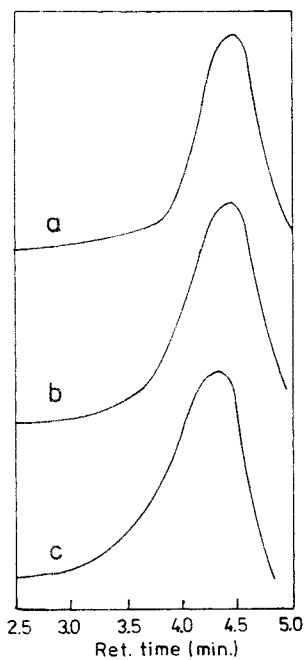


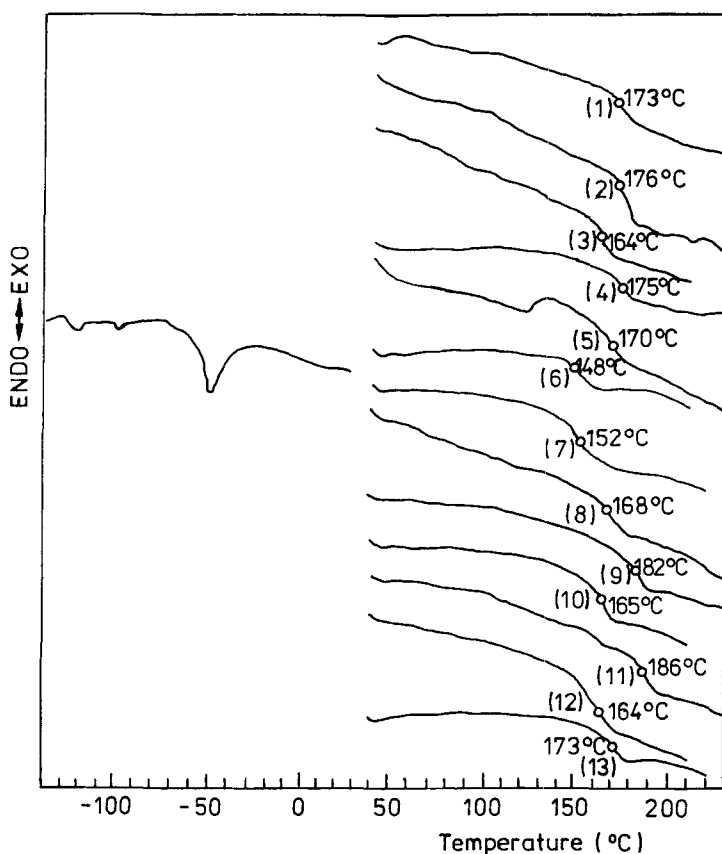**Figure 4.** GPC traces for Cl-PDMS (a), H-PDMS (b) and PSF-PDMS (c)

**Figure 5.** DSC traces of PSF-PDMS block copolymers (run II ).

observed for all samples in the temperature range 150-180°C and corresponds to the PSF oligomers.

The thermal stability of the PSF-PDMS block copolymers was studied by thermogravimetric (TGA) and differential thermal (DTA) analysis. The samples were heated at a constant temperature rate of 12°/min. in air. The initial decomposition temperatures and the temperature % weight loss were determined from the thermograms and are listed in Table 4.

## CONCLUSIONS

Polysulfone-polidimethylsiloxane block copolymers (PSF-PDMS) with Si-O-C intersegment linkages were prepared by condensation reactions of hydroxy-

TABLE 4.  TGA Analysis of PSF-PDMS Block Copolymers.

| Sample | IDT* (°C) | TGA temperature (°C) for various % decompositions | | | | |
|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 |
| $P_1$ | 185 | 425 | 464 | 488 | 532 | 578 |
| $P_2$ | 368 | 482 | 500 | 512 | 522 | 560 |
| $P_3$ | 140 | 444 | 469 | 523 | 578 | 595 |
| $P_4$ | 158 | 471 | 498 | 512 | 543 | 597 |
| $P_5$ | 168 | 413 | 472 | 498 | 544 | 570 |
| $P_6$ | 173 | 439 | 483 | 502 | 515 | 548 |
| $P_7$ | 275 | 450 | 489 | 506 | 530 | 573 |
| $P_8$ | 152 | 336 | 433 | 482 | 508 | 521 |
| $P_9$ | 108 | 430 | 482 | 503 | 518 | 530 |
| $P_{10}$ | 152 | 456 | 496 | 510 | 521 | 572 |

* - IDT (°C) is the initial decomposition temperature determined from original thermograms (1% weight loss).

telechelic polysulfone with Si-H or Si-Cl terminated polydimethylsiloxanes in Bz-Cl catalyzed by dibuthyltin dilaurate or piperidine.  The PSF-PDMS block copolymers were characterized by GPC, IR, ^{1}H-NMR, ^{13}C-NMR and DSC analysis. The block copolymers were found to display microphase separation.  The TGA data indicate a better thermal stability for the synthesized PSF-PDMS block copolymers.

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