Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Butuc, E. , Cozan, V. , Giurgiu, D. , Mihalache, I. , Ni, Yushan and Ding, Mengxian(1994) 'Modified Polysulfones. I. Synthesis and Characterization of Polysulfones with Unsaturated end Groups', Journal of Macromolecular Science, Part A, 31: 2, 219 — 230

To link to this Article: DOI: 10.1080/10601329409349729

URL: http://dx.doi.org/10.1080/10601329409349729

J.M.S.—PURE APPL. CHEM., A31(2), pp. 219–230 (1994)

MODIFIED POLYSULFONES. I. SYNTHESIS AND CHARACTERIZATION OF POLYSULFONES WITH UNSATURATED END GROUPS

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ABSTRACT

Chloro-terminated polysulfones with various molecular weights were modified with poly(ethylene oxide) and poly[(ethylene oxide)-(propylene oxide)] macromers carrying α-hydroxyl and ω-allyl end groups via classical polycondensation reactions. The properties of modified polysulfones are compared with the unmodified ones, and an increase in hydrophilicity of the former materials was observed.

INTRODUCTION

In recent years many investigations have been done on the synthesis, curing, and characterization of reactive end-capping oligomers and polymers [1–4]. Indeed, oligomers with terminal groups that undergo thermally induced crosslinking or chain extension reactions without evolving volatile by-products are good precursors for high performance polymers and composite matrices. According to this concept and because of their good thermal and chemical stability, aromatic ether oligomers have been widely studied as main-chain polymers. They have been end-capped with nadimide [5], cyanato [6], ethynyl [7, 8], and vinyl [9] groups. With low or moderate molecular weight, they provide better solubility and a lower softening point, allowing better processibility than their high molecular weight thermoplastic homologs. After cure, they provide crosslinked materials where T_g, mechanical properties, and solvent resistance improvements are expected [10].

Ethynyl and vinyl end-capped polyaromatic ethers are good candidates as reactive oligomers [9, 11, 12]. The ethynyl and vinyl end groups are introduced by the reaction of an end-capping agent, such as 4-ethynylbenzoyl chloride, and *p*-chloromethylstyrene with a hydroxy-terminated aromatic polyether [9, 13], respectively. As reported [14], the allyl-ether function was chosen for some synthesis because of an expected improvement in the solubility and in order to use the products obtained for building new amphiphilic polymers.

The application of polysulfones (PSF) in obtaining membranes is restricted by their hydrophobicity and poor solubilities in dipolar aprotic solvents: *N*-methyl-2-pyrolidone (NMP), dimethylsulfoxide (DMSO), dimethylformanide (DMF). For these reasons we have taken an interest in the chemical modification of polysulfones.

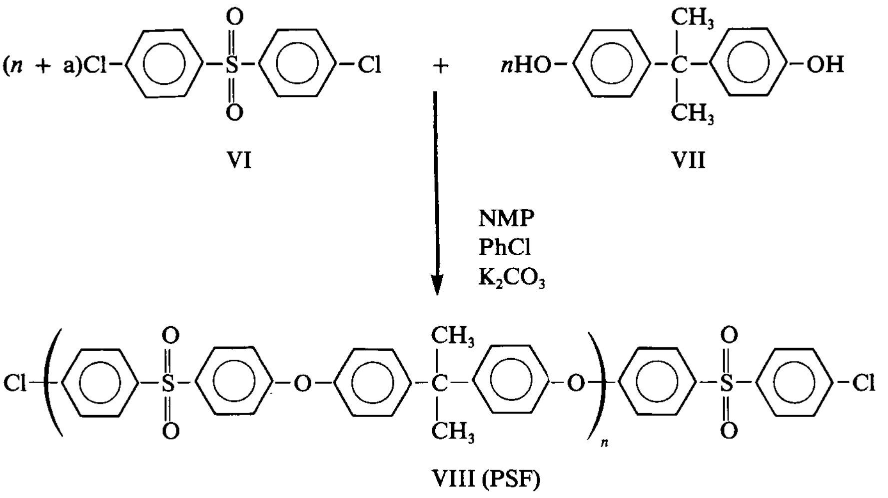
The purpose of this work is to present the one/two step synthesis of α,ω-diallyl-PEO-PSF (IX) and α,ω-diallyl-PEO-PPO-PSF (X) by condensing allyl-PEO-OH (IV) and allyl-PEO-PPO-OH (V) with 4,4′-dichlorodiphenyl sulfone (VI) and Bisphenol A (VII) (one-step synthesis, Scheme 3) or with chlorine-terminated polysulfone oligomers (VIII) (two-step synthesis, Schemes 1 and 2).

The modified polysulfones were characterized by elemental analyses, softening points, and reduced viscosities. Their structures were confirmed by IR and ^{1}H-NMR spectra. TGA data were used to compare the thermal stability of samples. Glass transition temperatures were obtained using DSC measurements. Water contact angles of modified polysulfones were measured to show any increase in their hydrophilicity.

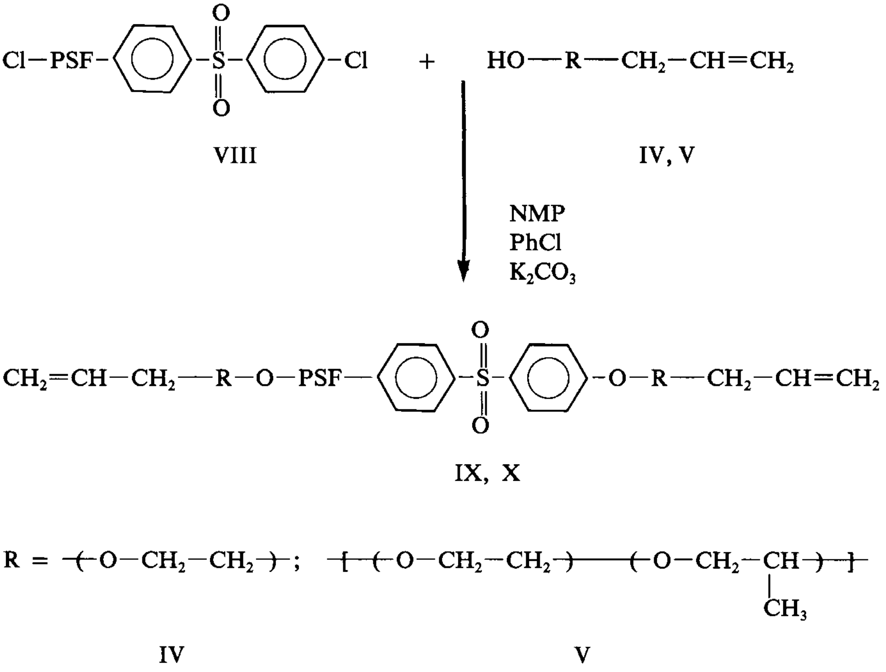
EXPERIMENTAL

Measurements

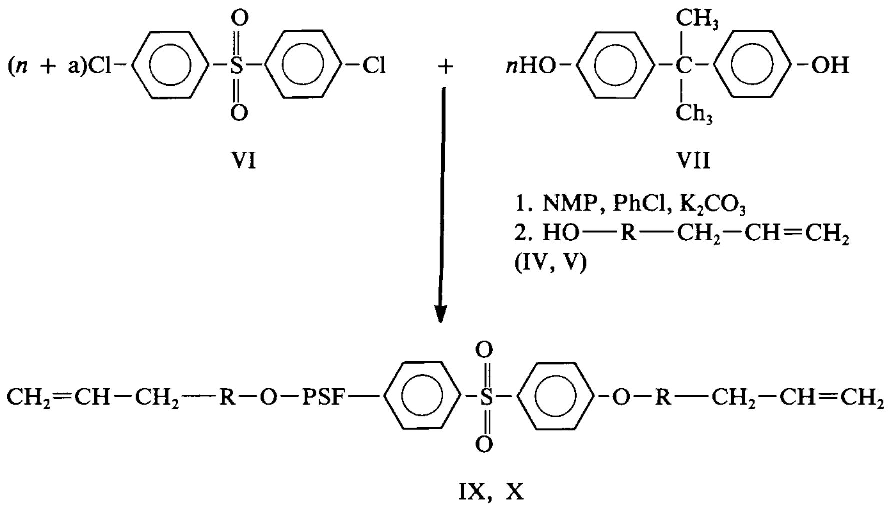
The IR spectra were recorded on a Specord M80 Carl Zeiss, Jena Spectrophotometer using the KBr pellet technique. Proton NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 50°C in $CDCl_3$ using TMS as the internal reference. The reduced viscosities of polymer solutions (0.2% w/v) in NMP were determined at 25°C by using an Ubbelohde Suspended Level Viscometer. The number-average molecular weights of polymers were determined by vapor-phase osmometry with a



SCHEME 1.



SCHEME 2.



SCHEME 3.

Knauer model 1974 osmometer using chloroform at 41 °C as solvent. The solubilities of modified polysulfones were examined using 0.1 g polymer in 1–2 mL solvent at room temperature. The melting and softening points were measured using a Gallenkamp hot-block melting-point apparatus. Thermogravimetric curves were obtained in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calorimetry (DSC) was carried out in air with a Perkin-Elmer 7 Series Thermal Analysis System at a heating rate of 20°C/min. Water contact angle measurements were carried out with an Erma Optical Works apparatus.

Reagents and Materials

4,4′-Dichlorodiphenyl sulfone (Aldrich) was recrystallized from toluene. 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A, Fluka) was used as received. NMP was

TABLE 1. The Characteristics of End-Capping Agent Macromers (IV, V) [15]

Macromer no.	$\overline{M}_n$[a]	I_{OH},[b] mg KOH/g	UD,[c] meq KOH/g	Viscosity,[d] cP
IV	1000	40.20	1.00	–
V	2850	31.75	0.35	347

[a] $\overline{M}_n$ was calculated by the formula $\overline{M}_n = 1000x/\mathrm{UD}$, where x = number of unsaturated end groups per macromolecule.

[b] I_{OH} = hydroxyl number determined by using a titration method.

[c] UD = unsaturation degree, determined by ^{1}H-NMR.

[d] Determined at 25 °C by using a Höppler viscometer.

TABLE 2. The Properties of the Unmodified PSF (VIII) and the Corresponding Modified Ones (IX, X)

Unmodified PSF				Modified PSF			
Polymer no.	$\overline{M}_n$[a]	Softening point, °C	η_{red},[b] dL/g	Polymer no.	Softening point, °C	η_{red},[b] dL/g	Conversion,[c] %
					Two-Step Synthesis		
VIII 1	38,000	246–248	0.49	X 1	149–152	0.31	100
VIII 2	36,900	205–209	0.41	X 2	178–182	0.28	67
VIII 3	31,400	–	0.37	X 3	178–181	0.17	88
VIII 4	20,400	–	0.27	X 4	203–205	0.17	52
VIII 5	16,000	168–172	0.24	X 5	199–210	0.32	32
VIII 6	5,100	110–115	0.09	X 6	129–133	0.16	24
				IX 1	95–97	0.14	100
					One-Step Synthesis		
				X 7	165–170	0.17	
				X 8	176–179	0.31	
				IX 2	102–104	0.27	

[a] Calculated from osmometric and viscometric measurements.

[b] Measured at a concentration of 0.2 g/dL in NMP at 25°C.

[c] The conversion was calculated from the chlorine content.

vacuum distilled over phosphorus pentoxide. Chlorobenzene (PhCl) (Aldrich) was used as received. Potassium carbonate was dried in vacuum before use.

Synthesis of Allyl-PEO-OH (IV) and Allyl-PEO-PPO-OH (V) Macromers

These macromers were prepared by anionic polymerization of ethylene oxide (II) or of II with propylene oxide (III) in the presence of allyl alcohol (I), as described in the literature [15]. Their characteristics are listed in Table 1.

Synthesis of Chloro-Terminated Polysulfone Oligomers (VIII)

Various chloro-terminated polysulfones (VIII) were prepared from the reaction of Bisphenol A with an excess of 4,4′-dichlorodiphenyl sulfone as described in the literature [16]. Their characteristics are listed in Table 2.

Synthesis of α,ω-Diallyl-PEO-PSF (IX) and α,ω-Diallyl-PEO-PPO-PSF (X)

The chloro-terminated polysulfones of various molecular weights (VIII) were modified into α,ω-diallyl-PEO-PSF (IX) and α,ω-diallyl-PEO-PPO-PSF (X), respectively, as follows: a flask fitted with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and stirrer was charged with 10 g macromer (IV, V), 60 mL

TABLE 3. Elemental Analysis of Polymers VIII, IX, and X

Polymer no.	S, %		Cl, %, Found
	Calculated	Found	
VIII 1	7.23	6.54	0.20
VIII 2	7.28	7.10	3.91
VIII 3	7.28	6.09	4.58
VIII 4	7.30	7.33	2.54
VIII 5	7.32	6.56	1.35
VIII 6	7.14	6.26	2.62
IX 1	5.85	5.35	0
IX 2	5.57	6.07	0.56
X 1	5.20	5.57	0
X 2	6.56	6.53	1.29
X 3	6.56	6.04	0.97
X 4	6.56	6.36	1.22
X 5	6.56	7.29	0.91
X 6	6.56	7.28	1.98
X 7	6.56	6.89	0.78
X 8	6.56	6.84	1.41

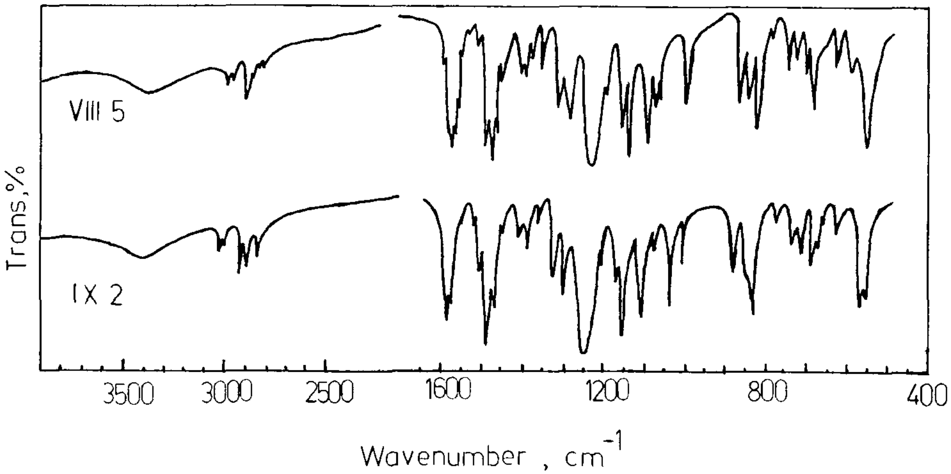


FIG. 1. The IR spectra of unmodified PSF (VIII 5) and modified PSF (IX 2).

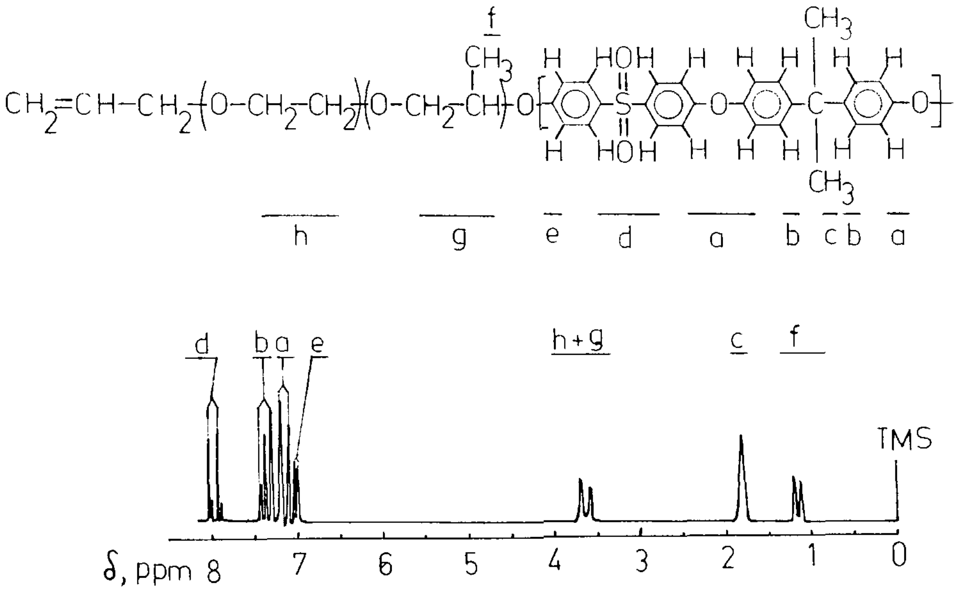


FIG. 2. The ^{1}H-NMR spectra of modified PSF (X).

NMP, and 60 mL PhCl. The system was continuously purged with dry nitrogen, slowly heated to 130–140°C to remove the moisture, and then cooled to about 100°C to add 10 g potassium carbonate anhydrous. The system was reheated to 140°C and maintained for about 2 hours (or as necessary) to distill all the water expected stoichiometrically into the trap. Sufficient PhCl was removed to increase the bath temperature to 150–155°C. Chloro-terminated polysulfone oligomer (30 g) (VIII) dissolved in 70 mL PhCl was added to the flask as fast as possible. PhCl was distilled to maintain the reaction temperature between 150 and 155°C for 3 hours. Then the temperature was raised to 180°C and maintained for 4 hours while PhCl

TABLE 4. The ^{1}H-NMR Protons Intensities Ratios (r)

Polymer no.	r
X 1	7.3
X 2	5.7
X 3	5.2
X 4	11.5
X 5	4.5
X 6	4.9
X 7	2.7
X 8	3.8
IX 2	1.2

TABLE 5. The Thermal Properties of Polysulfones VIII, IX, and X

Polymer no.	TGA temperature (°C) for various % decompositions 10	20	30	40	50	T_g,[a] °C
VIII 1	490	500	510	518	550	188
VIII 2	490	505	515	540	590	182
VIII 3	460	488	500	540	585	–
VIII 4	482	496	503	512	545	–
VIII 5	440	488	510	520	533	–
VIII 6	265	482	510	520	530	–
IX 1	342	392	426	483	512	73
IX 2	385	419	475	504	520	68
X 1	415	470	487	502	544	87
X 2	452	503	518	527	552	114
X 3	402	464	485	508	552	107
X 4	430	475	490	507	555	155
X 5	400	480	509	525	560	108
X 6	400	490	509	520	535	105
X 7	376	460	500	518	533	99
X 8	375	490	510	525	540	107

[a]DSC measurements in air.

was removed from the trap. The mixture was allowed to cool and then filtered to remove the inorganic salts. The solution is coagulated in a high-speed blender containing methanol at a v/v 7/1 ratio. The precipitate was filtered, washed with water and hot methanol, and finally dried in a vacuum oven at 80°C for 20 hours.

The characteristics of the modified polysulfones (IX, X) are listed in Table 2.

One-Step Synthesis of α,ω-Diallyl-PEO-PSF (IX) and α,ω-Diallyl-PEO-PPO-PSF (X)

Bisphenol A, 0.10 mol (22.83 g) (VII), 0.18 mol (31.82 g) 4,4′-dichlorodiphenyl sulfone (VI), and 0.2 g + 15% potassium carbonate anhydrous were charged with 100 mL NMP and 100 mL PhCl in a 500-mL three-neck flask equipped as described above. The system was purged with dry nitrogen for 10 minutes. The solution was heated at 155°C for 8 hours. During this time, PhCl-H_2O azeotrope was collected in the trap. Then the temperature was raised to 180°C. After 5 hours, PhCl was drained, and the temperature was increased to 187°C for 2 hours. The reaction mixture was then cooled to 140°C, and 20 g of end-capping agent (IV, V) was added in 30 mL PhCl. The reaction was continued at 140–150°C for 4 hours while PhCl was removed from the trap. The mixture was allowed to cool and then filtered to remove the inorganic salts. The solution was coagulated into a large excess of MeOH. The resulting polymer was filtered, washed with water and MeOH, and finally dried in vacuum at 80°C for 12 hours. A typical synthesis gave a yield of 97–99%.

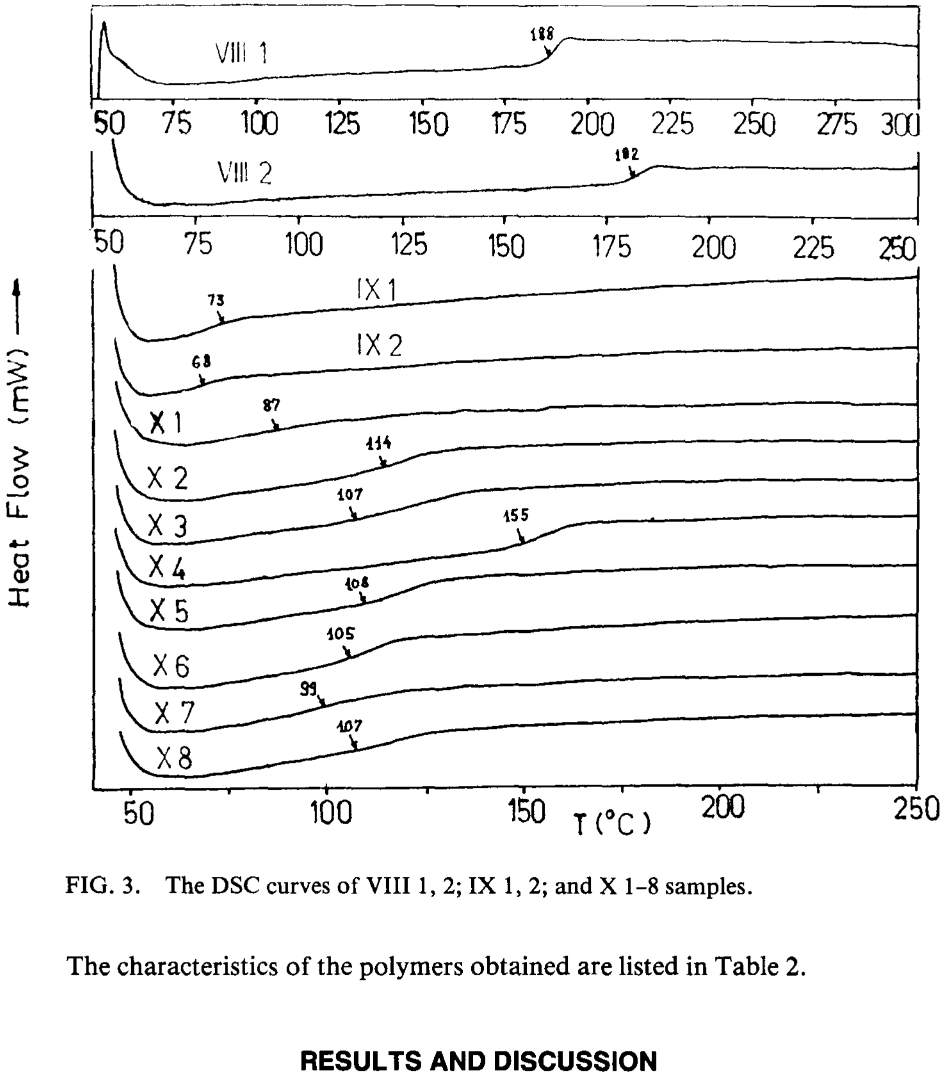


FIG. 3. The DSC curves of VIII 1, 2; IX 1, 2; and X 1-8 samples.

The characteristics of the polymers obtained are listed in Table 2.

RESULTS AND DISCUSSION

Modified α,ω-diallyl-PEO-PSF (IX) and α,ω-diallyl-PEO-PPO-PSF (X) were obtained in two-step (Schemes 1 and 2) and one-step syntheses (Scheme 3). In the last case the excess of aromatic dihalide and Bisphenol A in the presence of NMP, PhCl, and potassium carbonate was allowed to react, leading to chloro-terminated PSF which was then condensed with end-capping agents (IV and V) and the reaction was continued until completion, leading to modified PSF (IX and X). In this way only one treatment and purification step was required, limiting the operation and the solvent amounts used. This constitutes a more direct and less expensive route than the previously related one. Elemental analyses of the IX and X sample series (Table 3) showed good agreement in the %S content with the exception of the VIII 3, X 5, and X 6 samples. In the case of the VIII 3 sample, we suppose that this disagreement in the %S content could be due to an incomplete purification of the sample. Concerning the X 5 and X 6 samples, we think that the small difference in

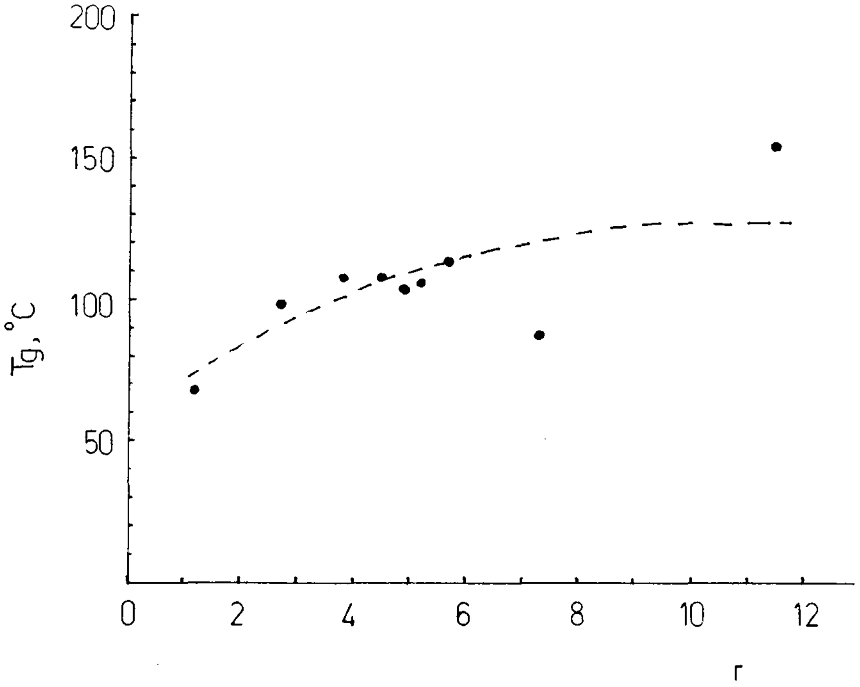


FIG. 4. The variation of T_g versus r for modified PSF (IX, X).

TABLE 6. The Water Contact Angle (α°) of Modified Polysulfones IX and X

Polymer no.	Modified PSF	Mixture[b] (water α = 10°; 21°)
X 1	81	70; 59; 64.5[a]
X 2	Brittle	72
X 3	Brittle	70; 75; 73; 73[a]
X 4	82	71
X 5	15; 16	78; 65; 71[a]
X 6	47	
X 7	Brittle	Brittle
X 8	75 (thin); 66	Brittle
IX 1	78; 76	77
IX 2	76; 75	
VIII 1	84; 88; 77; 73 (thin)	

[a] Average value.

[b] Mixtures of modified PSF (IX, X) with unmodified PSF (VIII 1).

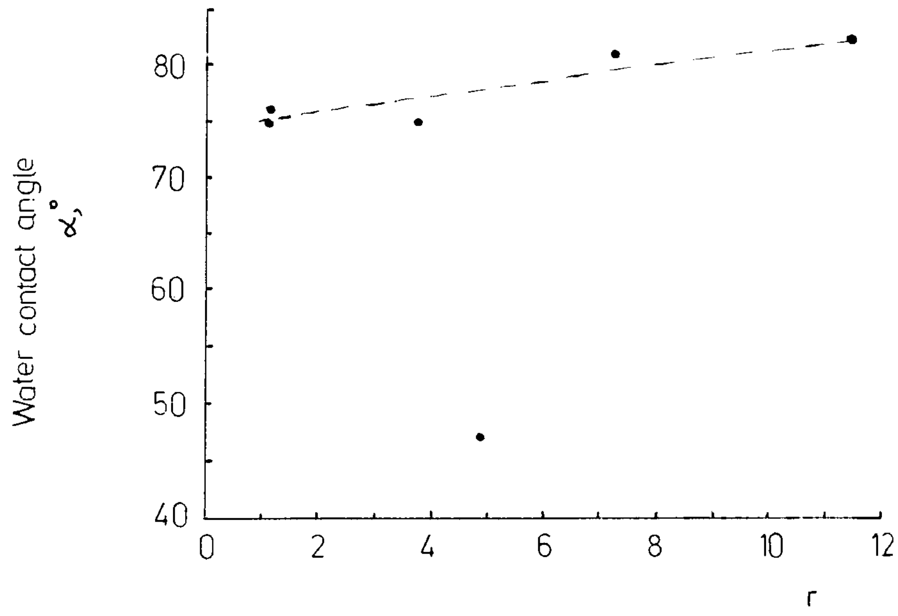


FIG. 5. The variation of water contact angle ($\alpha°$) versus r in the IX, X sample series.

the %S content could be attributed to the low conversion of polymers VIII 5 and VIII 6, respectively; this fact is confirmed by the unexpected increase of the reduced viscosities of the X 5 and X 6 samples. Concerning the reduced viscosity of modified PSF (IX, X) versus the unmodified ones (VIII) (Table 2), a decrease of η_{red} values was observed with the exception of the X 5 and X 6 samples. The decrease of the η_{red} values is possibly due to the plastifying effect of the ether-aliphatic chains. The increase of η_{red} values for the X 5 and X 6 samples versus the VIII 5 and VIII 6 ones is possibly due to the higher reactivity of the latter ones.

The IR spectrum (Fig. 1) of the modified PSF (IX 2) showed the appearance of the characteristic absorption of aliphatic-ether groups at about 1040 cm^{-1}. Both the unmodifed PSF (VIII 5) and the modified one (IX 2) showed the absorptions at 1330 and 1155 cm^{-1} assigned to the SO_2 groups.

The ^{1}H-NMR spectra showed resonance signals of the phenyl, $-CH_2-\overset{|}{CH}-O-$ (g), $-CH_2-CH_2-O-$ (h), $CH_3-\underset{|}{\overset{|}{C}}-CH_3$ (c), and $-CH_3$ (f) protons of relative intensities corresponding to the number and type of protons (Fig. 2). We calculated the ratios (r) of the protons intensities: aromatic (PSF)/aliphatic (PEO-PPO); values are listed in Table 4.

All the modified polysulfones showed very good solubility in dipolar aprotic solvents such as NMP and DMSO.

The thermal stabilities of PSF (VIII, IX, X) were evaluated by TGA in air at a heating rate of 12°C/min (Table 5). The temperature for 10% weight loss (T_{10}) is considered to be the polymer decomposition temperature and is used for comparing the thermal stabilities of different polymers. The modified PSF (IX, X) presented expected lower T_{10} values than the unmodified PSF ones (VIII), except for the X 6 sample which is higher than VIII 6.

DSC measurements showed a single glass transition temperature (T_g) in the range of 68 to 188°C, indicating a single-phase morphology (Fig. 3, Table 5). The T_g values of modified PSF (IX, X) (Fig. 4) showed a decrease as the content of ether-aliphatic chains increased. This fact could be due to an increase of the flexibility of the macromolecules.

Water contact angle ($\alpha°$) values are listed in Table 6. They show a decrease with a decrease of r (Fig. 5), proving an increase of the hydrophilic character of the modified PSF obtained.

CONCLUSIONS

Chloro-terminated polysulfones (PSF) were modified with poly(ethylene oxide) and poly[(ethylene oxide)-(propylene oxide)] macromers carrying α-hydroxyl and ω-allyl end groups via classical polycondensation reactions. Good improvement in their hydrophilicity and solubility in aprotic dipolar solvents (NMP, DMSO) was obtained.

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Received January 11, 1993
Revision received April 6, 1993