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Chemical Modification of Polysulfones by Bisphenolic Copper Chelates

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Chloro-terminated polysulfones with various molecular weights were chemically modified with bis(2,4-dihydroxybenzaldehyde)copper(II). The properties of modified polysulfones are compared with the unmodified ones, and an increase in glass transition temperatures, softening points and reduced viscosities of the former materials was observed. In addition, the chelate-modified polymers exhibited excellent thermal stability properties and semicrystalline patterns. Also, they provided transparent and flexible films. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The development of new chelate polymers has been of great interest due to their thermal stability, electrical conductivity and catalytic action, mainly in some of the chemical reactions occurring in biological materials.[1–3] Yet considerable difficulty has been reported in utilizing their excellent properties due to the insolubility of the chelate polymers, which hinders their incorporation into useful devices.

Coordination polymers prepared in early work were insoluble and high-molecular-weight products were not obtained since precipitation from solution occurred at an early stage. However, the interest in these materials continued.[4–7]

Some of these problems could be avoided if the chelate moieties were covalently incorporated into polymer systems, especially in thermo-oxidatively stable polymers. The introduction of chelate units on the polymer chain could lead to new electrical and optical characteristics, to improved mechanical properties and to heat resistance. The potential applications of chelate polymers are, for example, as surface coatings on metals and glasses, adhesives, high-temperature lubricants, electrical insulators, semiconductors.[8]

However, the application of the chelate polymers is restricted by their low molecular weight and insolubility. In contrast polysulfone is one of the useful high-performance engineering thermoplastics with high molecular weights that can be processed by conventional molding and solution casting techniques. For these reasons we have taken an interest in the chemical modification of polysulfones by bisphenolic chelates.

The present paper describes the synthesis and characterization of some bisphenol A-based polysulfones bearing chelate units in the polymer main chain. The chelate-modified polysulfones were synthesized from chloro-terminated polysulfones and the sodium salt of bis(2,4-dihydroxybenzaldehyde)Cu^{2+} by polycondensation reaction. The effect of the incorporation of bisphenolic chelate moieties on the properties of the resulting polymers is discussed.

EXPERIMENTAL

Materials

4,4′-Dichlorodiphenylsulfone (Aldrich) was recrystallized from toluene. 2,2-Bis(4-hydroxyphenyl)-propane (Bisphenol A, Fluka), 2,4-dihydroxybenzaldehyde (Fluka), dichloromethane (Aldrich), chlorobenzene (Aldrich) and dimethyl sulfoxide (Aldrich) were used as received. *N*-Methyl-2-pyrrolidone (NMP) was vacuum-distilled over phosphorus pentoxide. Anhydrous potassium carbonate was dried in a vacuum oven before use.

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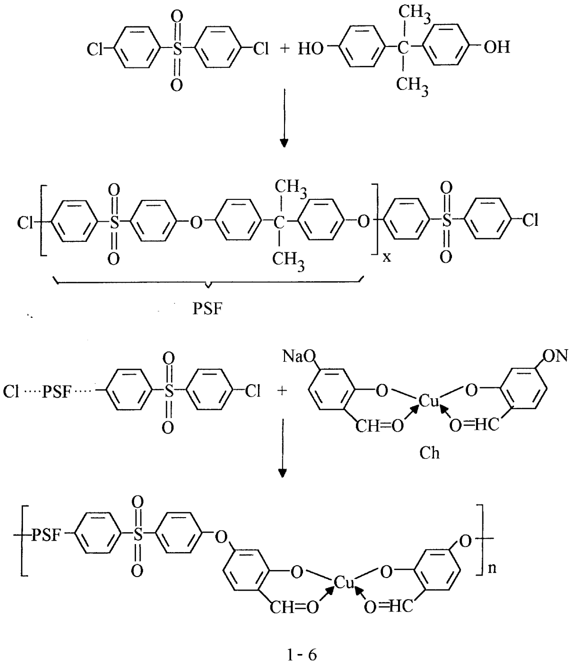
Syntheses

Chloro-terminated polysulfones (PSFs) were prepared from the reaction of bisphenol A with an excess of 4,4′-dichlorodiphenylsulfone in the presence of anhydrous potassium carbonate as described in the literature.[9,10] Bis(2,4-dihydroxybenzaldehyde)Cu^{2+} and its sodium salt were obtained according to previously reported procedures.[11,12]

Chelate-modified polysulfones (PSF–Ch**1**–**6**) were prepared by reacting a solution of chloro-terminated polysulfone (5 g) in dichloromethane with a solution of the sodium salt of the bisphenolic copper complex (Ch in scheme 1, below; 0.5 g) in dimethyl sulfoxide. The resulting homogeneous reaction mixture was firstly maintained at room temperature for 5 h under stirring and then was heated at 35 °C for 8 h. The mixture was allowed to cool and filtered to remove the inorganic salts. The solution was then coagulated in a high-speed blender containing methanol in a 1:7 (v/v) ratio. The precipitate was filtered, washed with water and methanol, and finally dried in a vacuum oven at 50 °C for 24 h.



Scheme 1 Preparation of chelate-modified polysulfones PSF–Ch **1**–**6**.

Instruments

^1H NMR spectra were recorded on a JEOL C60-HL spectrometer using dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as internal standard. IR absorption spectra were obtained in KBr pellets, on a Specord M80 spectrophotometer. Reduced viscosities of the polymers were determined at a concentration of 0.2% in *N*-methyl-2-pyrrolidone at 25.0 ± 0.1 °C using an Ubbelohde suspended-level viscometer. The softening points were measured with a Gallenkamp hot-block melting-point apparatus. Thermogravimetric analysis (TGA) was carried out using an MOM Derivatograph, at a heating rate of 12 °C min^{-1}, in air. Differential scanning calorimetry (DSC) measurements were done by a Mettler TA Instrument DSC 12E with a heating rate of 20 °C min^{-1} in air and the second heating cycle was used to determine the glass transition temperatures (T_g) of the samples. X-ray measurements were made with a TUR M62 diffractometer using Ni-filtered CuK_α radiation (36 kV, 25 mA).

RESULTS AND DISCUSSION

The starting chloro-terminated polysulfones were prepared using reported procedures[9,10] by the reaction of bisphenol A with 4,4′-dichlorodiphenylsulfone in DMSO/chlorobenzene at 160 °C using anhydrous potassium carbonate as base (Scheme 1). The resulting polysulfones showed number-average molecular weights (M_n) ranging between 38 000 and 3800. The end-capped chlorine content of starting polysulfones is given in Table 1.

The chelate-modified polysulfones were obtained by the reaction between chloro-terminated polysulfones of different molecular weights and the sodium salt of bis(2,4-dihydroxybenzaldehyde)-Cu^{2+} according to Scheme 1. Some of their characteristics are listed in Table 1. Properties of the corresponding parent polymers are also shown in Table 1 for comparison. The resulting chelate-modified polymers were characterized by reduced viscosities, ^1H NMR and IR absorption spectra, DSC, TGA and X-ray measurements.

The reduced viscosities of the chelate-modified polysulfones are higher than those of unmodified starting polymers (Table 1). The increase in viscosities is due to the incorporation of bisphenolic chelate moieties in polymer chains, which may result in a significant straightening of those chains

Table 1 Characteristics of chelate-modified polysulfones

Starting polysulfones					Chelate-modified polysulfones			
Sample	Cl (%)	M_n[a]	η_{red} (dl g^{-1})	Softening point (°C)	Sample	η_{red} (dl g^{-1})	Softening point (°C)	CuO[b] (%)
PSF**1**	0.20	38000	0.497	246	PSF–Ch**1**	0.630	227	1.5
PSF**2**	1.38	36900	0.415	205	PSF–Ch**2**	0.696	279	2.6
PSF**3**	1.27	37000	0.510	205	PSF–Ch**3**	0.550	215	2.0
					PSF–Ch**3A**	0.520	200	2.5
PSF**4**	2.25	16000	0.240	170	PSF–Ch**4**	0.420	195	3.3
PSF**5**	3.17	5100	0.090	110	PSF–Ch**5**	0.250	160	3.5
PSF**6**	2.22	3800	0.093	100	PSF–Ch**6**	0.300	170	4.0

[a] Calculated from osmometric and viscometric measurements.
[b] Determined from TGA measurements.

Table 2 Thermal properties of modified polymers

	T_g (°C)		$T_{10\%}$ (°C)		^1H NMR ratios		
Sample	PSF	PSF–Ch	PSF	PSF–Ch	r_o	r_c	Δr
1	188	190	512	500	2.31	2.35	0.04
2	182	188	475	465	2.70	2.82	0.125
3	177	181	490	468	2.75	2.89	0.140
4	148	172	472	470	2.67	2.84	0.173
5	125	128	475	497	2.67	2.89	0.220
6	121	129	470	478	2.60	2.83	0.230

and the formation of higher-molecular-weight products by coupling of the chains through chelate units.

The changes in reduced viscosities are in agreement with the modifications observed in the NMR spectra. Thus, ^1H NMR spectra of the chelate-bearing polysulfones showed an increase in the ratio of aromatic proton intensity to aliphatic isopropylidene protons compared with parent polysulfones. In this way, the corresponding ratios both for unmodified polysulfones (r_o) and for chelate-modified polymers (r_c) were calculated (Table 2). The difference between these ratios ($\Delta r = r_c - r_o$) could be considered as a semi-quantitative measure of the chelate content introduced into the polymer chain. In IR absorption spectra it was difficult to observe the appearance of new characteristic bands because of the low content of chelate units in the polymer backbone.

When the molecular weight of the parent polysulfones is lower and the chlorine content is higher, as in the case of samples PSF–Ch**4**–**6**, the resulting modified polymers exhibit the highest values of reduced viscosity and Δr, which agrees with an significant increase in the chelate content of these polymers.

Although the chelate-modified polysulfones PSF–Ch**3** and PSF–Ch**3A** come from the same polysulfone initially, their characteristics are somehow different because the synthesis conditions are different. In the case of sample PSF–Ch**3A** the reaction time was much longer and its chelate content became higher (Table 1).

The chelate-modified polysulfones have excellent solubilities in dipolar aprotic solvents such as DMSO, DMF and NMP, and in chloroalkylhydrocarbons. These materials afford tough and transparent films by casting from solution.

Thermal properties of these polymers were evaluated by DSC and TGA measurements. The representative DSC scans have been plotted in Fig. 1 for some modified polymers. As can be seen from Table 2, the glass transition temperature of the chelate-bearing polysulfones ranged between 128 °C (PSF–Ch**5**) and 190 °C (PSF–Ch**1**). The introduction of the chelate moieties into the polysulfone backbone leads to an increase in the glass transition temperature of the modified polymer as expected, probably due to the decrease in the flexibility of the polymer chains. The most significant increase in T_g values was observed for polysulfones with lower starting molecular weights (i.e. higher Δr values), while a small increase in T_g occurred for higher-molecular-weight polysulfones (Table 2).

Thermogravimetric analysis data of chelate-

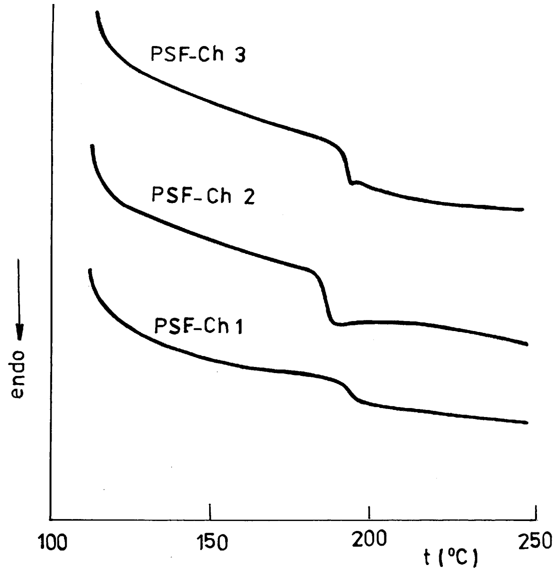


Figure 1 DSC thermograms of chelate-modified polysulfones.

modified polysulfones are presented in Tables 2 and 3 and selected TGA traces are presented in Fig. 2. The temperature of 10% weight loss ($T_{10\%}$) is generally considered to be the copolymer decomposition temperature and it is used in comparing the thermal stabilities of various copolymers. The introduction of chelate units into the polysulfone chains generally produces some decrease in the decomposition temperature, but this remains sufficiently high and still provides a large 'window' between the decomposition temperature and the glass transition temperature.

The results of thermogravimetric analysis revealed that the modified chelate polysulfones have good thermal stabilities, with polymer decomposition temperature ($T_{10\%}$) in excess of 460 °C, except for PSF–Ch**3A**, which exhibits the onset of decomposition at a lower temperature (435 °C). This is presumably because of the presence of a greater content of chelate in the sample. In the same time the T_g value increases (189 °C) as well as the difference Δr (0.175) in comparison with PSF–Ch**3**. For these chelate-bearing polymers the thermograms manifest two decomposition steps. By comparison with the initial polysulfones, the chelate-modified polymers have lower weight losses in the first stage of degradation, and higher in the second (Table 3). For the chelate-modified polymers resulting from high-molecular-weight polysulfones, the weight loss of *ca* 37% was detected in the first step, while for other modified polymers this loss reached 45%.

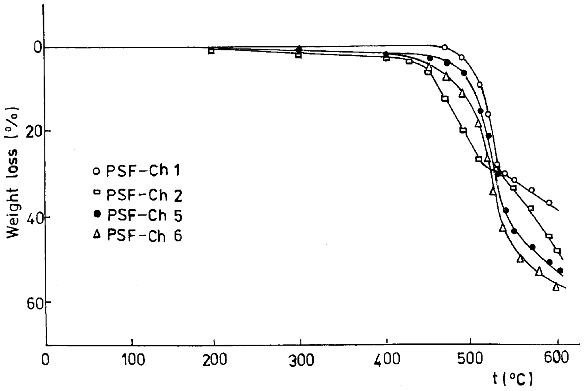


Figure 2 Thermogravimetric analysis of selected modified polymers.

The representative X-ray diffractograms for the modified polysulfones PSF–Ch**2** and PSF–Ch**6** are presented in Fig. 3. The chelate monomer is highly crystalline,[13] while the unmodified polysulfones are amorphous.[14] The chemical modification of the polysulfones with this bisphenolic complex led to partially crystalline polymers. Also, the semicrystalline patterns can be attributed to the relatively

Table 3 Thermogravimetric analysis of some unmodified and modified chelate polysulfones

	Weight loss (%)							
Sample	200 °C	300 °C	400 °C	450 °C	500 °C	520 °C	540 °C	560 °C
PSF**1**	0.0	0.0	0.0	0.5	3.0	16.5	39.0	49.5
PSF**3**	2.5	4.0	4.3	4.5	12.5	29.5	45.7	50.0
PSF**4**	2.5	4.0	4.5	7.0	17.0	34.0	44.5	47.5
PSF**6**	0.0	2.0	4.0	8.0	18.5	36.0	47.0	52.0
PSF–Ch**2**	1.2	1.5	3.0	6.0	24.5	29.0	32.0	36.5
PSF–Ch**3**	2.0	3.5	4.5	7.5	20.0	29.5	38.5	44.5
PSF–Ch**3A**	0.5	2.0	4.5	14.5	34.5	41.5	45.0	50.0
PSF–Ch**4**	2.5	4.0	5.5	7.5	18.0	34.5	42.0	48.0

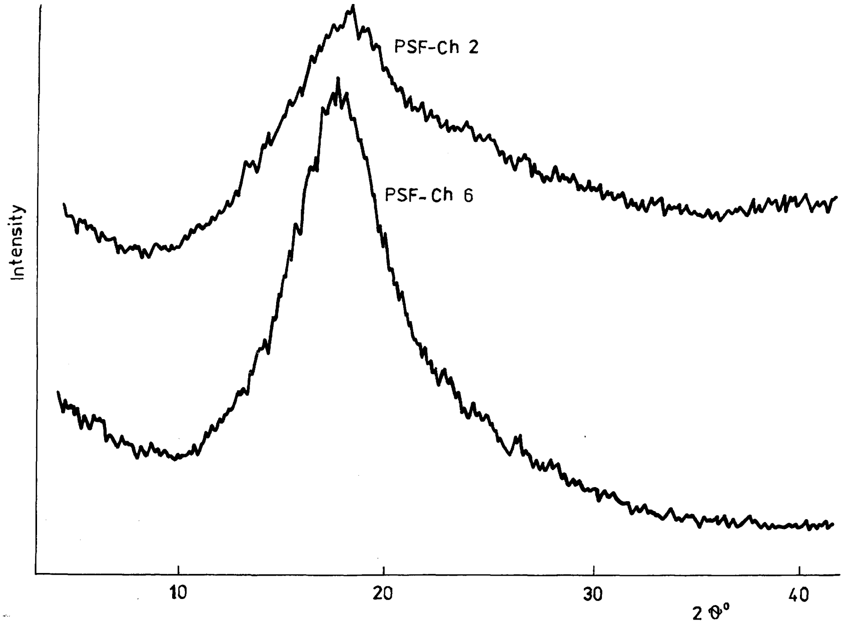


Figure 3 X-ray diffractograms of two chelate-modified polysulfones.

rigid structures of the modified polymer chains. The higher the chelate content in modified polysulfones, the greater the degree of order in these samples.

For these chelate-modified polysulfones the temperature dependence of the electrical conduction and Seebeck coefficient was investigated.[15] The highest increases in the reduced viscosity and glass transition temperature determine better electrical characteristics. For example, the lower-molecular-weight polysulfones modified by chelate moieties show smaller activation energies and high conductivity values.[15]

The introduction of copper(II) chelate units into the backbone of bisphenol A-based polysulfones by polycondensation reaction led to new chelate polymers, which exhibited higher viscosities, softening points and glass transition temperatures in comparison with the starting polysulfones. The modified chelate polysulfones keep their high thermal stabilities and they are soluble in aprotic dipolar and halogenated solvents, forming transparent and flexible films.

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