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Pendant functional group copolyether sulfones: III. Modified copolyether sulfones with bisphenolic copper chelate

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New copolyether sulfones having copper(II) chelate units as pendant groups were synthesized by a chemical modification reaction of chloromethylated polysulfones with the sodium salt of copper(II) bis(2,4-dihydroxybenzaldehyde) in dichloromethane/dimethyl sulfoxide as solvent system, at room temperature. The resulting copolymers were confirmed by IR absorption spectra and characterized by softening points, solubilities, differential scanning calorimetry and thermogravimetric analysis measurements. A slow increase of glass transition temperature values was observed in comparison with the starting chloromethylated polysulfones, and the thermal stability in air showed a slow, but insignificant, decrease. A significant increase in solvent resistance was observed. The glass transition temperature values, which do not exceed 200 °C, provide processing possibilities. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: polysulfone; copolyether sulfone; chloromethylation; copper(II) chelate; chemical modification; pendant groups

INTRODUCTION

Among the amorphous high-performance thermoplastics, aromatic polysulfones (polysulfone (PSF), polyethersulfone (PES), polyphenylsulfone (PPSF)) have achieved a remarkable position by virtue of their excellent properties, such as transparency, mechanical toughness and rigidity, high glass transition temperatures, very good thermooxidative, hydrolytic, and chemical resistance, easy processability and a high thermal stability that allows melt processing at temperatures up to 400 °C.[1–5]

Chemical modification of the polymers proved to be a useful way to change their properties, such as solubility, thermal behavior, hydrophilicity, etc.[5] Also by this process, it is possible to increase the reactivity of the main chain by introducing new reactive functional groups that permit further chemical reactions by crosslinking.

The chemical modification of polysulfones has been reported using sulfonation,[6,7] nitration,[8–10] and by the introduction of various functional groups, such as COOH,[11,12] F,[13] CF_3,[14] and aliphatic unsaturated end groups.[15]

Chloromethylation of polysulfone, as an example of chemical modification, has been performed by many research groups by different synthetic means.[16–25] We reported the chloromethylation of the polysulfone Udel P1700 using a paraformaldehyde/chlorotrimethylsilane mixture as a chloromethylation agent and tin(IV) chloride as catalyst.[26,27] The main application of such polymers resulted from the high reactivity of the chloromethylene functionality introduced on the polymer backbone, with many further reactions with appropriate partners being possible under mild conditions.

Introduction of chelate units on the polymer structure could lead to new electrical and optical characteristics, improved mechanical properties and heat resistance. Potential applications of chelate polymers are, for example, as surface coatings on metals and glasses, adhesives, high-temperature lubricants, electrical insulators and semiconductors etc.[28–30]

In a previous paper, the synthesis and some properties of bisphenol A-based polysulfones bearing copper(II) chelate moieties in the backbone were presented.[31] The electrical properties of these chelate-modified polysulfones were also reported.[32]

One of the drawbacks of such polymers is poor resistance to solvents, and some potential applications will suffer in this respect.

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Considering the problems discussed above, we propose in this paper to synthesize chelate-modified polysulfones using chloromethylated polysulfones (CMPSFs), by introducing the chelate units as pendant groups in the polymer chain. The bifunctional nature of this monomer should also induce some degree of crosslinking and, consequently, an increase in solvent resistance.

EXPERIMENTAL

Materials and reagents

Copper(II) bis(2,4-dihydroxylbenzaldehyde) and its sodium salt were obtained according to previously reported procedures.[28,29] To a solution of 2,4-dihydroxybenzaldehyde in methanol (27.6 g, 0.2 mol/100 ml), a solution of copper(II) acetate in methanol (18.16 g, 0.1 mol/100 ml) was added slowly, under stirring, at room temperature. The reaction mixture was maintained for 2 h at reflux, then allowed to cool. The green solid that separated out was filtered, washed with 100 ml methanol and dried under vacuum at 60 °C for 18 h (yield 28 g, 85%). The sodium salt of the copper chelate was prepared by dissolving 0.5 g (1.5 mmol) of copper chelate in 29.5 ml sodium hydroxide (aqueous solution, 0.1 M), filtering the resulted solution, and adding it over 100 ml acetone under vigorous stirring. The sodium salt that separated out was filtered, washed with acetone and then dried under vacuum at 60 °C for 24 h. Polysulfone Udel-P1700 (Union Carbide, M_n 38 000 by GPC) (PSF) was purified by reprecipitation with methanol from chloroform solution as described.[26] Paraformaldehyde, chlorotrimethylsilane (Merck), tin(IV) chloride (Fluka), dimethyl sulfoxide (DMSO; Aldrich) were used as received.

Instruments

IR absorption spectra were recorded in KBr pellets, on a Specord M80 spectrophotometer. The reduced viscosities of chloromethylated polysulfone solutions (0.2% w/v) in *N*-methylpyrrolidine-2-one (NMP) were determined at 25 ± 0.1 °C by using an Ubbelohde suspended level viscometer. The softening points were measured with a Gallenkamp hot-block melting-point apparatus. Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 20 °C min^{-1} in nitrogen; the temperature range was between 20 and 250 °C. After the first heating cycle the sample was quenched to room temperature. A second heating cycle was used to determine the glass transition temperatures T_g of the samples. Thermogravimetric analysis (TGA) was carried out using a MOM Derivatograph, at a heating rate of 12 °C min^{-1} in air. X-ray measurements were performed with a TUR M62 diffractometer using Ni-filtered Cu Kα radiation (36 kV, 25 mA).

Syntheses

Chloromethylation of polysulfone

Into a glass flask equipped with stirrer and reflux condenser were introduced 0.5 g (1.13 mmol) polysulfone Udel dissolved in 16.5 ml chloroform. The solution was heated at 50–52 °C, then 0.339 g (11.3 mmol) paraformaldehyde, 1.23 g (11.3 mmol) chlorotrimethylsilane and 0.0589 g (0.23 mmol) tin(IV) chloride were added. Determination of the chlorine content was used to monitor the evolution of chemical modification.[33] Once the reaction was completed, the mixture was poured into methanol under stirring and the separated polymer was filtered, washed with methanol and finally dried in vacuum at 40 °C for 18 h.

Chemical modification of chloromethylated polysulfones with the sodium salt of bis(2,4-dihydroxybenzaldehyde)Cu^{2+}

All samples were prepared in the same manner. A typical example is as follows: to a solution of the CMPSF (e.g. CMPSF-4), 0.8 g, (1.71 mmol) in dichloromethane/DMSO (10 : 1, v/v) was added 0.5 g (1.36 mmol) sodium salt of the copper chelate, under stirring, in nitrogen. The reaction mixture was stirred for about 10 h at room temperature. In time, the occurrence of modified polymer was observed as the solid separates. The solid was filtered, washed six times with methanol : water (10 : 1, v/v), then four times with methanol and dried at room temperature first in atmospheric air, then at 60 °C under vacuum. The final purification was realized by stirring the sample slurry in dichloromethane at room temperature for 2 h, followed by filtering and drying at room temperature first, then at 40 °C under vacuum for 18 h. Yield 0.87 g, 81%.

RESULTS AND DISCUSSION

Two main aspects must be taken into account concerning the synthesis of CMPSFs: (1) the resulting chloromethylated polymer must be soluble (avoiding crosslinking); (2) optimal synthesis conditions must be forward (polymer concentration, catalyst concentration, molar ratio polymer/chloromethylation agent, time) that lead to a maximum degree of substitution (DS), while the polymer remains soluble. After considerable work in this area,[26] we found optimal synthesis conditions (polymer concentration 2%, molar ratio polymer/paraformaldehyde/chlorotrimethylsilane 1 : 10 : 10, 0.20 mol tin(IV) chloride) as presented in Table 1. Some characteristics of CMPSFs are listed in Table 2. As can be seen from Table 2, there is a good correlation between the DS values calculated using different methods. The reduced viscosity showed higher values with increasing DS, whereas T_g and T_{10} values, on the contrary, exhibited a decreasing tendency, as noted.[22]

The chelate-modified polysulfones (PSFChs) were obtained by the reaction between CMPSFs of different DSs and the sodium salt of copper(II) bis(2,4-dihydroxybenzaldehyde) according to Scheme 1. Some of their characteristics are

Table 1. Synthesis conditions of CMPSFs

Code	Polymer concentration (%)	Molar ratio, polymer/ $(CH_2O)_n$/ Me_3ClSi	$SnCl_4$ (mol)	Time (h)	Chlorine[a] (%)	DS[b]	Remarks
CMPSF-1	5	1:3:3	0.50	24	11.86	1.77	Crosslinked
CMPSF-2	2	1:3:3	0.50	24	8.32	1.17	Crosslinked
CMPSF-3	2	1:3:3	0.20	5	2.69	0.35	Soluble
CMPSF-4	2	1:3:3	0.20	15	4.16	0.52	Soluble
CMPSF-5	2	1:3:3	0.20	28	5.20	0.66	Soluble
CMPSF-6	2	1:3:3	0.20	72	7.85	1.03	Soluble
CMPSF-7	2	1:10:10	0.20	72	10.35	1.42	Soluble
CMPSF-8	2	1:10:10	0.10	72	12.47	1.77	Soluble

[a] Chlorine content determined by Schoniger's modified method.[33]

[b] $\mathrm{DS} = \frac{\mathrm{Cl\%} \times M_{\mathrm{PSF}}}{100 \times 35.45 - M_{\mathrm{CH_2Cl}} \times \mathrm{Cl\%}}$, where M_{PSF} is the molecular weight of structural unit of polysulfone (442.51) and $M_{\mathrm{CH_2Cl}}$ is the molecular weight of chloromethylene group (49.48).

Table 2. Characterization of some CMPSFs

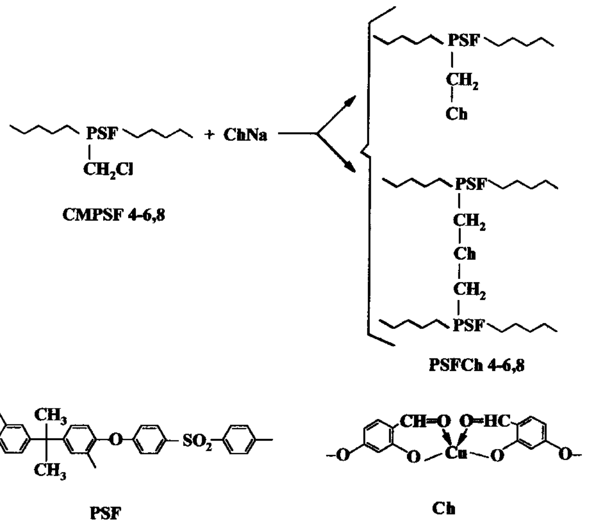
Code	η_{red}[a] (dl g^{-1})	DS Chlorine method	 ^{1}H NMR[b]	T_g[c] (°C)	T_{10}[d] (°C)
CMPSF-4	0.55	0.52	0.56	183	440
CMPSF-5	0.60	0.66	0.71	170	430
CMPSF-6	0.66	1.03	1.23	179	421
CMPSF-8	0.93	1.77	1.97	158	390

[a] Reduced viscosity measured at 0.2% concentration in NMP at 25 °C.

[b] Calculated from ^{1}H NMR spectral data using $\mathrm{DS} = 3A_{\mathrm{CH_2Cl}}/A_{\mathrm{(CH_3)_2C}}$, where $A_{\mathrm{CH_2Cl}}$ is the area corresponding to CH_2Cl protons (δ4.45 ppm) and $A_{\mathrm{(CH_3)_2C}}$ is the area corresponding to $(CH_3)_2C<$ protons (δ1.70 ppm).

[c] Glass transition temperature from DSC measurements (second heating cycle, heating rate 20 °C min^{-1}, heating range between 20 and 250 °C).

[d] Temperature from TGA measurements corresponding to 10% weight loss.



Scheme 1. Preparation of PSFChs.

presented in Table 3. The structures of the resulting chelate-modified polymers were confirmed by IR spectroscopy. DSC measurements performed on chelate-modified polymers provided useful information about the changes that occurred in the glass transition temperature, as a result of the chemical modification reaction. The thermal stability, in atmospheric air, of both CMPSFs and PSFChs was evaluated by using TGA measurements, in the temperature range 20–900 °C. The solubility of PSFCh polymers was studied for five common solvents, at room temperature, at a concentration of 1% (w/v).

One remark must be made on the synthesis path chosen, i.e. room temperature synthesis. We believe that such a mild synthetic variant would have possible applications on surface modifications of polysulfones in membrane building.

From Scheme 1 one can see that, even though stoichiometric amounts of reaction partners were used, some crosslinking

Table 3. Characteristics of PSFChs

Sample	A_{1660}/A_{1500}[a]	TGA Cu (%)[b]	T_g[c] (°C)	T_{10}[d] (°C)
PSFCh-4	0.13	5.0	187	440
PSFCh-5	0.12	5.7	177	413
PSFCh-6	0.20	8.0	192	388
PSFCh-8	0.23	10.0	173	370

[a] Absorbance ratio calculated[34] using $A = \log_{10}(\mathrm{AC}/\mathrm{AB})$ (where AC = the distance through the peak, from the wavenumber scale up to the intersection with the baseline, AB = the distance from the wavenumber scale up to the top of the peak).

[b] Copper content determined by TGA from the copper(II) oxide residue at 900 °C.

[c] Glass transition temperature determined by DSC in the second heating cycle at a heating rate of 20 °C min^{-1}.

[d] Temperature from TGA measurements corresponding to 10% weight loss.

reactions are unavoidable. The amounts of crosslinking structures for these polymers resulted in considerable increases in their solvent resistance.

The polymers obtained are insoluble in common solvents, such as chloroform, acetone, dimethylformamide, DMSO and NMP, making ^{1}H NMR spectroscopy impossible. This limitation in solubility was somewhat expected, and could be due to some crosslinked structures involved in the PSFCh polymers (Scheme 1).

IR spectra (Figure 1) showed characteristic absorption bands at 1660 cm^{-1} due to the stretching vibrations of the $-C{=}O$ groups from the chelate moieties. Unfortunately, the absorption band due to the $-CH_2-O-Ph$ group was not possible to monitor because of overlap with the $Ph-O-Ph$ groups. Calculation of the absorbance ratio $A_{C=O}$ (1660 cm^{-1}) versus A_{aromatic} (1500 cm^{-1} as reference) was possible by taking 1800–1350 cm^{-1} as the base line, free of any absorption. This ratio constitutes a sensitive measure of the chelate content chemically bonded in the polymer. As can be seen from Table 3, higher ratio values were obtained for polymers PSFCh-6 and PSFCh-8, obtained from starting CMPSF with higher DS (CMPSF-6: 1.23; CMPSF-8: 1.97; Table 2).

Glass transition temperature (Table 3) ranged between 173 and 192 °C. The introduction of chelate units as pendant or bridge moieties on the polysulfone backbone leads to an increase in the glass transition temperature for the modified polymer, as expected. Figure 2 depicts the gradient of increase in T_g values ($\Delta T_g = T_{g\mathrm{PSFCh}} - T_{g\mathrm{CMPSF}}$) versus copper content (%) determined by TGA. As can be seen, the higher the chelate content that is introduced by chemical modification, the higher the ΔT_g values that are obtained.

X-ray diffractograms of the chelate-modified polysulfones showed semicrystalline patterns for all samples. A representative X-ray diffractogram of sample PSFCh-6 is presented in Figure 3. The chelate monomer used is highly crystalline. The CMPSF is an amorphous polymer. As a result, the PSFCh imparts these specific morphological features of the starting partners, and shows a semicrystalline pattern. A similar behavior was noticed for linear PSFChs.[31]

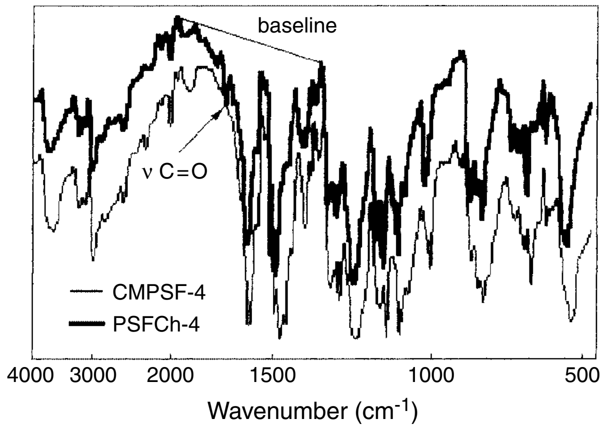


Figure 1. IR spectra of CMPSF-4 and the corresponding chelate-modified polymer PSFCh-4.

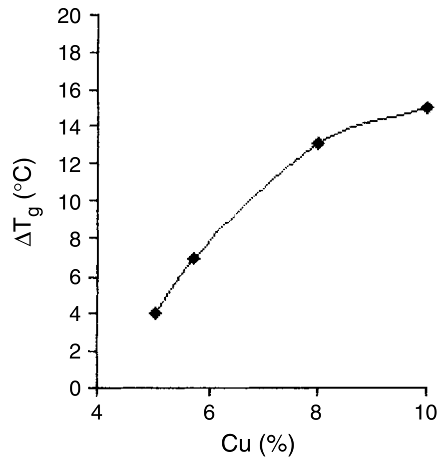


Figure 2. Dependence of increase in glass transition temperature ($\Delta T_g = T_{g\mathrm{PSFCh\text{-}i}} - T_{g\mathrm{CMPSF\text{-}}i}$) on the copper content (%).

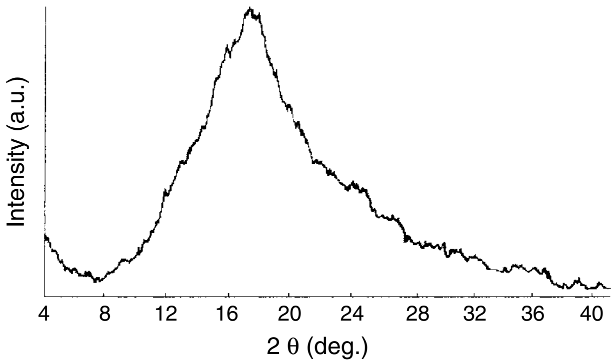


Figure 3. X-ray diffractogram of PSFCh-6.

TGA measurements were carried out in air with a heating rate of 12 °C min^{-1} from room temperature to 900 °C. At 900 °C, the residue formed contains only copper(II) oxide, thus providing a useful quantitative evaluation of the amount of chelate introduced by chemical modification. The copper content values listed in Table 3 agree well with the absorbance ratio values discussed above. The pattern of thermal behavior is depicted in Figure 4. An additional proof of the chemical reaction performed was provided by the thermal stability of a physical mixture of (CMPSF + chelate salt). In this case, a dramatic decrease in the mass at about 230 °C was recorded, whereas the chelate polymer followed a decomposition pattern similar to the CMPSF. In all cases the PSFChs exhibited a somewhat lower thermal stability in comparison with the starting CMPSFs, as observed for linear segmented chelate-polysulfones.[31]

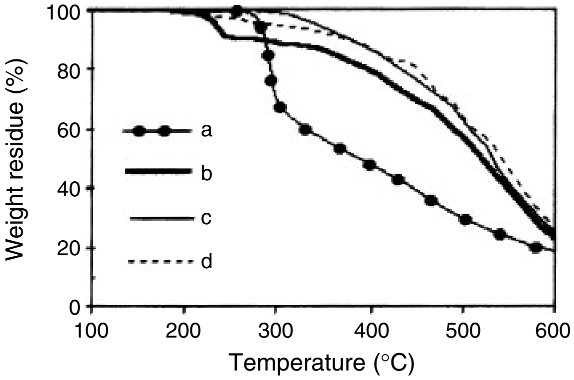


Figure 4. Representative TGA curves of: (a) copper(II) bis(2,4-dihydroxybenzaldehyde); (b) physical mixture (chelate + CMPSF-8); (c) chloromethylated polysulfone, CMPSF-8; (d) the corresponding chelate-modified polysulfone, PSFCh-8.

CONCLUSIONS

An attractive room-temperature synthesis was found for the chemical modification of CMPSFs with the sodium salt of copper(II) bis(2,4-dihydroxybenzaldehyde).

IR absorption spectra confirmed the proposed structures, allowing calculation of the absorbance ratio $A_{C=O\ 1660}/A_{1500}$ as a quantitative measure for evaluation of the chemical modification reaction.

The resulting polymers had higher T_g values compared with the starting CMPSFs, but they did not exceed 192 °C.

The PSFCh are semicrystalline, as evidenced by X-ray diffraction measurements. They exhibited little difference in their thermal stabilities compared with the starting CMPSF polymers, and showed an increase in their resistance to solvents.

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