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Synthesis and Properties of New Homo and Copolyether Sulfones Containing Cycloaliphatic Cardo Groups

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NOTES

SYNTHESIS AND PROPERTIES OF NEW HOMO AND COPOLYETHER SULFONES CONTAINING CYCLOALIPHATIC CARDO GROUPS

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Key Words: Cardo, Polysulfone, Copolyether Sulfone, Cycloaliphatic, Thermal Properties

ABSTRACT

New homo and copolyether sulfones containing cycloaliphatic cardo groups were prepared in the conventional literature manner by condensing the dipotassium salts of 1,1-bis(p-hydroxy-phenyl)cyclopentane (I a), 1,1-bis(p-hydroxyphenyl)cyclohexane (I b), 1,1-bis(p-hydroxyphenyl)cycloheptane (I c), and 2,2-bis(p-hydroxy-phenyl)-propane (Bisphenol A, III) with 4,4'-sulfonyl bis(4-chloro-phenyl) (II). The polymers were characterized by IR ^{1}H-NMR spectroscopy, elemental analysis, viscometry, solubility tests, softening points, DSC and TGA measurements.

INTRODUCTION

Among the heat-resistant polymers, aromatic polyethers are of great interest. They are known for their high resistance to heat and chemical attack, good mech-anical and dielectric properties and facile processability [1].

Several polysulfones with different phenylene connector groups in the bisphenol monomer, i.e., other than the isopropylidene unit of the familiar PSF were examined. The properties of the polymers are largely determined by their chemical structure.

It has been reported that heat stability is increased considerably when the polymer molecule contains cyclic side groups where one of the atoms also belongs to the main polymer chain. Polymers of this type are known as cardo polymers [2]. The introduction of cardo groups in different hetero- and carbochain polymers leads simultaneously to an increase of both heat resistance and solubility of polymers, which is of particular importance for aromatic polymers with rigid chains [2]. The properties of cardo polymers also depend on the backbone structure.

Aromatic polyethers containing various cardo groups along the chain, such as cyclohexyl [3-7], phthalide [8, 9], fluorene, phthalimide and anthrone [8] groups have been previously prepared. It was shown that the presence of cardo groups in the polymer chain increased significantly the softening point of aromatic polyethers.

The aim of this paper is to present the synthesis and properties of some new homo and copolyether sulfones with cyclopentylidene, cyclohexylidene and cyclo-heptylidene moieties as cardo groups.

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena spectrophotometer by using the KBr pellet technique. ^{1}H-NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 80 °C in DMSO-d_6, $CDCl_3$ or $(CD_3)_2CO$ using TMS as the internal reference. Melting and softening points were determined with a Gallenkamp hot-block melting point apparatus. The reduced viscosities of copolymer solutions (0.2% w/v) in NMP were determined at 25 (0.1°C by using an Ubbelohde suspended level viscometer. Polymer solubilities were determined for eight common solvents using 0.1 g polymer in 1-2 mL solvent at room temperature.Thermogravimetric analysis (TGA) was carried out in air with an F.Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calor-imetry (DSC) measurements were done by using a Mettler TA instrument DSC 12E with a heating rate of 20°C/min in nitrogen. Glass transition temperature (T_g) was taken at the inflection point of the dT versus temperature curve.

Synthesis of Cardo Bisphenols (I a-c)

The most common bisphenol synthesis is the condensation of a ketone with excess of phenol in the presence of an acidic condensing agent [10]. In this paper, the cardo bisphenols (I a-c) were synthesized according to the reported method [5].

1,1-Bis(p-hydroxyphenyl)cyclopentane (I a)

After washing with benzene, the monomer was crystallized from diluted acetic acid.

Mp 153-154°C (literature 154-155°C [11]). Analysis Calcd. for $C_{17}H_{18}O_2$, (%): C, 80.28; H, 7.13. Found (%): C, 79.80; H, 7.76. IR (KBr, cm^{-1}): 3100-3600 (OH); 2970, 2980 (CH_2), 1620, 1600, 1520, 1450 (C=C, aromatic); 1250 (C-O); 835 (aromatic ring). ^{1}H-NMR (DMSO-d_6, TMS, ppm): 1.63 (m, 4H, CH_2, β cyclopentane); 2.22 (m, 4H, CH_2 , α cyclopentane); 6.62 (d, 4H, ortho to OH); 7.045 (d, 4H, ortho to quaternary carbon); 8.80 (s, 2H, OH).

1,1-Bis(p-hydroxyphenyl)cyclohexane (I b)

The monomer was crystallized from benzene, mp 185-187°C (literature 185-186°C [12]. Analysis Calcd. for $C_{18}H_{20}O_2$, (%): C, 80.56; H, 7.51. Found (%): C, 80.47; H, 7.69. IR (KBr, cm^{-1}): 3200-3600 (OH); 2995, 2980 (CH_2), 1615, 1600, 1520, 1450 (C=C, aromatic); 1250 (C-O); 845, 830 (aromatic ring). ^{1}H-NMR (DMSO-d_6, TMS, ppm): 1.55 (s, 6H, CH2, β+χ cyclohexane); 2.72 (s, 4H, CH_2, α cyclohexane); 6.62 (d, 4H, ortho to OH); 7.01 (d, 4H, ortho to quaternary carbon); 8.80 (s, 2H, OH).

1,1-Bis(p-hydroxyphenyl)cycloheptane (I c)

The monomer was crystallized from ethanol, mp 189-194°C. Analysis Calcd. for $C_{19}H_{22}O_2$, (%): C, 80.81; H, 7.85. Found (%): C, 79.95; H, 7.92. IR (KBr,cm^{-1}): 3100-3600 (OH); 2945, 2880 (CH_2), 1610, 1600, 1595, 1515, 1445 (C=C, aromatic); 1250 (C-O); 826, 830 (aromatic ring). ^{1}H-NMR ($(CD_3)_2CO$, TMS, ppm): 1.57 (s, 8H, CH_2, β+χ cycloheptane); 2.25 (s, 4H, CH_2, α cycloheptane); 6.72 (d, 4H, ortho to OH); 7.00 (d, 4H, ortho to quaternary carbon).

Synthesis of Homo and Copolymers (IV a-c, V a-c)

All polymers were synthesized by a classical procedure [13]. An extraction in a Soxhlet with methanol for at least 24 hours was performed, then the polymers were dried in a vacuum oven at 80°C overnight. Their properties are listed in Table 1.

RESULTS AND DISCUSSION

The preparation of homopolymers (IV a-c) was based on the polycondensation reaction of 1,1-bis(p-hydroxyphenyl)cyclopentane (I a), 1,1-bis(p-hydroxyphenyl)cyclohexane (I b), 1,1-bis(p-hydroxyphenyl)cycloheptane (I c)

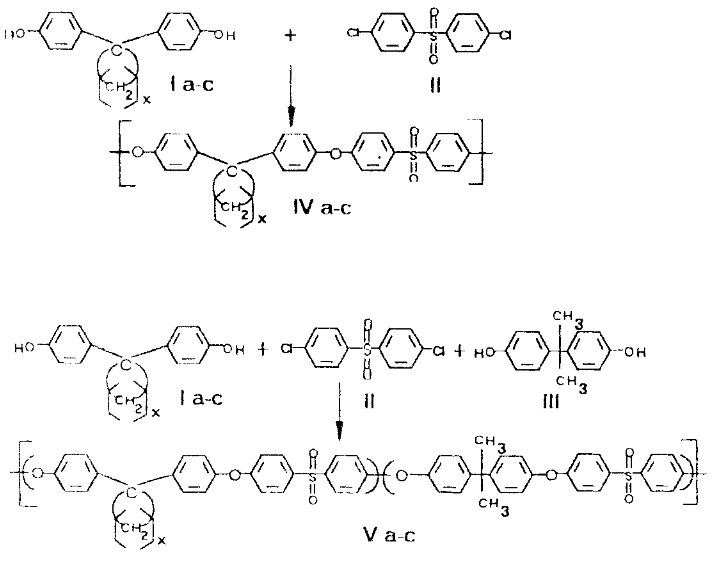
TABLE 1. The Properties of Homo and Copolymers (IV a-c, V a-c)

Polymer	Color	Yield, %	Softening range,°C	Reduced viscosity,[a] dL/g	R[c]
IV a	brown-black	85	175-210	0.18[b]	-
IV b	white	83	230-240	0.24	-
IV c	grey-ochre	95	183-205	0.15	-
V a	grey	81	235-245	0.21	0.67
V b	white	97	215-250	0.31	1.08
V c	ochre	90	198-230	0.25	3.00

[a] Measured in NMP at a concentration of 0.2 g/dL at 25(0.1 °C.

[b] Partially soluble.

[c] R = (cycloalkyl units / Bis A units), calculated from ^{1}H-NMR data.



x	I	IV	V	I/III
4	Ia	IVa	Va	25/75
5	Ib	IVb	Vb	50/50
6	Ic	IVc	Vc	75/25

Scheme 1

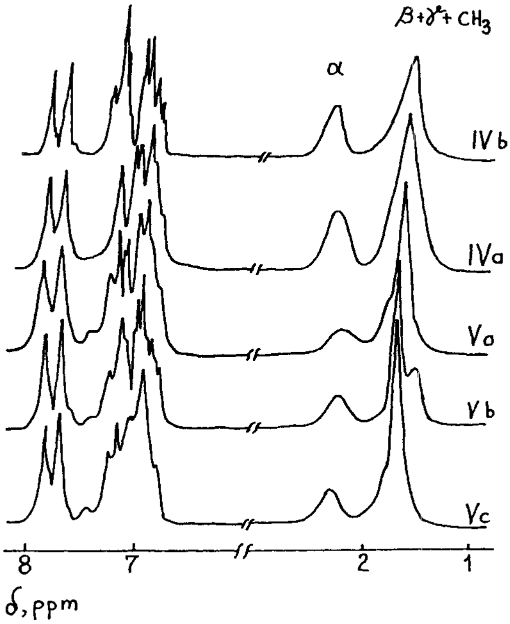


Figure 1. ¹H-NMR spectra of polymers IV a,b and Va-c.

bisphenols with 4,4'-sulfonyl bis(4-chlorophenyl) (II) in a DMSO-PhCl mixture, in presence of anhydrous K_2CO_3 (Scheme 1). The same procedure was applied for the synthesis of copolymers (V a-c) by the reaction of cardo bisphenols (I a-c), bisphenol A (III) with 4,4'-sulfonyl bis(4-chlorophenyl) (II) in a DMSO-PhCl mixture, in the presence of anhydrous K_2CO_3 (Scheme 1). IR, ¹H-NMR spectra and elemental analysis data confirmed the expected structures.

From the ¹H-NMR spectra of the copolymers V a-c (Figure 1), the ratio of the corresponding integrals of peaks for cycloalkylidene (cyclalk) units versus isopropylidene Bisphenol A (Bis A) units was calculated and used to estimate the ratio (R) of the corresponding degrees of polymerization (R = cyclalk/Bis A). The obtained values are listed in Table 1. As can be seen, for the copolymer V a, the R value (0.67) indicates a greater content in Bisphenol A units as compared to the copolymers V b and V c.

Elemental analysis data (Table 2) showed a good agreement between calculated and found values.

The reduced viscosity values ranged between 0.15 and 0.31 dL/g. These values are not very high, possibly due to a lower reactivity of the cardo bisphenols

TABLE 2. Elemental Analysis of Homo and Copolymers (IV a-c, V a-c)

Polymer	Empirical formula	(formula weight)	S,% Calcd	S,% Found	Cl,% Found
IV a	$(C_{29}H_{24}SO_4)_n$	$(468.55)_n$	6.84	7.64	0.70
IV b	$(C_{30}H_{26}SO_4)_n$	$(482.57)_n$	6.64	6.76	2.03
IV c	$(C_{31}H_{28}SO_4)_n$	$(496.60)_n$	6.46	7.24	0.80
V a	$(C_{56}H_{44}S_2O_8)_n$	$(911.06)_n$	7.87	6.93	0.94
V b	$(C_{57}H_{46}S_2O_8)_n$	$(925.08)_n$	7.73	6.98	3.36
V c	$(C_{58}H_{48}S_2O_8)_n$	$(939.11)_n$	7.61	7.05	1.25

TABLE 3. The Solubility of Homo and Copolymers (IV a-c, V a-c)[a]

Test solvent	Solubility[b] parameter, δ	Homopolymer IV a	IV b	IV c	Copolymer V a	V b	V c
Chloroform	9.21	PS	S	S	S	S	S
PhCl	9.57	PS	S	S	S	S	S
Cyclohexanone	9.89	PS	S	S	S	S	S
1,4-Dioxane	10.01	I	S	S	S	S	S
Nitrobenzene	10.67	I	S	S	S	S	S
NMP	11.17	PS	S	S	S	S	S
DMF	12.15	PS	PS	S	S	S	S
DMSO	13.04	PS	PS	PS	I	PS	S

[a] I = insoluble; PS = partially soluble; S = soluble.

[b] Solvent solubility parameter in $(\mathrm{Cal/cm^3})^{1/2}$ after Hansen [15].

[14]. The room temperature solubility tests were performed using eight common solvents (Table 3). The homopolymer IVa showed the lower solubility, possibly due to the higher rigidity of the cyclopentane ring.

All polymers showed high softening points, as it can be seen from Table 1. Glass transition temperatures (T_g) of polymers (Table 4) ranged between 166 and 220°C. While the copolymer Va possessed a higher T_g (220°C) than the parent

TABLE 4. The Thermal Properties of Homo and Copolymers (IV a-c, V a-c)

Polymer code	TGA temperatures (°C) for various % decomposition 10	20	30	40	50	T_g^a(°C)
IVa	400	460	505	550	585	230
IVb	487	503	515	525	543	247
IVc	460	483	496	510	545	247
Va	435	480	495	520	575	210
Vb	495	510	520	530	549	216
Vc	478	498	508	518	535	221

[a]DSC measurements under nitrogen at a heating rate of 20°C/min, second heating cycle.

homopolymer IV a (166°C), the other copolymers (V b,c) present only slightly different values (184 vs. 200, and 178 vs. 176 °C, respectively). The increased T_g value of the copolymer Va can be explained through a higher solubility of the growing chain during the reaction, leading to a higher molecular weight.

The thermal stability of the polymers in air was checked by thermogravimetric analysis (TGA). The temperature at which 10% weight loss occurred (T_{10}) was considered as a useful parameter to characterize the thermal stability of the polymers. As can be seen from Table 4, T_{10} values of homopolymers (IV a-c) ranged between 400 and 495°C; a good level of thermal stability. The T_{10} values of polymers can be arranged in the following order: for IV series, IV b > IV c > IV a; for V series, V b > V c > V a. The copolymers with Bisphenol A units (V a-c) had higher T_{10} values than their corresponding homopolymers.

CONCLUSIONS

Homo and copolyether sulfones containing cyclopentyl, cyclohexyl and cycloheptyl cardo groups were prepared by the classical polycondensation reaction of bisphenols (I a-c, III) with 4,4'-sulfonyl bis(4-chlorophenyl) (II). The expected structures were confirmed using current analysis methods. All polymers showed a good solubility, except for homopolymer (IV a) with cyclopentyl cardo groups. The introduction of cycloaliphatic cardo groups into the polymer chain led to an increases of the softening points.

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