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SYNTHESIS, BIOLOGICAL ACTIVITY, AND CHEMICAL RESISTANCE OF CARDO POLYSULFONATES BASED ON BISPHENOL-C AND ITS DERIVATIVES

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NOTE

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ABSTRACT

Cardo polysulfonates (PS-1, PS-2, PS-4, PS-7, and PS-9) of 1,1′-bis(R,R′,4-hydroxy phenyl)cyclohexane (R = H, CH_3,Cl and Br; and R′=H, Cl and Br) with 4,4′-diphenyl ether disulfonyl chloride (DPESC) and 4,4′-diphenyl disulfonyl chloride (DPSC) have been synthesized by interfacial polycondensation of corresponding bisphenol (0.005 mol) and DPESC/DPSC (0.005 mol) by using water-1,2-dichloro-ethane/chloroform/dichloro methane (4:1 v/v) as an interphase, alkali (0.012−0.016 M) as an acid acceptor and cetyl trimethyl ammonium bromide (50 mg) as an emulsifier at 0°C for 3 hours. IR and NMR spectral data support the structures. The intrinsic viscosities of the said polymers are determined in different solvents at three different temperatures: 30°, 35°, and 40°C, and it is found that little solvent and temperature effect is observed on viscosities. All the polysulfonates possess good antibacterial activity against E. coli and S. aureus microbes and excellent resistance to hydrolytic attack against acids, alkalis and salt.

Key Words: Cardo polysulfonates; IR; NMR; Viscosity; Biological activity; Hydrolytic stability

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INTRODUCTION

Recently, much attention is being paid towards polymers containing cardo (Latin meaning a loop) groups [1], due to their excellent physicochemical properties and promising industrial applications as coatings, adhesives, thermoplastic molding compositions alone or mixed with fillers, films, fibers, packaging, glass reinforced plastics and antifriction self-lubricating materials. It has been proposed that cyclic side groups in the main chain is regarded as loops (cardo groups). The introduction of such groups in different hetero and carbo chain polymers: polyesters, polyethers, polyamides, polyimides, polycarbonates, polysulfones, polysulfonates result in very specific properties such as excellent solubility, excellent thermal, mechanical and electrical properties, high flexibility, excellent chemical resistance, which signify the industrial importance of this class of polymers [1].

The literature survey on cardo polymers reveals that most of the work is confined on the aromatic polyesters, polyamides, etc. and little work has been reported on aromatic cardo polysulfonates [2–5]. Recently, some work on cardo polysulfonates has been published from our laboratory [6–10]. With a view to synthesize and characterize more new polysulfonates, present communication deals with synthesis of cardo polysulfonates of bisphenol-C and its derivatives (Scheme 1).

EXPERIMENTAL

Materials

The chemicals used were of laboratory grade and purified prior to use by methods in the literature [11]. 1,1′-Bis(4-hydroxy phenyl) cyclohexane (BC) [12, 13], 1,1′-bis(3-methyl-4-hydroxy phenyl)cyclohexane (MeBC) [12, 13], 1,1′-bis(3,5-dichloro-4-hydroxy phenyl) cyclohexane (ClBC) [14], 1,1′-bis(3-methyl-5-chloro-4-hydroxy phenyl) cyclohexane (ClMeBC) [14], 1,1′-bis(3,5-dibromo-4-hydroxy phenyl) cyclohexane (BrBC) [15, 16], 4,4′-diphenyl ether disulfonyl chloride (DPESC) [17] and 4,4′-diphenyl disulfonyl chloride (DPSC) [18] were synthesized and repeatedly purified from appropriate solvent systems. The emulsifier cetyl trimethyl ammonium bromide (CTAB) (Sisco Chemical) was used as received.

Polymer Synthesis

To a cooled (0°C) and clear solution of bisphenol (0.005 mol) in 0.012–0.016 M sodium hydroxide (50 mL), CTAB (50 mg) was added with vigorous stirring for 10 minutes. A solution of DPESC/DPSC (0.005 mol) in 1,2-dichloro-ethane/chloroform/dichloromethane (12.5 mL) was added

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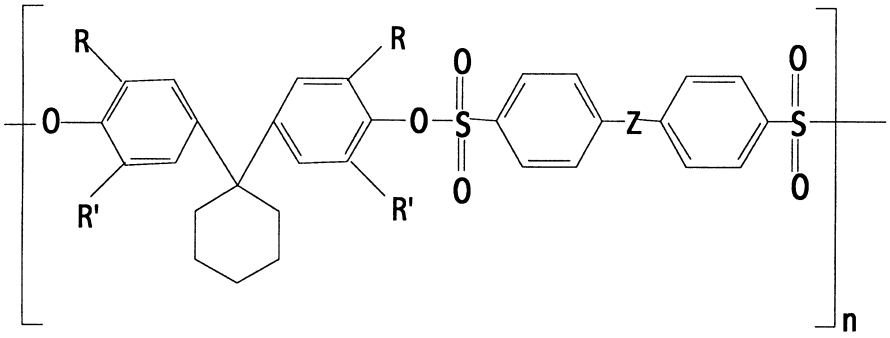

PS-1: R=R'= H and Z=O

PS-2: R=CH_3, R'=H and Z=O

PS-3: R=R'= Cl and Z=O

PS-4: R=CH_3, R'=Cl and Z=O

PS-5: R=R'= Br and Z=O

PS-6: R=R'= H and Z= -

PS-7: R=CH_3, R'=H and Z= -

PS-8: R=R'= Cl and Z= -

PS-9: R=CH_3, R'= Cl and Z= -

PS-10: R=R'= Br and Z= -

Scheme 1.

dropwise over 10 minutes. The emulsion was vigorously stirred for 2 hours at 0°C. The organic layer was run into a large excess of methanol to precipitate the polymer. The separated polymer was filtered, washed well with water, and finally washed with methanol and dried at 50°C. A good result was obtained in the 1,2-dichloro ethane system. The polymers were further purified repeatedly by dissolving in chloroform and precipitating in methanol. The yield was ~90–92%. PS-5, PS-6, PS-8, and PS-10 found low molecular weight even after changing the interphase systems. PS-3 formed an insoluble gel in all the solvent systems studied. Molecular weight of polymer depends on the reactivity of the initial compounds [19]. The termination reactions take place mainly with participation of $SOCl_2$ groups. Molecular weight increases with increasing reactivity of the bisphenols. The molecular weight may decrease with increasing contribution of termination reactions and vice versa depending on the ratio of the propagation and termination rate constants.

The polymers are found to be highly soluble in common organic solvents like chloroform, 1,2-dichloroethane, dichloro methane, tetrahydrofuran, DMSO, etc. High molecular weight fractions were obtained by soxhlet extraction in chloroform-methanol of varying proportion (50:50, 60:40, 70:30, 80:20, 100:0 v/v). The polymers form tough and transparent films from solutions. PS-1, PS-2, PS-4, PS-7, and PS-9 are used for their further physico-chemical characterization.

Measurements

The IR spectra (KBr pellets) of PS-1, PS-2, PS-4, PS-7 and PS-9 were scanned on a Carl Zeiss specord FTIR spectrophotometer. The NMR spectra of polysulfonates were scanned on a Bruker FTNMR (300 MHz) spectrometer by using $CDCl_3/CDCl_3-DMSO\text{-}d_6$ as a solvent and TMS as an internal standard. The viscosity measurements at three different temperatures: 30°, 35°, and 40°C were carried out with an Ubbelohde type suspended level viscometer [20] and the intrinsic viscosities were determined by Huggins relationship [21]. The biological activities of polysulfonates and standard drugs were tested by the cup-plate method [22, 23] against different microbes at 37°C by using DMF as a solvent. The sample loaded in the cup was 50 μg (0.1 mL). The chemical resistance of polysulfonates was tested at room temperature for a varying period in 10% each of acids, alkalis, salt, as well as water. Polymer films for chemical resistance was prepared from concentrated solutions and dried prior to their use.

RESULTS AND DISCUSSION

The characteristic IR (KBr pellets) absorption bands (cm^{-1}) of PS-1, PS-2, PS-4, PS-7, and PS-9 are reported in Table 1. The NMR chemical shifts, types of protons and multiplicity of the said polymers are also reported in Table 1. Thus, the structures of the polymers are supported by IR and NMR spectral data.

The solution viscosity is an important tool in characterizing molecular interaction occurring in the solution and it is a direct measure of hydrodynamic volume of molecules. The intrinsic viscosity [η] and Huggins constant (k) of polymers were determined in chloroform (CF), 1,2-dichloro ethane (DCE), tetrahydrofuran (THF) at three different temperatures: 30°, 35°, and 40°C. The data are reported in Table 2. Not much of temperature and solvents effect are found on the intrinsic viscosity (Table 2). The viscosity of a polymer solution depends on its molecular weight, temperature, concentration, and nature of a solvent, and on its thermodynamic affinity for a polymer. The viscosity of dilute solutions is greatly affected by the mole-

Table 1. The IR and NMR Spectral Data of Polymers

Polymer	Characteristic IR Absorption Bands, cm^{-1}	NMR Chemical Shifts, ppm.
PS-1	1379.5(-O-SO_2-,ν_s) 1188.1(-O-SO_2-,ν_{as}) 1250.7(C-O-C,str.)	1.466–1.590(6H,d,β + γ-CH_2-); 2.175 (4H, s, α-CH_2-); 6.901–6.930(4H,d,Ar-H(a),J = 8.6); 7.088–7.117(4H,d,Ar-H(d),J = 8.7); 7.140–7.169(4H,d,Ar-H(c),J = 8.7); 7.813–7.841(4H,d,Ar-H(b),J = 8.6); 7.262 ($CDCl_3$)
PS-2	1371.9(-O-SO_2-,ν_s) 1181.9(-O-SO_2-,ν_{as}) 1240.6(C-O-C,str.)	1.473–1.578(6H,d,β + γ-CH_2-); 2.079–2.168 (10H,d,α-CH_2- + -CH_3); 6.916–7.033(6H,m,Ar-H(MeBC)); 7.118–7.147(4H,d,Ar-H(a),J = 8.8); 7.870–7.899(4H,d,Ar-H(b),J = 8.8); 7.259 ($CDCl_3$)
PS-4	1373.3(-O-SO_2-,ν_s) 1170.5(-O-SO_2-,ν_{as}) 1245.9(C-O-C,str.) 751.9(C-Cl, str.)	1.476–1.579(6H,d,β + γ-CH_2-); 2.081–2.175 (10H,d,α-CH_2- + -CH_3); 6.919–7.035(4H,m,Ar-H(ClMeBC)); 7.119–7.149(4H,d,Ar-H(a),J = 8.7); 7.871–7.900(4H,d,Ar-H(b),J = 8.7); 7.259 ($CDCl_3$)
PS-7	1374.6(-O-SO_2-,ν_s) 1178.0(-O-SO_2-,ν_{as})	1.471–1.575(6H,d,β + γ-CH_2-); 2.014–2.162 (10H,d,α-CH_2- + -CH_3); 6.912–7.035(6H,m,Ar-H(MeBC)); 7.725–7.753(4H,d,Ar-H(b),J = 8.2); 7.940–7.968(4H,d,Ar-H(a),J = 8.3); 7.260 ($CDCl_3$)
PS-9	1373.7(-O-SO_2-,ν_s) 1178.5(-O-SO_2-,ν_{as}) 756.1(C-Cl, str.)	1.471(6H,s,β + γ-CH_2-); 2.061–2.174 (10H,d,α-CH_2- + -CH_3); 6.899–7.055(4H,m,Ar-H(ClMeBC)); 7.808–7.830(4H,d,Ar-H(b),J = 6.3); 7.929–7.957(4H,d,Ar-H(a),J = 8.3); 7.585 ($CDCl_3$) 3.027(moisture in DMSO)

cular weight and molecular shape of the dissolved polymer. [η] and the slope of η_{sp}/C vs. C line depends on the nature of a solvent. This is due to the fact that the polymer coil swells differently in different solvents and therefore has different sizes. For flexible polymers, high values of k′ are the characteristic of the poor solvents and this is not observed in polymers with rigid chains and strong specific interactions. Thus, the poorer the solvent, the higher the value of k′. The nature and extent of solvent-polymer interactions will be different in all the polymers under investigation due to different substituents, as well as

Table 2. The Intrinsic Viscosities and Huggins Constant of Polymers in Different Solvents at Different Temperatures

	30°C		35°C		40°C	
Polymer	[η]	k	[η]	k	[η]	k
Chloroform						
PS-1	0.27	1.10	0.29	0.39	0.23	0.59
PS-2	0.30	6.8	0.57	0.30	0.51	0.27
PS-4	0.27	1.10	0.32	0.83	0.33	0.35
PS-5	–	–	0.09	0.93	–	–
PS-6	–	–	0.13	0.37	–	–
PS-7	0.24	0.87	0.34	− 0.02	0.27	0.03
PS-8	–	–	0.11	0.44	–	–
PS-9	0.32	2.2	0.29	0.39	0.26	0.04
PS-10	–	–	0.06	3.03	–	–
Tetra Hydrofuran						
PS-1	0.39	0.13	0.34	0.13	0.28	0.16
PS-2	0.75	0.23	0.54	0.55	0.40	0.37
PS-4	0.39	0.13	0.31	0.00	0.36	0.11
PS-5	–	–	0.05	0.47	–	–
PS-6	–	–	0.14	0.10	–	–
PS-7	0.34	0.09	0.34	0.13	0.28	0.16
PS-8	–	–	0.10	0.21	–	–
PS-9	0.45	0.07	0.38	0.21	0.24	0.26
PS-10	–	–	0.07	0.99	–	–
1,2-Dichloro ethane						
PS-1	0.44	0.21	0.35	− 0.04	0.37	0.37
PS-2	0.62	0.16	0.60	0.17	0.51	0.04
PS-4	0.37	0.04	0.36	0.00	0.35	1.02
PS-5	–	–	0.05	1.49	–	–
PS-6	–	–	0.15	0.10	–	–
PS-7	0.28	0.00	0.23	0.24	0.23	0.25
PS-8	–	–	0.10	1.04	–	–
PS-9	0.37	0.04	0.33	− 0.09	0.29	0.25
PS-10	–	–	0.07	− 0.79	–	–

backbone structure and therefore, it is difficult to decide thermodynamic goodness of the solvents of polydisperse polymers on the basis of k′ values. Powerful solvent-polymer interaction results into an extension of a coil and hence, high viscosity. On the basis of experimental observations, and keeping in mind only chain extension, the thermodynamic goodness is THF>DCE>CF except PS-1 where it is DCE>THF>CF. Moreover, no systematic trend in k values is observed indicating polydisperse nature of the polymers as well as specific interactions occurring in the solution and hence, the degree of solvophilicity of a polymer at a specified temperature. For the

sake of comparison, [η] of PS-5, PS-6, PS-8, and PS-10 are determined at 35°C in solvent systems studied. From Table 2, it is clear that these polymers possess quite low molecular weights.

Biological Activity

The biological activity of PS-1, PS-2, PS-4, PS-7, and PS-9 and standard drugs: amoxycilin (S_1), ampicillin (S_2), ciprofloxacin (S_3) and erythromycin (S_4) were screened against different microorganisms: Escherichia coli, Becillus megaterium, Proteus vulgaris, Staphylococcus aureus and Aspergillus niger by using DMF as a solvent at 37°C. The detailed experimental method is described in our earlier publication [6]. The sample concentration was 50 μg. The zones of inhibition of microbial growth of standard samples along with polymer samples are reported in Table 3.

From Table 3, it is evident that PS-1, PS-2, PS-7, and PS-9 are found as active as S_1, S_2, and S_4 against E.coli while PS-2, PS-4, PS-7, and PS-9 are found as active as S4 against S.aureus but none of them are found as antibacterial. The structure, nature of substituents molecular weight, and molecular weight distribution [25, 26] of polymer affect the biological activities. In the present case, the observed activity might be due to methyl, chlorine and sulfonate linkages in the polymers, and to some extent, phenolic and sulfonyl end groups.

Acid, Alkali, and Salt Resistance

The resistance to hydrolytic attack of PS-1, PS-2, PS-4, PS-7, and PS-9 films was determined by a change in weight method at room temperature in

Table 3. A Comparative Zones of Inhibition for Standard and Polymers Against Different Microorganisms

Sample	Zones of Inhibition, mm				
	E. coli	*B. mega*	*P. vulgaris*	*S. aureus*	*A. niger*
PS-1	18	15	12	14	12
PS-2	19	13	13	18	11
PS-4	14	14	12	17	10
PS-7	17	12	10	19	11
PS-9	16	11	12	20	12
DMF	11	11	11	11	11
Amoxycilin S_1	17	22	24	26	–
Ampicillin S_2	17	24	22	30	–
Ciprofloxacin S_3	30	31	29	26	–
Erythromycin S_4	18	26	35	19	19

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Table 4. Chemical Resistance of Polymers by Change in Weight Method at Room Temperature

	% Wt. Change														
	PS-1			PS-2			PS-4			PS-7			PS-9		
Solution, %	After One Day	After One Week	After One Month	After One Day	After One Week	After One Month	After One Day	After One Week	After One Month	After One Day	After One Week	After One Month	After One Day	After One Week	After One Month
HCl	4.2	6.3	7.5	8.0	9.2	10.5	5.1	6.4	7.9	3.9	4.5	6.0	5.6	6.2	7.8
H_2SO_4	1.8	2.6	3.4	3.5	4.0	5.3	2.0	3.6	4.2	2.5	3.2	4.7	3.2	4.1	5.3
HNO_3	3.8	4.6	5.8	2.8	3.7	5.1	1.4	2.5	3.8	1.4	2.2	3.5	2.2	3.6	4.7
NaOH	3.3	4.3	5.2	1.4	2.3	3.0	1.6	2.1	4.0	0.6	1.1	1.4	0.8	1.7	2.2
KOH	2.3	2.8	3.1	1.0	1.5	1.9	−0.4	−0.1	0.1	−0.1	0.1	0.4	−0.4	0.0	0.4
NaCl	2.0	2.6	3.2	1.1	1.5	1.8	−1.2	−0.5	0.0	−0.6	−0.3	0.0	0.0	0.2	0.4
H_2O	0.2	0.4	0.5	0.1	0.3	0.6	0.1	0.2	0.3	0.0	0.0	0.1	0.1	0.2	0.3

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pure water and in 10% each of aqueous hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, potassium hydroxide and sodium chloride after 24 hours, one week and one month. The percent weight gained or loss is reported in Table 4. From Table 4, it is clear that the % water uptake also increased with time except PS-7. The lone pairs in sulfonate and ether linkages and chlorine are electronegative groups, while methyl, methylene and phenyl groups are electropositive groups. The strong interaction of hydrogen ions and negative ions of alkali and salt with the said groups in the polymer cause the solvation phenomenon. The degree of solvolysis will be predominant in the case of dipole-dipole interaction of the opposite type. In the present case, predominant solvolysis is observed in acidic solutions especially in HCl and minimum in alkali and salt solutions. Negative weight loss in NaOH and NaCl solutions indicates partial degradation of sulfonate linkages at the surfaces up to a definite time span and after that solvation phenomenon is predominant. From Table 4, it is evident that H-bond formation between water and polymer is less favorable as compared to acids, alkalis and salt. Thus, polysulfonates under investigation possess excellent hydrolytic stability towards acids, alkalis and salt under investigation.

CONCLUSION

Polysulfonates possess excellent solubility in common organic solvents, good antibacterial activity against E.coli and S.aureus microbes, and excellent resistance to hydrolytic attack towards acids, alkalis and salt. Further work on thermal, mechanical and electrical properties of the said polymers is in progress and will be published elsewhere.

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