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Synthesis and Characterization of Cardo Polysulfonates of 1,1'-Bis(4-Hydroxy Phenyl)Cyclohexane with 1,3-Benzene and 2,4-Toluene Disulfonyl Chlorides

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SYNTHESIS AND CHARACTERIZATION OF CARDO POLYSULFONATES OF 1,1′-BIS(4-HYDROXY PHENYL)CYCLOHEXANE WITH 1,3-BENZENE AND 2,4-TOLUENE DISULFONYL CHLORIDES

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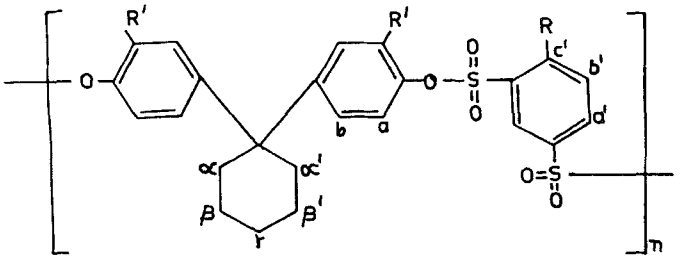
ABSTRACT

Cardo polysulfonates (PSBCB and PSBCT) of 1,1′-bis(4-hydroxy phenyl)cyclohexane with benzene-1,3 and toluene-2,4-disulfonyl chlorides have been synthesized by interfacial polycondensation of 1,1′-bis(4-hydroxy phenyl)cyclohexane (0.005 mol) with benzene-1,3/toluene-2,4-disulfonyl chlorides (0.005 mol) using water–chloroform (4:1, v/v) as interphase, alkali (0.015 mol) as acid acceptor, and cetyl trimethyl ammonium bromide (0.125 g) as emulsifier at 0°C for 3 hours. The structures of the polymers were supported by IR and NMR spectral data. The PSBCT was fractionated into several fractions by using 1,2-dichloroethane as solvent and *n*-butanol as precipitant. The fractions were characterized by GPC and viscometry in different solvents at four

different temperatures. Viscosity studies showed that the PSBCT is flexible in solutions and has a specific solvent effect. PSBCB and PSBCT have good biological activity against *E. coli* and *S. citrus* organisms, and they possess excellent hydrolytic stability toward acids and alkalis.

INTRODUCTION

Aromatic polysulfonates are well known for their promising industrial applications [1–7] as coating, adhesive, thermoplastic molding compositions alone or mixed with fillers, films, packaging, bonding materials for glass reinforced plastics, and antifriction self-lubricating materials. They possess unique stability toward hydrolytic attack [1, 2, 8, 9]. A literature survey on polysulfonates containing cardo (Latin, meaning "loop") showed that not much work has been carried out on this class of polymers. In continuation with our earlier work [10], the present paper describes the synthesis and characterization of cardopolysulfonates of 1,1′-bis(4-hydroxy phenyl)cyclohexane with benzene-1,3-disulfonyl chloride and toluene-2,4-disulfonyl chloride of the following structure.



I PSBCB: R = H, R′ = H

II PSBCT: R = CH_3, R′ = H

III PSMBC: R = R′ = CH_3

EXPERIMENTAL

Materials

The chemicals used were of laboratory grade and were purified prior to use by literature methods [11]. 1,1′-Bis(4-hydroxy phenyl)cyclohexane (BC), benzene-1,3-disulfonyl chloride (BDSC), and toluene-2,4-disulfonyl chloride (TDSC) were synthesized according to reported methods [12–15]. The emulsifier cetyl trimethyl ammonium bromide (Sisco Chemicals) was used as such.

Polymer Synthesis

To a cooled and clear solution of BC (0.005 mol) in 0.015 M NaOH (50 mL), cetyl trimethyl ammonium bromide (0.125 g) was added with vigorous agitation. A solution of BDSC/TDSC (0.005 mol) in chloroform (12.5 mL) was added dropwise

over a period of 20 minutes and the emulsion was agitated vigorously at 0°C for 3 hours. The organic layer was separated and poured into isopropanol to precipitate the polymer. The polymer was filtered, washed with water and methanol repeatedly, and dried at 50°C. The polymer was further purified by dissolving it in chloroform and precipitating it with isopropanol. The yield was 90–92%.

The polymers, hereafter designated as PSBCB and PSBCT, are soluble in common organic solvents like chloroform (CF), 1,2-dichloroethane (DCE), trichloroethylene (TCE), chlorobenzene (CB), *o*-dichlorobenzene, 1,4-dioxane (DO), and tetrahydrofuran (THF). The polymers form tough and transparent films from chloroform solution.

PSBCT (1%) was fractionated by fractional precipitation with 1,2-dichloroethane as solvent and *n*-butanol as precipitant at 30 ± 0.2°C. A standard procedure was used, and 11 fractions were collected.

MEASUREMENTS

The IR spectra of PSBCB and PSBCT (thin films) were scanned on a Shimadzu DR-1, 435 IR Spectrometer. The NMR spectra of PSBCB and PSBCT were scanned in $CDCl_3$ on a Hitachi R-1200(60 MHz) Spectrometer using TMS as an internal standard. The viscosity measurements were carried out with an Ubbelohde-type suspended level viscometer [16]. The intrinsic viscosity [η] of each fractions in different solvents at 30, 35, 40, and 45°C was determined according to the Huggins [17] relationship. Gel permeation chromatographic measurements were made on a Water Associates GPC-150 equipped with a set of three different columns containing μ-Styragel (10^6, 10^5, and 10^4 Å) at 25°C, using THF as the solvent.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra (thin films) of PSBCB and PSBCT. The observed characteristic absorption bands (cm^{-1}) are for PSBCB: 1383 $\left(-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}, \nu_s\right)$, 1183 $\left(-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-, \nu_{as}\right)$, and 1150 (C—H i-p-d, Ar); and for PSBCT: 1388 $\left(-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-, \nu_s\right)$, 1367 (C—H, δ_s, $-CH_3$), 1183 $\left(-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-, \nu_{as}\right)$ and 1150 (C—H i-p-d, Ar) besides the normal modes of the alkane, alicyclic, and aromatic groups.

Figure 2 shows the NMR spectra ($CDCl_3$) of PSBCB and PSBCT. PSBCB and PSBCT show four and five distinct signals, respectively, in Fig. 2. The signals are assigned as follows. For PSBCB: two singlets at δ 1.441 (6H, β + γ—CH_2—) and δ 2.139 (4H, α—CH_2—) and two multiplets at δ 7.189-6.730 (8H, a and b Ar—H) and at δ 8.093-7.375 (4H, a′, b′, c′, and d′ Ar—H). For PSBCT: three singlets at

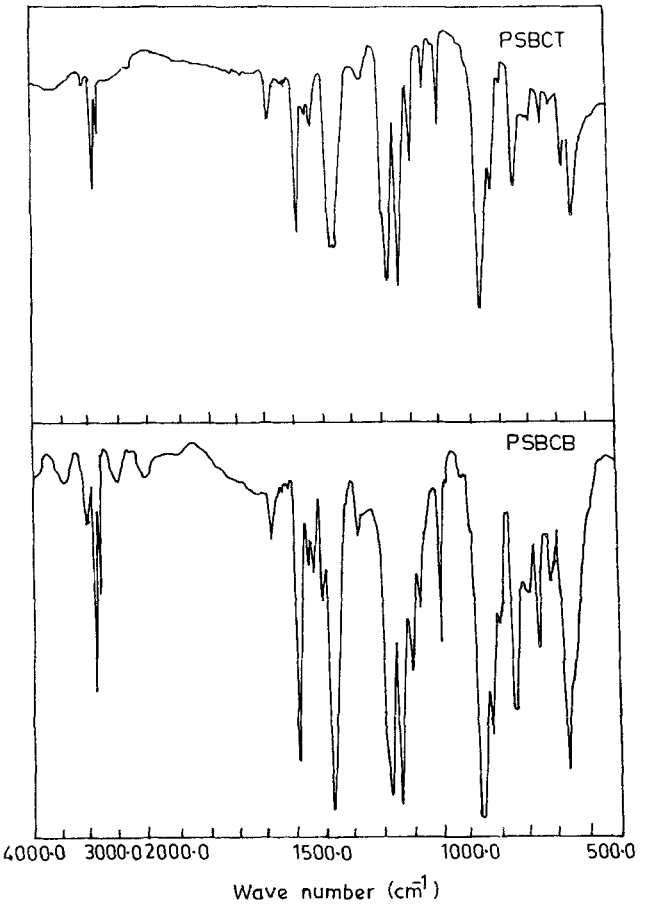


FIG. 1. IR spectra (thin film) of PSBCB and PSBCT.

δ 1.438 (6H, β + γ—CH_2—), δ 2.124 (4H, α—CH_2), and δ 2.764 (3H, —CH_3), and two multiplets at δ 7.143–6.703 (8H, a and b Ar—H) and δ 8.093–7.375 (3H, a′, b′, and d′ Ar—H). The residual solvent signal is overlapped at δ 7.375 in both spectra. Each type of proton is assigned in the spectrum itself. Thus, the structures of PSBCB and PSBCT are confirmed by IR and NMR spectral data.

Figure 3 shows a typical GPC chromatogram of fraction F-4. All chromatograms of PSBCT were Gaussian in nature and were skewed to the right. The Gaussian nature of GPC chromatograms justifies the selection of column porosity. The number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights and the polydispersities of some of the selected fractions are reported in Table 1. From Table 1 it is clear that fractions F-1A and F-2 are highly heterogeneous compared to the others. This is mainly due to poor fractionation as reflected by the skewness in the chromatograms.

Solution viscosity is a measure of the size or extension into space of polymer molecules. It is empirically related to molecular weight for linear polymers. Solution

viscosity constitutes an extremely valuable tool for the molecular characterization of polymers. The viscosity of polymer solutions at the molecular level is a direct measure of the hydrodynamic volume of polymer molecules. The intrinsic viscosities and Huggins constant k of PSBCT fractions were determined in CF, DCE, THF, and DO at four different temperatures: 30, 35, 40, and 45°C. The data are reported in Table 2. On the basis of $[\eta]$ in Table 2, the thermodynamic quality of the solvents is in the order CF > THF > DCE > DO.

Experimental $[\eta]$ is correlated with $\overline{M}_w$ by the empirical Mark-Houwink-Kuhn-Sakurada (MHKS) relationship [18] ($[\eta] = KM_w^a$). Linear least square plots of log $[\eta]$ against $\overline{M}_w$ are shown in Fig. 4. The slopes and the intercepts of the plots yielded values of exponent a and constant K. The relationships at 30°C are

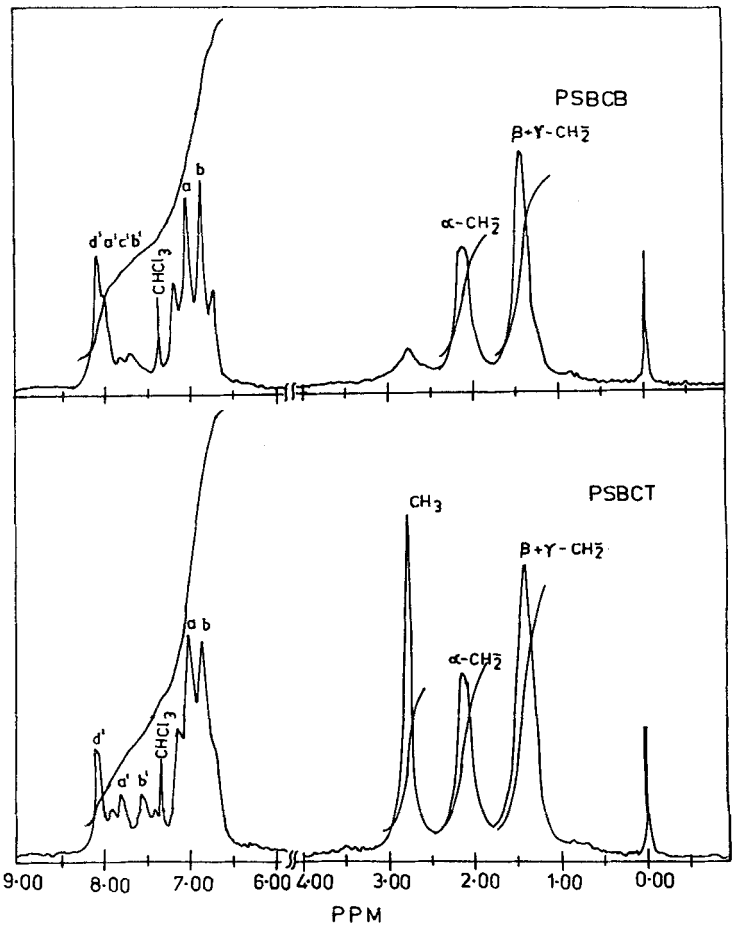


FIG. 2. NMR spectra of PSBCB and PSBCT in $CDCl_3$ at 60 MHz.

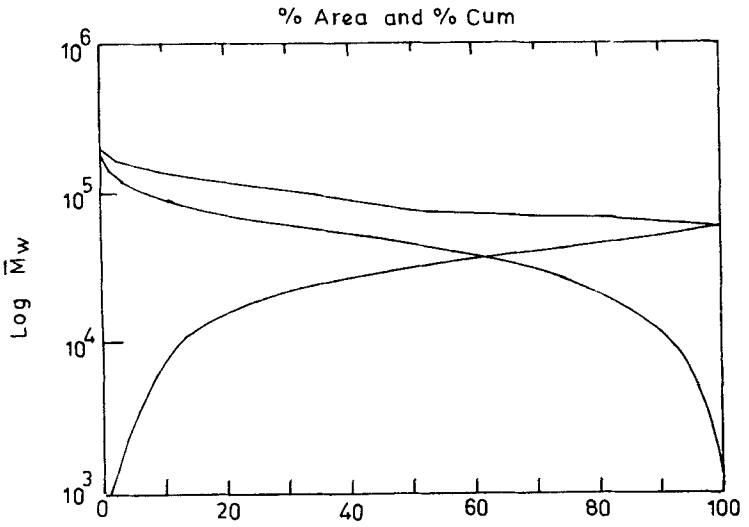


FIG. 3. Plots of log $\overline{M}_w$ against % area and % cumulative for F-4.

$$[\eta] = 1.63 \times 10^{-4} \overline{M}_w^{0.54} \quad \text{(CF)}$$
$$= 15.5 \times 10^{-4} \overline{M}_w^{0.54} \quad \text{(THF)}$$
$$= 11 \times 10^{-4} \overline{M}_w^{0.55} \quad \text{(DCE)}$$
$$= 1.6 \times 10^{-4} \overline{M}_w^{0.64} \quad \text{(DO)}$$

In general, $[\eta]$ of a polymer decreases with a decrease in molecular weight and an increase in temperature above the θ temperature in a particular solvent. The dielectric constant of the solvent also influences $[\eta]$ of the polymer. From Table 2 it is clear that the variation of $[\eta]$ with increasing temperature is not very significant except for the chloroform system (excluding F-6). Thus, not much effect of temperature is observed in a particular solvent. GPC molecular weights are valid as long as the relative magnitude is of concern because separation is based on molecular size and not on molecular weight. Polymer chains adopt an extended chain configura-

TABLE 1. Molecular Weights and Molecular Weight Distributions of PSBCT Fractions Obtained from GPC Data in Tetrahydrofuran at 25°C

Fraction	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
F-1A	20.143	2.934	6.87
F-2	8.809	1.585	5.56
F-4	4.739	2.072	2.29
F-5	4.285	1.690	2.53
F-6	2.869	1.246	2.30

TABLE 2. Intrinsic Viscosity [η] and Huggins Constant k [17] for PSBCT Fractions at Different Temperatures

Solvent	Temp., °C	F-1A		F-2		F-4		F-5		F-6	
		[η]	k	[η]	k	[η]	k	[η]	k	[η]	k
CF	30	1.08	0.62	0.69	0.41	0.61	0.15	0.46	0.10	0.35	0.11
	35	0.91	0.70	0.63	0.44	0.47	0.14	0.38	0.17	0.34	0.10
	40	0.85	0.71	0.57	0.49	0.43	0.14	0.34	0.19	0.35	0.12
	45	0.75	0.62	0.55	0.45	0.39	0.19	0.34	0.20	0.33	0.11
THF	30	1.03	0.35	0.76	0.18	0.53	0.13	0.43	0.05	0.37	0.10
	35	0.99	0.31	0.74	0.21	0.52	0.13	0.45	0.13	0.34	0.10
	40	0.99	0.41	0.76	0.20	0.46	0.18	0.46	0.10	0.35	0.10
	45	1.12	0.10	0.73	0.22	0.45	0.17	0.42	0.03	0.37	0.05
DCE	30	0.86	0.10	0.53	0.33	0.38	0.21	0.35	0.22	0.31	0.26
	35	0.85	0.10	0.54	0.34	0.32	0.23	0.28	0.27	0.24	0.25
	40	0.70	0.22	0.49	0.35	0.31	0.20	0.28	0.24	0.27	0.15
	45	0.62	0.29	0.44	0.40	0.28	0.21	0.34	0.22	0.33	0.20
DO	30	0.24	0.10	0.19	0.10	0.16	0.04	0.11	0.11	0.11	0.10
	35	0.25	0.10	0.21	0.05	0.16	0.05	0.10	0.13	0.10	0.24
	40	0.25	0.18	0.20	0.02	0.15	0.10	0.10	0.14	0.10	0.32
	45	0.27	0.02	0.21	0.02	0.14	0.04	0.10	0.12	0.10	0.24

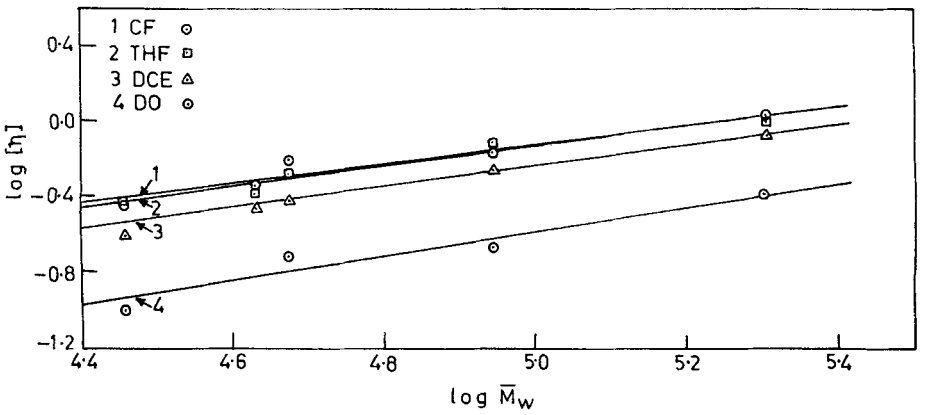


FIG. 4. Plots of log [η] against log $\bar{M}_w$ for PSBCT at 30°C in different solvents.

tion in a good solvent and a compact coil configuration in a poor solvent, which causes lowering of $[\eta]$. From Table 2 it is clear that no systematic trend in $[\eta]$ is observed due to the high polydispersity of polymer fractions and the specific solvent–polymer interaction in a particular solvent at a particular temperature. In earlier work on PSMBC(III) [10] we also observed such an effect. The exponent a is a measure of the degree of expansion of polymer chains in a good solvent at a particular temperature. For flexible polymers, $0.5 < a < 0.8$. The constant K is a measure of the solvent–solute interaction, and in the present case it is about ten times higher in the dioxane system.

BIOLOGICAL ACTIVITY

The biological activities [19] of PSBCB and PSBCT were tested against different microorganisms (*Escherichia coli, Becillus megaterium, Salmonella typhose, Staphylococcus citrus,* and *Aspergillus niger*) using DMF as the solvent at 37°C. The sample concentration was 50 μg. The zones of inhibition of the bacterial growth of the standard samples and the polymer samples are reported in Table 3. From Table 3 it is observed that the antimicrobial activity of PSBCB and PSBCT are comparable with standard drugs against *E. coli* and *S. citrus*. PSBCB and PSBCT have moderate activity against *A. niger*.

Polymeric materials possess some unique characteristics which exert a profound influence on biological activities [20, 21] in a number of cases. The nature, molecular weight, and molecular weight distribution of polymers, the degree of crosslinking, the stereochemical configuration, etc. have significant roles in their biological activities. From Table 3 it is clear that PSBCB and PSBCT have somewhat more biological activity than PSMBC [10]. PSMBC chains assume a coiled configuration in DMF, and its fractions are less heterogeneous compared to PSBCT fractions. The observed greater activity may be due to the nature and configurations of PSBCB and PSBCT chains. Their molecular weights are comparable with PSMBC (83,500–24,900) [10].

TABLE 3. Comparative Zones of Inhibition for Standards and Polymers Against Different Strains of Microorganisms

	Cultures				
Sample	*S. typhose*	*E. coli*	*S. citrus*	*B. mega*	*A. niger*
Norfloxacin	28	26	33	23	18
Chloramphenicol	25	24	24	26	21
Ampicillin	17	24	22	17	20
Griseofulvin	12	25	22	10	23
DMF	10	10	10	10	10
PSBCT	11	22	20	11	16
PSBCB	12	22	21	11	16
PSMBC(III) [10]	11	18	18	11	14

TABLE 4. Hydrolytic Stability of PSBCB and PSBCT Films toward Alkalies and Acids

	Weight loss, %				
	After 1 week			After 1 month	
10% acid/alkali	PSBCT	PSBCB	PSMBC[a]	PSBCT	PSBCB
H_2SO_4	0.65	1.00	100	0.94	1.60
HCl	1.00	0.75	–	1.44	0.83
HNO_3	0.90	0.75	14.1	1.18	0.97
NaOH	0.25	0.35	0.7	0.40	0.58
KOH	0.34	0.50	–	0.36	0.56

[a]After refluxing for 24 hours.

ACID AND ALKALI RESISTANCE

The hydrolytic stabilities of PSBCB and PSBCT films were determined at room temperature in 10% solutions each of aqueous sulfuric acid, nitric acid, hydrochloric acid, sodium hydroxide, and potassium hydroxide. The percentage weight losses after 7 days and 1 month are reported in Table 4 along with PSMBC-(III) [10]. From Table 4 it is clear that PSBCB and PSBCT have excellent hydrolytic stabilities in the above-mentioned acids and alkalies. PSBCB and PSBCT have excellent acid and alkali resistance and are comparable with aromatic polysulfonates which contain rigid moieties [6, 8] ($< 1\%$ weight loss after 1 week).

In conclusion, PSBCB and PSBCT have excellent solubilities in common organic solvents, good biological activities against *E. coli* and *S. citrus* organisms, and excellent hydrolytic stabilities toward acids and alkalies.

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