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Synthesis and physico-chemical properties of copoly(ester-sulfonates) of 1,1′-bis (3-methyl-4-hydroxy phenyl) cyclohexane with 2,4-toluene disulfonyl and terephthaloyl chlorides

B.G. Manwar, S.H. Kavthia, P.H. Parsania *

Department of Chemistry, Saurashtra University, Rajkot, 360 005 Gujarat, India

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Abstract

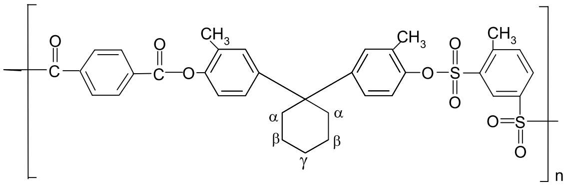
Copoly(ester-sulfonates) of varying compositions have been synthesized by interfacial polycondensation technique by using H_2O–$CHCl_3$ as an interphase, alkali as an acid acceptor and sodium lauryl sulfate-cetyl trimethyl ammonium bromide as mixed emulsifiers at 0 °C for $4\frac{1}{2}$ h. Copolymers are characterized by IR and NMR spectral data, viscosity in three different solvents at three temperatures and little solvent and temperature effect is found on $[\eta]$; and density (1.3430–1.3406 g/cm^3) by floatation method. Copolymers possess excellent solubility in common solvents and chemical resistance against water, acids, alkalis and salts. They possess moderate to good tensile strength (10.6–79.5 N/mm^2), excellent volume resistivity (7.5–28×10^{16} Ω cm), electric strength (53–118 kV/mm) and dielectric constant (1.3–1.58). They are thermally stable up to about 349–373 °C in an N_2 atmosphere and possess high T_g (136–196 °C). DTA endo/exothermic transitions supported either decomposition or formation of new product(s). Physical properties of copolymers are improved with increasing terephthlate content.

Keywords: Copoly(ester-sulfonates); IR, NMR; Viscosity; Density; Thermal analysis, Mechanical and electrical properties

1. Introduction

A considerable research interest has been increased in the field of aromatic copoly(ester-sulfonates) due to their outstanding applications as thermoplastic molding compositions, packaging films, fibers, coating and adhesives [1–6]. Incorporation of cardo groups in the main chain leads to improved physico-chemical properties: excellent solubility, hydrolytic stability, high T_g and thermal stability, excellent mechanical and electrical properties, etc. [7], which signify their industrial applications in variety of fields.

To our knowledge no work has been reported on aromatic cardo copoly(ester-sulfonates). The present work describes the synthesis and physico-chemical properties of copoly(ester-sulfonates) of 1,1′-bis (3-methyl 4-hydroxy phenyl) cyclohexane with toluene-2,4-disulfonyl and terephthaloyl chlorides (I) of varying mole compositions.



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* Corresponding author. Tel.: +91-281-2581097; fax: +91-281-2578512.
E-mail address: phparsania@sancharnet.in (P.H. Parsania).

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CP-1: [100:90:10]
CP-2: [100:80:20]
CP-3: [100:70:30]
CP-4: [100:60:40]
CP-5: [100:50:50]
CP-6: [100:40:60]
CP-7: [100:30:70]
CP-8: [100:20:80]
CP-9: [100:10:90]

2. Experimental

2.1. Material

The chemicals used were of laboratory grade and were purified prior to their use [8]. 1,1′-Bis (3-methyl-4-hydroxy phenyl) cyclohexane (MeBC) [9,10], toluene-2,4-disfulfonyl chloride (TDSC) [11] and terephthaloyl chloride (TC) [12] were synthesized according to reported methods and were repeatedly recrystallized from appropriate solvent systems. The emulsifiers sodium lauryl sulfate (Sisco-Chem.) and cetyl trimethyl ammonium bromide (Sisco-Chem.) were used as received.

2.2. Polymer synthesis

In a 250 ml three-necked flask equipped with a high speed mechanical stirrer and a thermometer, a 0.005 mol MeBC and 0.012 mol sodium hydroxide were dissolved in 50 ml of distilled water. The solution was cooled to 0 °C and 30 mg cetyl trimethyl ammonium bromide and 20 mg sodium lauryl sulfate were added; and the solution was stirred vigorously for about 15 min. Then, a solution of TDSC-TC (90:10 to 10:90 mol%) was added dropwise over 10 min. and the emulsion was vigorously stirred for 4.5 h 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. CP-1 to CP-9 were further purified repeatedly by dissolving in chloroform (CF) and precipitating in methanol. The yields were 85–91%. CP-1 to CP-9 are soluble in common organic solvents like chloroform, 1,2-dichloroethane (DCE), tetrahydrofuran, DMF, DMSO, etc.

A tough and transparent films of CP-1 to CP-3 and CP-7 to CP-9 were cast from concentrated chloroform (~4%) solutions on a leveled clean glass plate. CP-4 to CP-6 are found to be low molecular weights under identical reaction conditions and formed brittle films.

2.3. Measurements

The IR spectra (thin films) of copolymers were scanned on a Carl Zeiss FTIR spectrophotometer and the NMR spectra were scanned on a Brucker FTNMR (300 MHz) spectrometer by using $CDCl_3$ as a solvent and TMS as an internal standard. The viscosity measurements in various solvents at three different temperatures: 30, 35 and 40 °C were made with an Ubbelohde type suspended level viscometer [13] and intrinsic viscosities were determined by Huggins relationship [14]. The chemical resistance of copolymer films was carried out at room temperature for varying period in water and 10% each of acids, alkalis and salt solutions. The density measurements were carried out by floatation method [15]. The TG-DTA (15 °C/min) and DSC (10 °C/min) measurements were made on Mettler TS systems in nitrogen atmosphere. The electric strength (ASTM-D-149-92), dielectric constant (ASTM-D-150-92), volume resistivity (ASTM-D-257-92) and tensile strength measurements of 15 mm wide and 50 μm thick films were made at room temperature on a high volume Tester (Automatic (Mumbai)) by using 25/75 mm brass electrodes, Schering Bridge (Tettex Switzerland), Hewlet Packard High Resistance Meter at 500 V DC after 60 s and Instron Universal Testing Machine, Model No. 1186 at a testing speed of 50 mm/min, respectively.

3. Results and discussion

3.1. IR and NMR spectral study

Fig. 1. shows typical IR spectra of CP-1 and CP-9. The characteristic observed absorption bands (cm^{-1}) are 1178–1200 ($–SO_2$, ν_{as}), 1373–1389($–SO_2–$, ν_s); 1263 (C–O, str.) and 1738–1740 (C=O, str.) besides normal modes of alkane, alicyclic and aromatic groups. Fig. 2. shows NMR spectra of CP-1 and CP-9. CP-1 to CP-9 showed seven signals at δ 1.58–1.45 (6H, d, $\beta+\gamma$, $–CH_2–$); 2.21–2.00 (10H, m, $\alpha–CH_2–+CH_3$); 2.81 (3H, s, $Ar–CH_3$); 7.20–8.30 (d, MeBC + TC + TDSC). The signal due to residual chloroform appeared at about δ 7.26 and overlapped with aromatic protons. From Fig. 2, it is clear that NMR spectra of copolymers are very complex. The copolymer compositions are not determined due to complex nature and unreliable integrated peak areas of the spectra.

3.2. Solution viscosity

Viscosity of a solution is a transport property and is a measure of the hydrodynamic volume of a macromolecule. It also furnishes information pertaining to polymer–solvent interactions and thus behavior of polymer chain in the solution. Hydrodynamic volume of a molecule in solution depends on nature of solvents, temperature, nature of the functional groups present, etc. The viscosity measurements were made in three different solvents: chloroform, 1,2-dichloroethane and tetrahydrofuran at three different temperatures: 30, 35 and 40

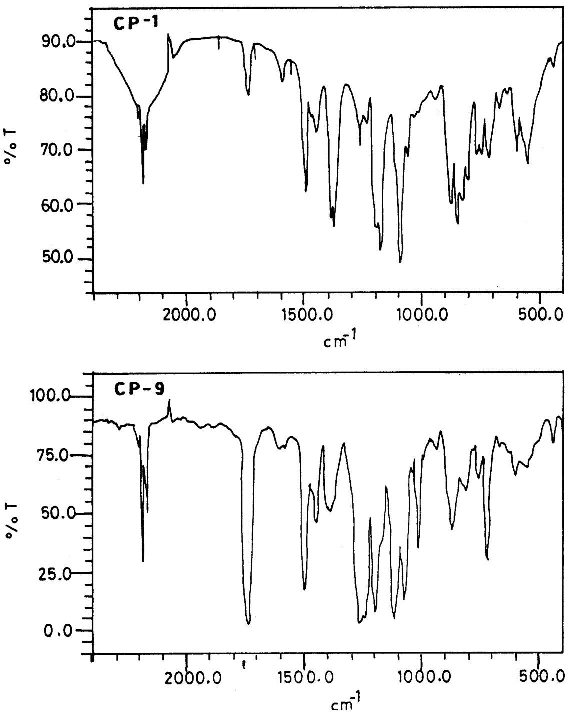

Fig. 1. IR spectra (thin films) of CP-1 and CP-9.

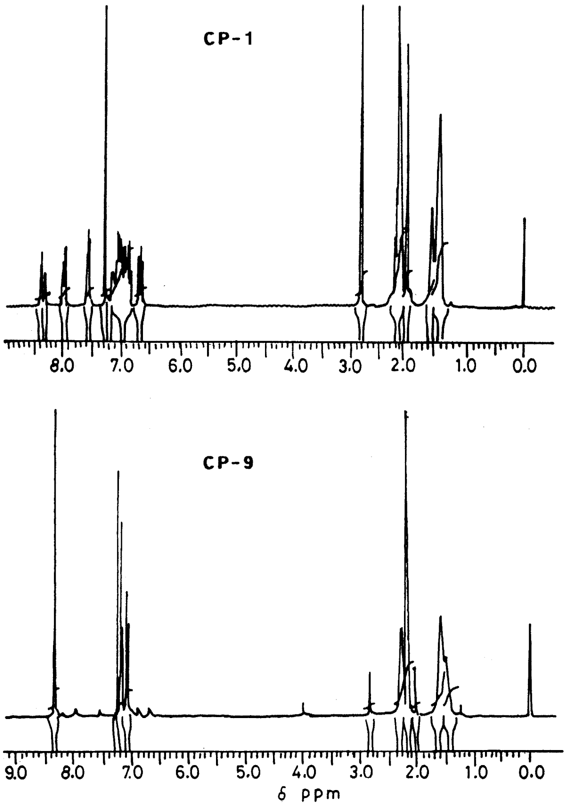

Fig. 2. NMR spectra ($CDCl_3$) of CP-1 and CP-9.

°C. The intrinsic viscosity [η] and Huggins constant (k') for each system were determined according to Huggins relationship. The least square values are reported in Table 1. From Table 1, it is evident that [η] and k' have increased with increasing TC content in the copolymers. The observed thermodynamic goodness of [η] is THF > DCE > CF. Little temperature and solvent effect is observed on [η] indicating flexible nature of the copolymer chains. Random values of k' indicated polydisperse nature and specific solvent–polymer interactions in the solutions.

3.3. Chemical resistance

The resistance to hydrolytic attack of CP-1 to CP-3 and CP-7 to CP-9 films was determined by a change in weight method at room temperature in pure water and 10% each of aqueous HCl, H_2SO_4, HNO_3, CH_3 COOH, NaOH, KOH and NaCl solutions after 24 h, one week and one month. The percent weight gained or loss is reported in Table 2. From Table 2, it is observed that CP-1 to CP-3 and CP-7 to CP-9 have suffered ±1.9% weight changes indicating excellent hydrolytic stability towards said reagents. A slight weight loss or gain for a given sample is due to either surface degradation or solvation of ions with polar groups present in the copolymer chains. In accordance to other cardo polysulfonates [16–18], CP-1 to CP-3 and CP-7 to CP-9 possess excellent chemical resistance to acids, alkalis and salt solutions.

3.4. Density measurements

The densities of CP-1 to CP-3 and CP-7 to CP-9 films were determined by floatation method using CCl_4-n-hexane system at room temperature according to reported method [15]. The experimental densities along with standard deviation are reported in Table 3. From Table 3, it is evident that density has decreased with increasing TC content in the copolymers due to difference in intrinsic volume of TDSC and TC moieties.

3.5. Thermal analysis

Typical DSC and TG-DTA thermograms of CP-1 and CP-9 are presented in Figs. 3 and 4. The DSC and DTA transitions are reported in Table 4. T_g is found to increase with increasing TC content in the copolymer. DSC endo/exothermic transitions for a given copolymer are due to some physical change as confirmed by no weight loss in TG curve over that transition region. Similarly DTA endo/exothermic transitions have showed decomposition as supported by weight loss in

Table 1
The intrinsic viscosity and Huggins constant for CP-1 to CP-3 and CP-7 to CP-9 in different solvents at three different temperatures

Polymer	CF		DCE		THF	
	[η]	k′	[η]	k′	[η]	K′
	30 °C					
CP-1	0.61	0.63	0.65	0.59	0.84	0.12
CP-2	0.74	0.45	0.84	0.12	0.87	0.21
CP-3	0.87	0.30	0.87	0.32	0.99	0.16
CP-7	0.99	0.27	0.98	0.30	1.14	0.12
CP-8	0.98	0.31	1.11	0.17	1.26	0.08
CP-9	1.08	0.26	1.21	0.12	1.38	0.06
	35 °C					
CP-1	0.51	1.24	0.62	0.65	0.77	0.23
CP-2	0.61	0.88	0.68	0.60	0.85	0.21
CP-3	0.72	0.70	0.81	0.42	0.95	0.19
CP-7	0.98	0.26	0.97	0.30	1.12	0.11
CP-8	1.07	0.16	1.03	1.26	1.21	0.10
CP-9	1.17	0.13	1.19	0.13	1.34	0.07
	40 °C					
CP-1	0.48	1.42	0.63	0.54	0.72	0.31
CP-2	0.60	0.89	0.66	0.64	0.79	0.31
CP-3	0.65	1.02	0.79	0.46	0.88	0.28
CP-7	0.92	0.34	0.95	0.31	1.12	0.09
CP-8	1.03	0.19	1.03	0.24	1.21	0.08
CP-9	1.18	0.10	1.16	0.14	1.29	0.08

Table 2
Chemical resistance of copolymers by change in weight method at room temperature

Solution %	% Weight change								
	After 24 h	After one week	After one month	After 24 h	After one week	After one month	After 24 h	After one week	After one month
	CP-1			CP-2			CP-3		
H_2O	−0.13	−0.97	−0.16	−0.47	−0.81	−0.11	−0.43	−1.50	−0.52
HCl	−1.62	−1.83	−0.38	−1.41	−1.12	−0.26	−0.41	−1.69	−0.02
H_2SO_4	−0.72	−1.42	−0.14	−0.96	−1.65	−0.60	−0.60	−1.22	−0.28
HNO_3	−2.12	−0.79	−1.89	−0.73	−0.81	0.77	−0.15	−0.39	−0.24
CH_3COOH	0.05	0.34	0.05	0.24	0.35	0.71	0.29	1.42	1.69
NaOH	−1.19	−0.70	−0.85	−0.37	−1.35	−0.17	−0.53	−2.11	−0.76
KOH	−1.99	−0.86	−0.24	−0.30	−0.80	−0.11	−0.23	−0.44	−0.59
NaCl	−0.89	−0.85	−1.46	−0.60	−0.15	−0.30	−0.36	−1.08	−0.21
	CP-7			CP-8			CP-9		
H_2O	−0.48	−0.41	−0.79	−0.71	−0.37	−0.12	−0.61	−0.88	−0.37
HCl	−0.07	−0.26	−0.36	−0.40	−0.64	−0.31	−0.36	−0.46	−0.05
H_2SO_4	−0.74	−0.68	−0.65	−0.16	−0.29	−0.45	−0.30	−0.11	−0.28
HNO_3	−0.30	−0.41	−0.74	−0.36	−0.69	−0.33	−0.16	−0.08	−0.39
CH_3COOH	0.45	0.52	0.85	0.38	0.39	0.27	0.14	0.31	0.23
NaOH	−0.28	−0.15	−0.03	−0.42	−0.48	−0.52	−0.54	−0.30	−1.05
KOH	−0.12	−0.87	−1.23	−0.47	−0.75	−0.70	−0.45	−0.51	−0.76
NaCl	−0.81	−1.02	−0.88	−1.00	−1.21	−0.75	−0.36	−0.41	−0.28

TG curves while physical change has supported no weight loss in TG curves for a given system.

The initial decomposition temperature, decomposition range, % weight loss and temperature of maximum weight loss (T_{max}) for copolymers are reported in Table 4. Copolymers are thermally stable up to about 349°–373 °C and have involved two step decomposition. It is interesting to note that the thermal stability and T_{max} are

Table 3
The densities of CP-1 to CP-3 and CP-7 to CP-9 determined by floatation method at 30 °C

Polymer	ρ, g cm^{-3}	Polymer	ρ, g cm^{-3}
CP-1	1.3430 ± 0.004	CP-7	1.3410 ± 0.0003
CP-2	1.3423 ± 0.0003	CP-8	1.3409 ± 0.0004
CP-3	1.3419 ± 0.0004	CP-9	1.3406 ± 0.0005

increased with increasing terephthlate content in copolymers. The observed thermal stability of copolymers is in accordance with cardo polysulfonates of bisphenol-C (PS) [19] and cardo polyester of MeBC and TC (HP). T_g is comparable when TC content is less than 50% mol composition but it is high for high TC content.

3.6. Mechanical and electrical properties

The tensile strength, electric breakdown voltage, volume resistivity and dielectric constant data of CP-1 to CP-3 and CP-7 to CP-9 films along with homo polysulfonate (PS) of MeBC and TDSC are reported in Table 5. From Table 5, it is clear that CP-1 to CP-3 and CP-7 to CP-9 possess moderate to good tensile strength. The tensile strength is increased with increasing TC content in the copolymers. They possess excellent BDV and volume resistivity and low dielectric constant. Volume resistivity and BDV are found to increase with increasing TC content. They possess somewhat good electrical properties as compared to homo polysulfonates [19]. Thus mechanical and electrical properties are improved by copolymerization. Copolymers possess comparable tensile strength and superior BDV and volume resistivity and low dielectric constant as compared to some industrial plastics [20] indicating their industrial usefulness as insulators.

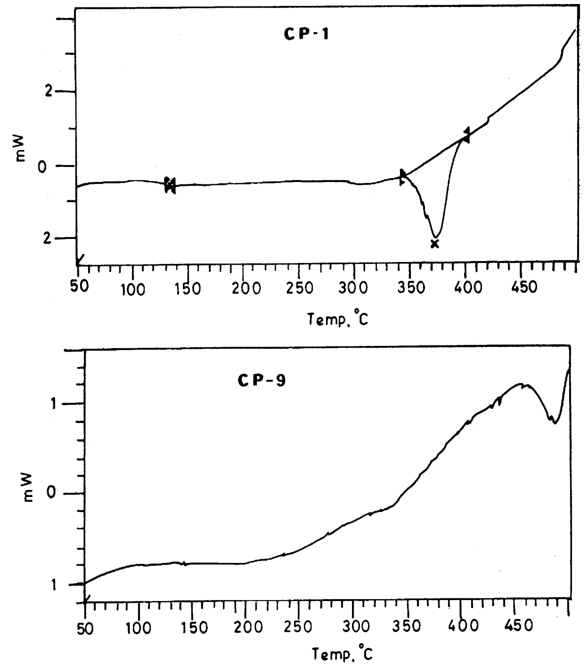

Fig. 3. DSC thermograms of CP-1 and CP-9 at a heating rate of 10 °C/min in an N_2 atmosphere.

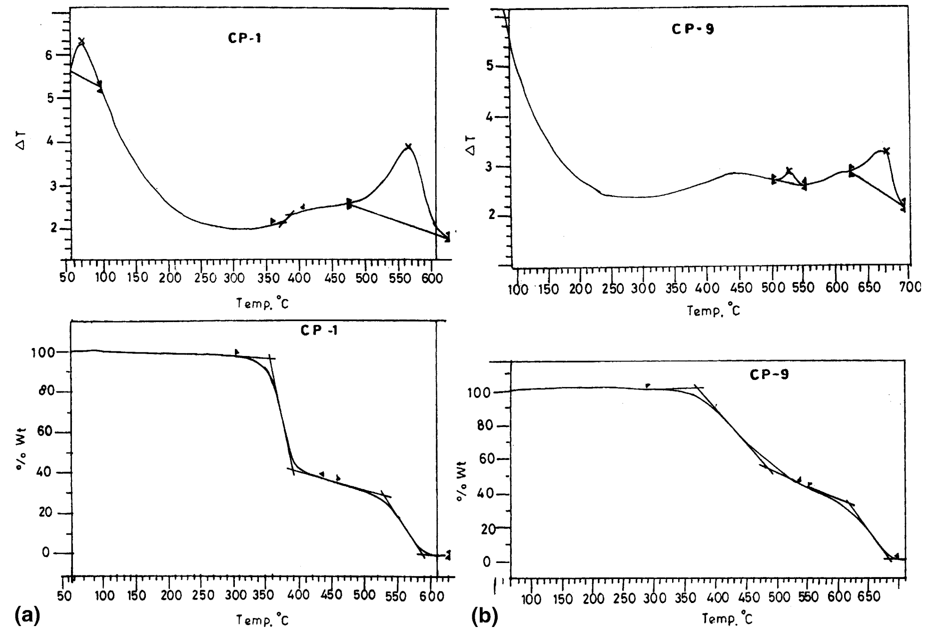

Fig. 4. TG-DTA thermograms of (a) CP-1 and (b) CP-9, at a heating rate of 15 °C/min in an N_2 atmosphere.

Table 4
DSC and DTA transitions; and TGA data for PS, HP and CP-1 to CP-9

Polymer	DSC			DTA		TGA			
	T_g	Transition	Transition temp., °C	Transition	Temp., °C	IDT, °C	Decompn. range, °C	% Wt loss	T_{max}, °C
PS[19]	141.0	Exo	292.9	Exo	386.2	356	356–388	60.9	376.5
				Exo	580.0	525	525–598	26.9	570.2
HP	–	–	–	Exo	515.4	379.4	379–452	34.5	428.1
				Exo	605.0	569.7	569–614	33.0	599.5
CP-1	136.0	Endo	373.7	Exo	384.3	354	354–389	54.6	375.9
				Exo	570.9	528	528–588	28.8	561.3
CP-2	152.2	Endo	375.9	Endo	367.7	349	349–382	51.8	369.2
				Exo	536.4	506	506–600	–	–
CP-3	145.4	Endo	379.9	Endo	380.9	361	361–392	57.4	378.1
				Exo	553.9	518	518–566	22.8	550.1
CP-7	188.9	Exo	342.0	Endo	492.0	373	373–422	20.9	413.7
				Endo	566.1	487	487–495	23.6	490.0
CP-8	196.0	Exo	240.1	Endo	387.0	371	371–418	22.6	402.0
		Endo	445.4	Exo	520.2	–	–	–	–
CP-9	196.0	Endo	460.0	Exo	532.6	370	375–486	46.1	432.0
				Exo	681.4	619	619–686	31.5	668.6

Table 5
Mechanical and electrical properties of PS, CP-1 to CP-9

Polymer	Tensile strength, N/mm^2	Volume resistivity, Ω cm	BDV, kV/mm	ε 230 V/50 Hz atm.temp
PS	18.5	4.2×10^{15}	23.6	1.47
CP-1	10.4	7.5×10^{16}	53.0	1.37
CP-2	10.6	8.8×10^{16}	67.0	1.57
CP-3	18.0	8.9×10^{16}	76.0	1.35
CP-7	50.1	1.2×10^{17}	77.0	1.15
CP-8	51.6	1.6×10^{17}	86.0	1.58
CP-9	79.5	2.8×10^{17}	118.0	1.30

4. Conclusion

On the basis of observed data, it is concluded that copoly(ester-sulfonates) possess excellent solubility, hydrolytic stability, high thermal stability, moderate to good tensile strength and excellent electrical properties. Thus physico-chemical properties of polysulfonates are improved by copolymerizing with terephthlate moiety.

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