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Synthesis and Physico-chemical Properties of Copolyesters of 1,1′-*bis*(3-Methyl-4-hydroxy Phenyl)cyclohexane with 2,2′-*bis*(4-Hydroxy Phenyl)propane with Terephthaloyl Chloride

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ABSTRACT

Copolyesters 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 cetyl trimethyl ammonium bromide–sodium lauryl sulfate as mixed emulsifiers at 0°C for 4 h. Copolymers are characterized by IR and NMR spectral data, viscosity and density (1.2465–1.2403 g/cm^3) by a floatation method. Copolymers possess excellent solubility in common solvents and chemical resistance against water, acids, alkalis, and salt. They possess moderate to good tensile strength (9.3–61.8 N/mm^2), excellent volume resistivity (1.2×10^{15}–1.1×10^{17} Ωcm), electric strength (29.6–50.0 kV/mm), and dielectric constant (1.51–2.03). They are thermally stable up to about 303–307°C in an N_2 atmosphere and possess high T_g (176–190°C). DTA endo/exothermic transition(s) supported either decomposition or formation of new product(s).

Key Words: Copolyesters; IR; NMR; Chemical resistance; Density; Thermal analysis; Mechanical and electrical properties.

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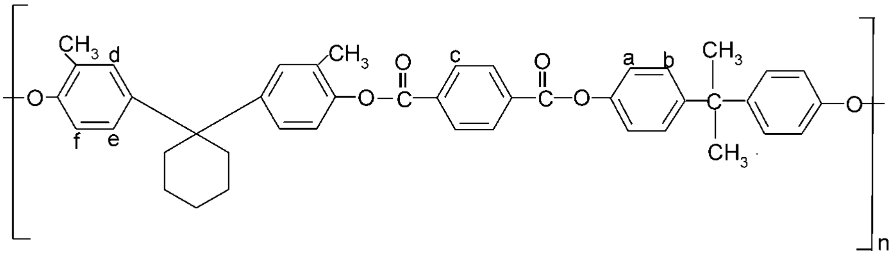
INTRODUCTION

High performance thermoplastics must possess excellent physical properties and regarded as a potential engineering plastic or as a matrix for advanced composites.[1] High performance polymers are well known for their high thermal stability, high T_g and T_m, high heat resistance and are soluble; and useful for modern technologies.[2–4] Introduction of rigid units such as cardo groups or heterocyclic rings into the polymer backbone leads to stiffer polymer backbone with high T_g and T_m. Among aromatic polymers cardo polymers occupy prominent place due to their excellent physical properties.[2]

Copolymerization or blending is another way of improving physical properties. Preparation of copolymers is a very important component of polymer design.[4] Properties of copolymers depend both on copolymer compositions and microstructures. The microstructure is determined by reaction conditions, equilibrium, comonomer reactivity ratio, etc.

Earlier we have reported some work on copolyesters of bisphenol-C with isophthaloyl and terephthaloyl chlorides.[5–7] To our knowledge, no work has been reported on copolyesters of bisphenol-A and bisphenol-C. With a view to improve physico-chemical properties of copolyesters, the present work reports the synthesis and physico-chemical properties of copolyesters of 1,1′-*bis*(3-methyl-4-hydroxy phenyl)cyclohexane (MeBC) and 2,2′-*bis*(4-hydroxy phenyl)propane (BA) with terephthaloyl chloride (I) of varying mole compositions.



BA : MeBC : TC	BA : MeBC : TC
CP-1: [20 : 80 : 100]	CP-2: [40 : 60 : 100]
CP-3: [50 : 50 : 100]	CP-4: [60 : 40 : 100]
CP-5: [20 : 80 : 100].	

Scheme 1.

EXPERIMENTAL

Materials

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

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Polymer Synthesis

In a 250mL three-necked flask equipped with a high speed mechanical stirrer and a thermometer; 0.005 mol (BA : MeBC, 20 : 80 to 80 : 20 mol%) and 0.012 mol sodium hydroxide were dissolved in 50 mL of distilled water. The solution was cooled to 0°C and 50, 100, 150, 200, 250 mg cetyl trimethyl ammonium bromide and 50, 75, 75, 100, 100 mg sodium lauryl sulfate were added and the solution was stirred vigorously for about 15 min. Then, a solution of 0.005 mol TC in chloroform (12.5 mL) was added dropwise over 10 min. The emulsion was vigorously stirred for 4 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-5 were further purified repeatedly by dissolving in chloroform and precipitating in methanol. The yields were ~80–87%. CP-1 to CP-5 are soluble in common organic solvents like chloroform, 1,2-dichloroethane, tetrahydrofuran, DMF, DMSO, etc.

Tough and transparent films of CP-1 to CP-5 were cast from concentrated chloroform (~4%) solutions on a leveled clean glass plate. The films were vacuum dried prior to their use.

Measurements

The IR spectra (KBr pellet) of copolymers were scanned on a Carl Zeiss Specord FTIR spectrophotometer. The NMR spectra of copolymers 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 chloroform at 30°C were made with an Ubbelohde type suspended level viscometer and intrinsic viscosities were determined by Huggins relationship. 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 a floatation method.[12] 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 resistance (ASTM-D-257-92) and tensile strength (IS 11298-87) measurements of 15 mm wide and 58–75 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 volt DC after 60 sec and Instron Universal Testing Machine, Model No. 1186 at a testing speed of 50 mm/min, respectively.

RESULTS AND DISCUSSION

IR and NMR Spectral Study

Figure 1 shows a typical IR spectrum of CP-3. The characteristic observed absorption bands (cm^{-1}) are 1263.3 (C–O str.) and 1739.7 (C=O, str.) besides normal modes of alkane,

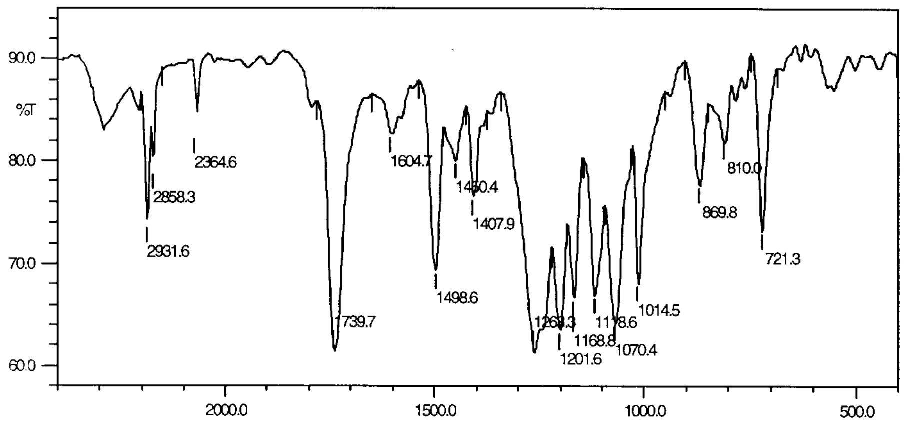

Figure 1. IR spectrum (KBr pellet) of CP-3.

alicyclic, and aromatic groups. Figure 2 shows a typical NMR spectrum of CP-3. CP-1 to CP-5 have shown eight signals at δ 1.596 (6H, *d*, $\beta + \gamma$-CH_2–); 1.737 (6H, *s*, –$C(CH_3)_2$–); 2.217 (6H, *s*, Ar-CH_3); 2.296 (4H, *s*, α-CH_2); 7.104–7.074 (2H, *d*, Ar-H(d), $J = 9$); 7.201–7.152 (8H, *m*, Ar-H(b + e + f), $J = 7.5$); 7.345–7.316 (4H, *d*, Ar-H(a), $J = 8.6$); 8.329 (4H, *s*, Ar-H(c)). The signals due to residual chloroform appeared at about δ 7.26 and overlapped with aromatic protons. In order to determine copolymer compositions, the signal due to isopropyl

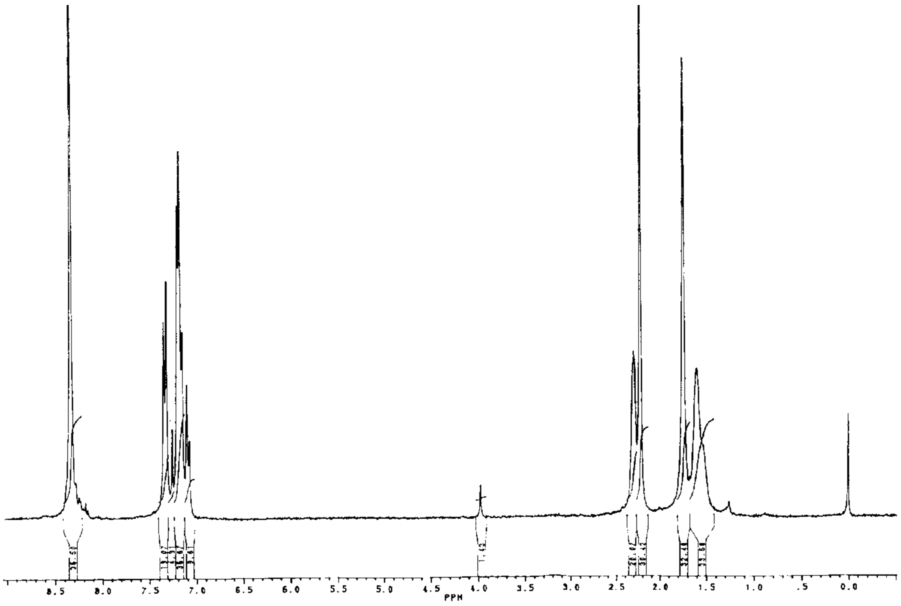

Figure 2. NMR spectrum ($CDCl_3$) of CP-3.

protons of bisphenol-A moiety and $\beta + \gamma$-CH_2- protons of MeBC moiety are identified for the determination of copolymer compositions according to following relationship:

$$\text{Composition} = \frac{A_A}{A_C}$$

where A_A and A_C are integrated peak areas for isopropyl and $\beta + \gamma$-CH_2-protons. Copolymer compositions determined according to the above relationship are reported in Table 1. From Table 1 it is clear that the copolymer compositions are in fairly good agreement with the feed compositions. Some disagreement in the composition is found due to unreliable integrated peak areas, which might be due to peak broadening problem.

Viscosity Measurements

Viscosity measurements of a dilute solution are a useful tool for understanding molecular interactions and behavior of polymer chains in solutions. The magnitude of viscosity provides an idea about molecular mass of the polymer. In order to understand the relative molecular masses of the copolymers CP-1 to CP-5 the intrinsic viscosity $[\eta]$ was determined in chloroform at 30°C. The observed $[\eta]$ values for CP-1 to CP-5 are 0.49, 0.66, 0.66, 0.56, and 0.74 dL/g, respectively. From these values it is clear that copolymers have moderately high molecular masses. $[\eta]$ has increased with increasing BA composition indicating somewhat more reactive nature of BA.

Chemical Resistance

The resistance to a hydrolytic attack of CP-1 to CP-5 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_3COOH, NaOH, KOH, and NaCl solutions after 24 h, 1 week and 1 month. It is observed that CP-1 to CP-5 have suffered ± 0.48% weight change 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 polymer chains. In accordance with other cardo copolyesters of bisphenol-C,[5–7] CP-1 to CP-5 possess excellent chemical resistance to acids, alkalis, and salt solutions.

Table 1. Copolymer compositions of CP-1 to CP-5.

			A_A/A_C	
Polymer	A_A	A_C	Experimental	Expected
CP-1	5.57	21.06	0.26	0.25
CP-2	13.39	22.23	0.60	0.67
CP-3	32.48	33.68	0.96	1.00
CP-4	36.97	28.65	1.30	1.50
CP-5	23.19	5.95	3.90	4.00

Density Measurements

The densities of CP-1 to CP-5 films were determined by a floatation method by using CCl_4-n-hexane binary system according to reported method.[12] The experimental densities along with standard deviation are reported in Table 2. From Table 2, it is evident that density has decreased as the composition of BA has increased in the copolymers due to a difference in intrinsic volume of MeBC and BA moieties. It might probably be due to increasing symmetric BA content in the copolyesters.

Thermal Analysis

Typical DSC and DTA-TG-thermograms of CP-3 are presented in Figs. 3 and 4, respectively. The DSC and DTA endo/exothermic transitions, initial decomposition temperature (IDT), the decomposition temperature range, percentage weight loss and temperature of maximum degradation (T_{max}) are reported in Table 3. DSC and DTA thermograms of CP-1 to CP-5 have showed either a small endothermic transition or change in slope, respectively at about 191° (186°), 190° (189°), 196° (183°), 205° (193°), and 176° (184°), which are due to a glass transition temperature indicating the onset of segmental motions. The figures in brackets are derived from DTA thermograms. Other DSC/DTA endo/exothermic transition(s) are due to either decomposition of polymer chains or some physical change (Table 3). The decompositions are confirmed by weight loss in TG thermograms over that of temperature ranges while physical change has indicated no weight loss in TG thermograms. Copolyesters possess lower TG than that of homo polyester of MeBC and TC (201.7°). From Fig. 4, it is evident that copolyesters have followed a three-step degradation pattern. First and second steps have overlapped to yield distorted sigmoidal TG curves. From Table 3, it is evident that CP-1 to CP-5 are thermally stable up to about 303–307°C. The thermal stability has increased with increasing composition of BA moiety in the copolymers but it is less than HP. A slight difference in T_{max} is observed for CP-2 to CP-5 and it is somewhat higher as compared to HP.[5] Copolymer microstructure influences thermal as well as tough properties.[4] Kinetic parameters are not determined due to distorted sigmoidal TG curves.

Table 2. The densities of CP-1 to CP-5 determined by floatation method at 30°C.

Polymer	$\rho\,(g\,cm^{-3})$
CP-1	1.2465 ± 0.0073
CP-2	1.2441 ± 0.0028
CP-3	1.2404 ± 0.0010
CP-4	1.2324 ± 0.0012
CP-5	1.2291 ± 0.0012

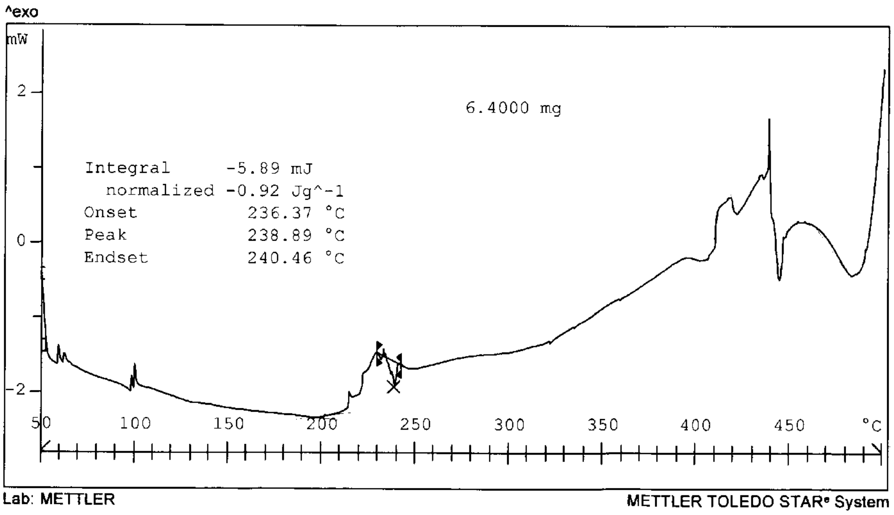

Figure 3. DSC thermogram of CP-3 at heating rate of 10°C/min in an N_2 atmosphere.

Mechanical and Electrical Properties

The tensile strength, electric breakdown voltage, volume resistivity, and dielectric constant data of CP-1 to CP-5 films are reported in Table 4. From Table 4, it is clear that CP-5 has low tensile strength indicating comparatively low molecular weight as supported by viscosity data. Other copolyesters possess comparable tensile strength with some useful

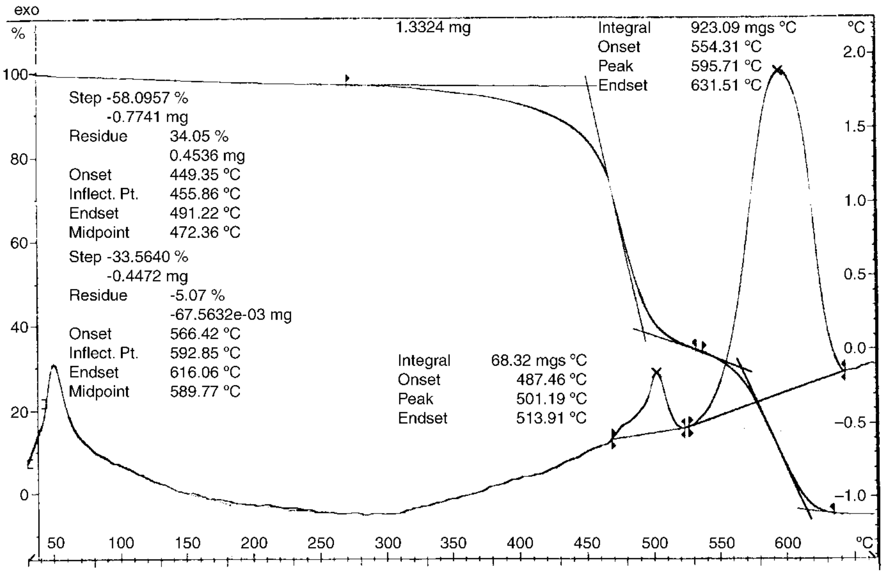

Figure 4. DTA-TG thermogram of CP-3 at heating rate of 15°C/min in an N_2 atmosphere.

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Table 3. Thermal data of HP and CP-1 to CP-5 derived from DSC and DTA-TG thermograms.

	DSC			DTA			TGA		
Polymer	T_g	Transition	Transition temperature (°C)	Transition	Transition temperature (°C)	IDT (°C)	Decomposition range (°C)	Percentage wt. loss	T_{max} (°C)
HP	—	—	—	Exo	515.4	379	379–452	34.5	428.1
	(201.7)			Exo	605.0	569	569–614	33.0	599.5
CP-1	191.0	Exo	455.5	Endo	543.5	305	305–412	15.5	405.0
	(186.6)			Exo	608.7	485	485–505	10.1	493.6
						574	574–619	30.7	592.6
CP-2	190.5	Exo	417.3	Exo	516.3	303	303–503	61.0	480.3
	(189.0)			Exo	613.2	585	585–636	28.8	608.9
CP-3	196.3	Endo	238.9	Exo	501.2	303	303–491	58.1	472.4
	(183.3)	Exo	416.7	Exo	595.7	566	566–616	33.6	589.8
		Exo	456.5						
CP-4	205.1	Exo	415.7	Exo	507.2	307	307–501	54.5	475.8
	(193.5)			Exo	626.1	575	575–629	25.6	609.2
CP-5	176.0	Exo	465.0	Exo	500.7	300	300–509	47.4	480.2
	(184.0)			Exo	638.0	600	600–654	28.1	623.2

Table 4. Mechanical and electrical properties of CP-1 to CP-5.

Polymer	Tensile strength (N/mm^2)	Volume resistivity (Ω cm)	BDV (kV/mm)	ε (230 V/50 Hz atm. temp.)
CP-1	52.9	1.2×10^{15}	40.6	2.03
CP-2	60.1	2.2×10^{15}	29.6	1.96
CP-3	41.0	6.2×10^{16}	41.9	1.83
CP-4	61.8	7.4×10^{16}	36.8	1.60
CP-5	9.3	1.1×10^{17}	50.0	1.51

plastics.[13] They possess good BDV and excellent volume resistance and low dielectric constant indicating excellent insulating property. Volume resistance is increased and dielectric constant decreased with an increasing BA content in copolyesters. Thus, copolyesters possess superior electrical properties as compared to some commercial plastics[13] signifying their industrial utility as excellent insulating materials.

CONCLUSION

On the basis of experimental findings, it is concluded that copolyesters possess excellent solubility, hydrolytic stability, electrical properties and good thermal, and mechanical properties.

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