Synthesis and Comparative Physicochemical Investigation of Partly Aromatic Cardo Copolyesters

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ABSTRACT: Copolyesters were synthesized through the condensation of 0.0025 mol of 1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane, 0.0025 mol of ethylene glycol/propylene glycol/1,4-butanediol/1,6-hexane diol, and 0.005 mol of terephthaloyl chloride with water/chloroform (4:1 v/v) as an interphase, 0.0125 mol of sodium hydroxide as an acid acceptor, and 50 mg of cetyl trimethyl ammonium bromide as an emulsifier. The reaction time and temperature were 2 h and 0°C, respectively. The yields of the copolyesters were 81–96%. The structures of the copolyesters were supported by Fourier transform infrared and ^{1}H-NMR spectral data and were characterized with the solution viscosity and density by a floatation method (1.1011–1.2697 g/cm^3). Both the intrinsic viscosity and density of the copolyesters decreased with the nature and alkyl chain length of the diol. The copolyesters possessed fairly good hydrolytic stability against water and 10% solutions of acids, alkalis, and salts at room temperature. The copolyesters possessed moderate-to-good tensile strength (11–37.5 MPa), good-to-excellent electric strength (19–45.6 kV/mm), excellent volume resistivity (3.8 × 10^{15} to 2.56 × 10^{17} Ω cm), and high glass-transition temperatures (148–195°C) and were thermally stable up to about 408–427°C in a nitrogen atmosphere; they followed single-step degradation kinetics involving 38–58% weight losses and 34–59% residues. The copolyesters followed 2.6–2.9-order degradation kinetics. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2463–2471, 2007

Key words: density; films; mechanical properties; polyesters; synthesis; thermal properties; viscosity

INTRODUCTION

Aromatic cardo (a Latin word meaning "loop") polymers[1–5] are well known for their excellent solubility, excellent thermomechanical and electrical properties, excellent chemical stability, high softening temperatures, and easy processability, which have led to their industrial importance.

Polymers of various stiffnesses can be synthesized with different kinds of disulfonyl chlorides/diacid chlorides and bisphenols. Terephthalate polyesters are useful as engineering thermoplastics because of their good chemical resistance, good thermal and dimensional stability, high strength and rigidity, and good surface hardness and gloss.[6,7] Aromatic polyesters are high-performance engineering plastics and have applications in a variety of fields.[8–17] Partly aromatic polyesters obtained from aliphatic glycols and aromatic dicarboxylic acids or esters are important commercially. They find their applications in precision molding for electrical and electronic devices, domestic and office appliances, and automotive parts. Partly aromatic polyesters can be synthesized with aliphatic diols and aromatic dicarboxylic acids.[18,19]

Rigid-chain polymers are difficult to process because of their limited solubility and high glass-transition temperatures (T_g's). One of the approaches to improving the solubility of these polymers without much loss of their high thermal stability is the introduction of polar and flexible groups or cardo groups into the backbone chain.[1,20–28] Another approach to modifying rigid polymers is blending with suitable polymers or copolymerization. Copolymerization and the use of asymmetric monomers are the most widely used approaches for obtaining manageable transition temperatures for processing and characterization.[20]

A literature survey on partly aromatic copolyesters containing cyclohexyl as a cardo group revealed that no work had been reported on terephthalate copolyesters of 1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane (MeBC) and aliphatic diols, and this prompted us to synthesize them and compare their physicochemical properties (Scheme 1).

EXPERIMENTAL

Materials

The chemicals used were laboratory-grade and were purified before their use by appropriate methods.[29] MeBC[30,31] and terephthaloyl chloride (TC)[32] were synthesized according to reported methods. MeBC
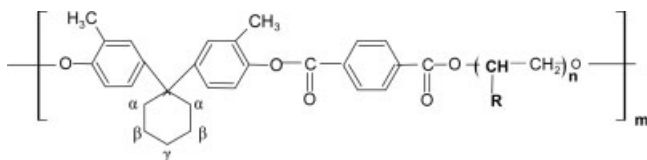
Scheme 1

was repeatedly recrystallized at least three times from benzene and methanol/water systems, and TC was recrystallized three times from a chloroform/n-hexane system. Other chemicals (Sisco-Chem, Mumbai, India), including cetyl trimethyl ammonium bromide (CTAB), ethylene glycol (EG), propylene glycol (PG), 1,4-butane diol (BD), and 1,6-hexane diol (HD), were used as received.

Copolyester synthesis

Into a 250-mL, three-necked flask equipped with a high-speed mechanical stirrer and a thermometer, 0.0025 mol (0.74 g) of MeBC, 0.0025 mol of EG/PG/BD/HD, and 0.0125 mol (0.5 g) of NaOH were dissolved in 50 mL of distilled water, and the solution was cooled to 0°C. CTAB (50 mg) was added, and the solution was stirred vigorously for about 15 min. To this solution, 0.005 mol (1.015 g) of TC in 12.5 mL of chloroform was added dropwise through a dropping funnel over 10 min. The emulsion was vigorously stirred for 2 h at 0°C. The organic layer was run into a large excess of methanol to precipitate the copolyester. The separated copolyester was filtered, washed well with water and finally with methanol, and dried at 50°C. The copolyesters were designated MET : $n = 1$ and R = H, MPT : $n = 1$ and R = CH$_3$, MBT : $n = 2$ and R = H, and MHT : $n = 3$ and R = H and were further purified thrice through dissolution in chloroform and precipitation in methanol. The yields were 81–96%. MET, MPT, MBT, and MHT were soluble in common solvents such as chloroform, 1,2-dichloroethane, and dichloromethane.

Film preparation

Thin and thick films of the copolyesters were cast from 1 and 4% chloroform solutions on a leveled glass plate. The rate of chloroform evaporation was controlled by the glass plate being covered. After 24 h, each film was peeled from the glass plate. A thick MHT film was brittle. The films were vacuum-dried before their use.

Measurements

The IR (thin films) spectra of MET, MPT, MBT, and MHT were scanned on a Shimadzu model 8400 Fourier transform infrared spectrometer (Kyoto, Japan). The ^{1}H-NMR spectra of the copolyesters were scanned on a Brucker FT-NMR (300 MHz) spectrom-

eter (Fallanden, Switzerland) with CDCl$_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. The viscosity measurements were carried out at three different temperatures—30, 35, and 40°C—in 1,2-dichloroethane and chloroform with an Ubbelohde suspended-level viscometer. The intrinsic viscosities were determined by the Huggins relationship. The density measurements were carried out at room temperature by a floatation method with a CCl$_4$/n-hexane system. The densities of the mixtures were determined by the usual method. The density and viscosity measurements were accurate to ± 0.0001 g/cm^3 and $\pm 0.1\%$, respectively. The hydrolytic stability of the copolyesters was determined at room temperature for various periods in water and aqueous HNO$_3$, H$_2$SO$_4$, HCl, KOH, NaOH, and NaCl (each at a 10% concentration). Tensile strength (IS 11298-Pt-2-1999), volume resistivity (ASTM D-257-92), and electric strength (IEC 243-Pt.1-1988) measurements were performed on an Instron model 1185 universal tensile testing machine (Kolkatta, India) at a speed of 50 mm/min, a Hewlett–Packard high-resistance meter (500-V direct current) (Garland, TX) after 60 s of charging in air at 25°C, and an Automatic (Mumbai, India) high-voltage tester in air at 27°C with 25/75-mm brass electrodes, respectively. Thermogravimetry (TG)/differential scanning calorimetry (DSC) measurements were performed on Universal V1.12E and V3 0.0G instruments (TA Instruments, Taichung, Taiwan) at a heating rate of 20°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Figure 1(a–d) shows Fourier transform infrared spectra of the copolyesters. The observed characteristic absorption peaks (cm^{-1}) are at 3355–3400 (OH stretching), 1792–1788 and 1740–1738 (C=O stretching), and 1246–1243 cm^{-1} (C—O stretching), in addition to normal modes of alicyclic, aliphatic, and aromatic groups.[33,34] The moderate peak at about 3355 cm^{-1}, due to OH stretching, indicates more unreacted OH and COOH end groups supporting the formation of moderately low-molecular-weight copolyesters, and this is supported by the low values of the intrinsic viscosities (Table I).

Figure 2(a–d) shows ^{1}H-NMR spectra of the copolyesters. Each of the copolyesters displays five distinct signals. Different types of protons are assigned in the corresponding spectra. Residual chloroform appears at about 7.44–7.26 ppm. The protons bonded to ester linkages are displayed in the upfield with an increase in the alkyl chain length. The signals due to aromatic protons of TC and MeBC moieties appear at about 8.33 and 7.35–7.07 ppm, respectively. For MET and MPT, protons bonded to ester linkages appear at 4.73 and 3.96 ppm, respectively, but for
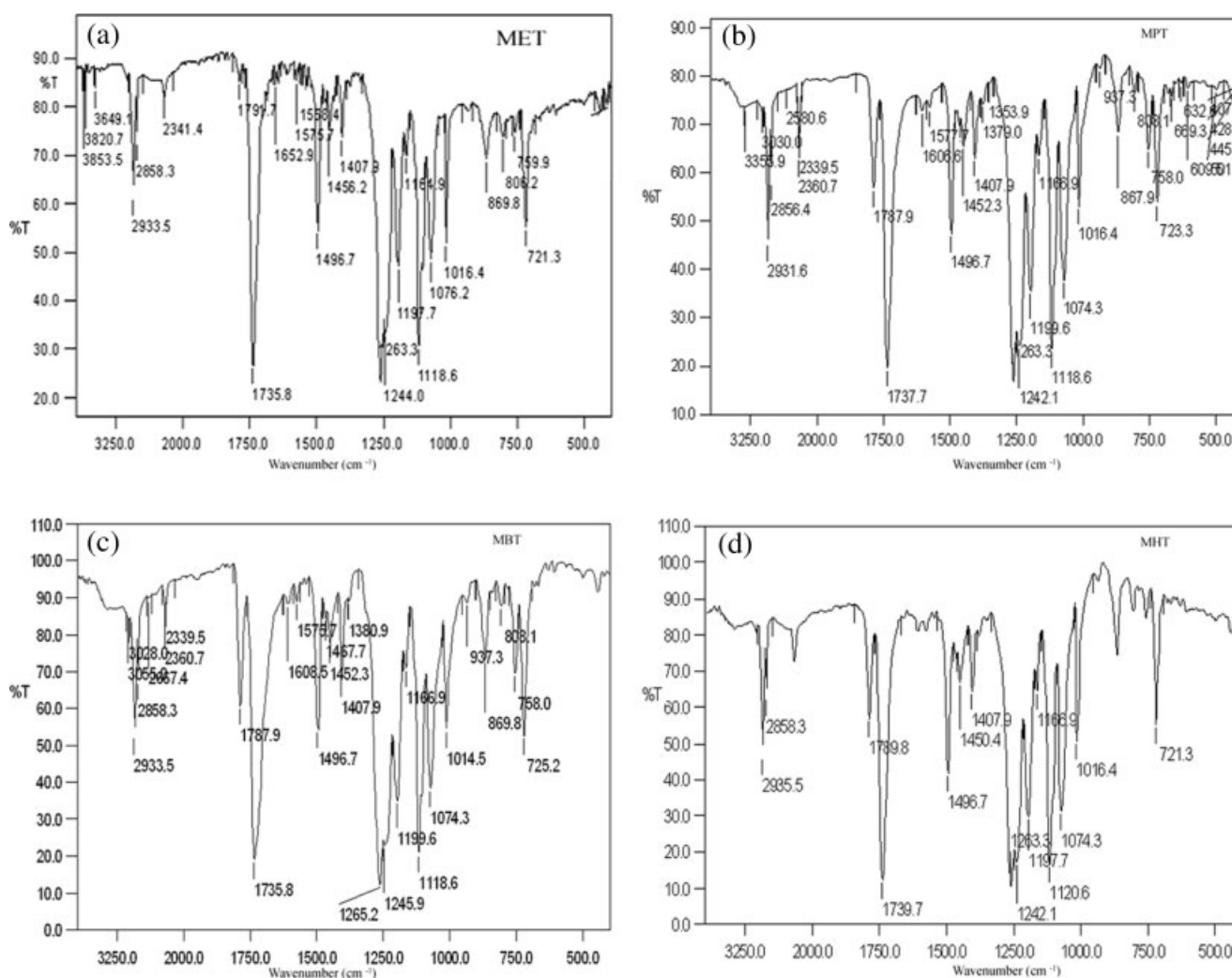
Figure 1 IR spectra of (a) MET, (b) MPT, (c) MBT, and (d) MHT.

MBT and MHT, they overlap with $\beta + \Upsilon$ —CH$_2$— protons of the cyclohexyl ring. An attempt has been made to evaluate the copolyester composition according to the following relationship:

$$\text{Composition} = (\text{Peak areas due to diol protons})$$
$$/(\text{Peak areas due to MeBC protons}) \quad (1)$$

For MET

$$\text{Composition} = \frac{A_2}{A_1 + A_3 + A_4} = \frac{24.9}{125.93} \cong 0.2$$

For MPT

$$\text{Composition} = \frac{A_2 + \frac{1}{3}A_4}{A_1 + A_3 + \frac{2}{3}A_4} = \frac{18.54}{69.24} \cong 0.27$$

For MBT

$$\text{Composition} = \frac{A_3 + \frac{2}{5}A_4}{A_1 + A_2 + \frac{3}{5}A_4} = \frac{25.1}{73.54} \approx 0.34$$

TABLE I
Values of the Intrinsic Viscosity and Huggins Constant for the Copolyesters in Two Different Solvents at Three Different Temperatures

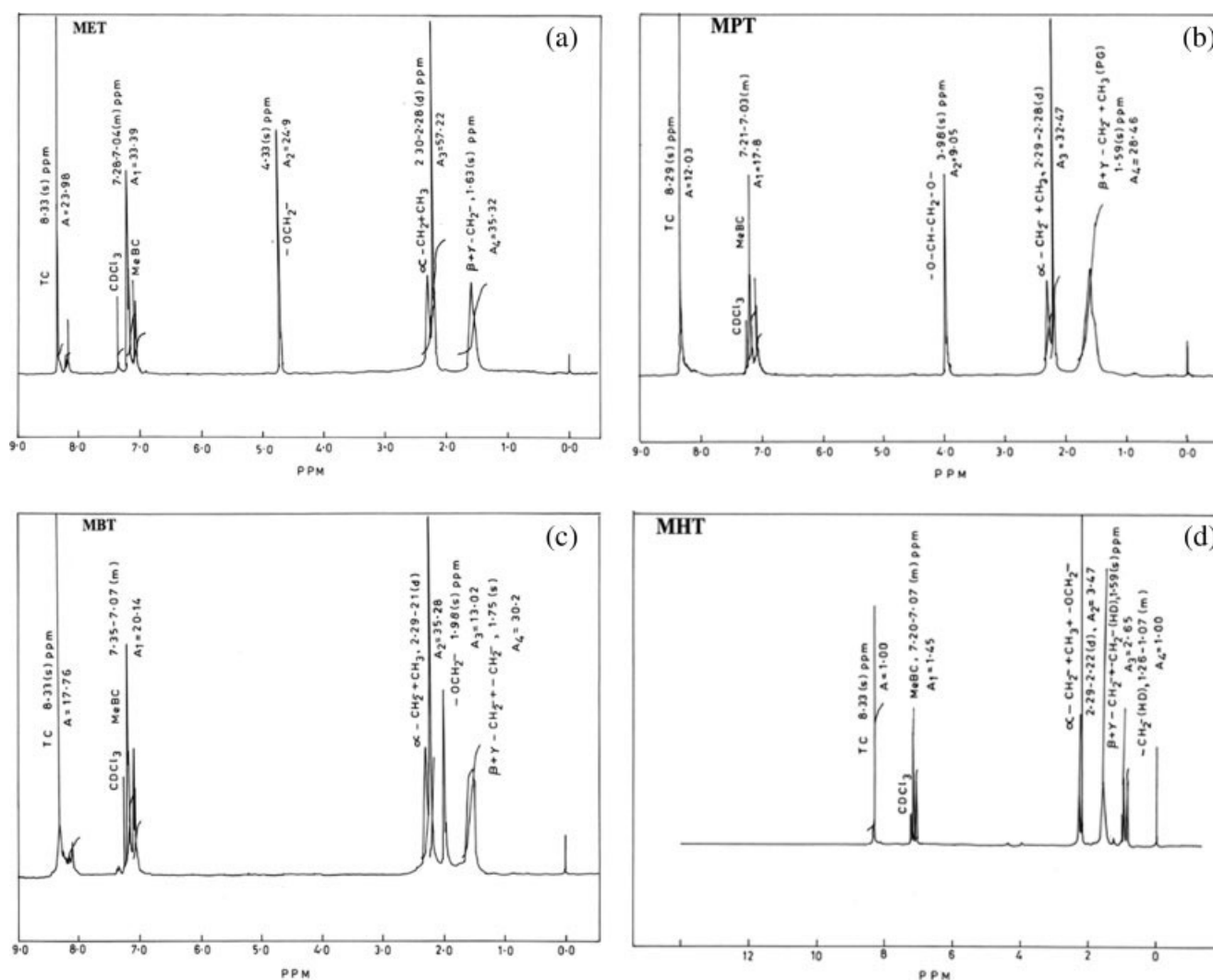| Copolyester	1,2-Dichloroethane		Chloroform	
	Intrinsic viscosity	Huggins constant	Intrinsic viscosity	Huggins constant
30°C				
MET	0.28	2.83	0.32	3.26
MPT	0.45	0.72	0.50	1.00
MBT	0.33	2.15	0.38	1.90
MHT	0.21	5.30	0.25	2.24
35°C				
MET	0.25	2.96	0.26	5.48
MPT	0.42	0.82	0.48	0.92
MBT	0.30	2.47	0.33	2.65
MHT	0.17	6.38	0.22	3.30
40°C				
MET	0.20	5.56	0.23	6.87
MPT	0.40	1.17	0.44	1.11
MBT	0.26	3.36	0.30	3.47
MHT	0.15	5.55	0.20	3.00

Figure 2 NMR spectra (CDCl$_3$) of (a) MET, (b) MPT, (c) MBT, and (d) MHT.

For MHT

$$\text{Composition} = \frac{\frac{2}{7}A_2 + \frac{2}{5}A_3 + A_4}{A_1 + \frac{5}{7}A_2 + \frac{3}{5}A_3} = \frac{3.05}{5.52} \approx 0.55$$

The expected copolyester compositions for MET, MPT, MBT, and MHT are 0.18, 0.27, 0.36, and 0.55, which are in good agreement with those observed within the experimental errors involved in determining the integrated peak areas. The physical and chemical properties of the copolymers strongly depend on the composition, the kinds of functional groups, and the arrangement of the structural units in the copolymer chains.[1] Thus, the IR and NMR spectral data support the structures of the copolyesters.

Solution viscosity

The solution viscosity is a transport property and is a measure of the hydrodynamic volume of a polymer in a given solvent. It is an important technique for the characterization of molecular interactions occurring in solutions and conformational changes. The structure of the polymer, nature of the solvent, temperature, presence of polar and pendant groups in the polymer molecule, and so forth are the decisive factors for molecular interactions and hence change with hydrodynamic volume and conformational changes in the solution. The intrinsic viscosities and Huggins constants of the copolyesters were determined according to the Huggins relationship and are reported in Table I, from which it is clear that the intrinsic viscosity is slightly greater in a chloroform system and decreases with temperature. The viscosity of a dilute solution is generally affected by the molecular weight and molecular shape of the dissolved polymer. For flexible polymers, high values of the Huggins constant are characteristic of a poor solvent, and this is not observed in polymers with rigid chains and strong specific interactions. The nature and extent of the solvent–polymer interactions in this study are different

because of the different backbone structures, which are supported by the different values of the intrinsic viscosity and Huggins constant. A small temperature effect on the intrinsic viscosity indicates the flexible nature of the copolyesters. An increase in the Huggins constant with an increase in the temperature indicates an increase in the molecular interactions in the solutions. Both the intrinsic viscosity and Huggins constant depend on the temperature, structure of the polymer, nature of the solvent, polydispersity, and so forth. The low values of the intrinsic viscosities and the moderate IR absorption peak at about 3355 cm^{-1} confirm the formation of copolyesters of moderate molecular weights. Cardo polyesters and copolyesters of small intrinsic viscosities (the intrinsic viscosity = 0.33–0.83 dL/g) are well documented in the literature.[3,5,35,36] From Table I, it is clear that the alkyl chain length and pendant methyl group (PG) of the aliphatic diols affected the molecular weights. The use of an asymmetric diol (PG) resulted in a considerable improvement in the molecular weight on the basis of the intrinsic viscosity. Because of a lack of facilities, the molecular weights of the copolyesters were not determined. From the observed copolymer compositions, it is expected that the distribution of monomers in the copolymer chains would be random, and this may not give correct molecular weight information because of different hydrodynamic volumes.

Density measurements

The densities of the copolyester films were determined by a floatation method at room temperature. In six different wide-mouth stoppered tubes, a small piece of a copolyester film and about 5 mL of CCl$_4$ were placed, and *n*-hexane was added dropwise with shaking until the film remained suspended throughout; it was allowed to equilibrate at room temperature for 24 h. The densities of the mixtures were determined by the usual method. The averages of six measurements along with the standard deviations from the mean are reported in Table II, from which it is evident that the density decreases with an increase in the alkyl chain length of the diol up to four carbons in the copolymer chains, indicating an increase in the chain flexibility, which is further supported by the viscosity data. Again, it increases with the alkyl chain length, indicating an increase in the chain packing density.

Hydrolytic stability

Most of the organic polymers are water-insoluble and have a tendency to absorb water depending on their molecular structure, the humidity, and the temperature. The moisture uptake tendency of the poly-

TABLE II
Densities of the Copolyesters by the Floatation Method at 30°C

Copolyester	Density (g/cm^3)
MET	1.2697 ± 0.0004
MPT	1.1984 ± 0.0010
MBT	1.1011 ± 0.0002
MHT	1.2389 ± 0.0004

mers strongly affects the physical properties of the polymers. The hydrolytic stability of copolyester films against various reagents was determined at room temperature by a change-in-weight method:

$$\Delta M \ (\%) = (M_2 - M_1/M_1) \times 100 \qquad (2)$$

where ΔM is the change in the weight, M_1 is the initial weight of the sample, and M_2 is the weight after the chemical treatment. To examine the hydrolytic stability of copolyester films against water and 10% solutions of HNO$_3$, H$_2$SO$_4$, HCl, KOH, NaOH, and NaCl at room temperature, preweighed films (4–5 mm) were kept in six different stoppered tubes containing the respective reagent with intermittent shaking. The films were taken out periodically, the surfaces were wiped with tissue paper, and the films were reweighed and reimmersed in the respective solutions. The weight changes (%) after 24 h, 1 week, and 1 month are reported in Table III; the weight changes range from +5.6 to −6.5% in different environments, indicating fairly good hydrolytic stability of the copolyesters in harsh acidic, alkaline, and saline environments. The use of PG instead of EG has been reported to improve the water resistance of polymers.[37,38] In fact, in this case, MPT has better water resistance than MET and MBT. From Table III, it is clear that MET has a weight-gain tendency in all the test media, whereas MPT has a weight-loss tendency, except in water, in which it has a weight-gain tendency. MBT has a weight-gain tendency in HNO$_3$, HCl, NaCl, and H$_2$O media, whereas in an H$_2$SO$_4$ medium, it has a weight-gain tendency. In alkaline media, MBT suffers a weight loss initially and then shows a weight-gain tendency. In all three copolyesters, the weight change is maximum up to 1 week, and then it decreases. The weight-gain tendency of the copolyesters is due to surface solvolysis by polar groups (ester, hydroxyl, and carboxyl groups) of copolyester molecules and water uptake through microcracks and microvoids, whereas the weight-loss tendency is due to hydrolysis of ester linkages, which indicates the leaching of small molecules. The extent of the water uptake mainly depends on the presence of hydrophilic polar groups, voids, additives, humidity, and temperature. Water may penetrate polymeric films through micro-

TABLE III
Chemical Resistance of the Copolyesters by the Change-in-Weight Method at Room Temperature

	Weight change (%)								
	After 24 h	After 1 week	After 1 month	After 24 h	After 1 week	After 1 month	After 24 h	After 1 week	After 1 month
Solution		MET			MPT			MBT	
HNO$_3$	3.2	4.1	3.6	−4.0	−3.2	−2.8	4.9	4.2	5.6
H$_2$SO$_4$	1.8	2.6	3.5	−3.9	−6.5	−4.3	−2.5	−3.1	−4.6
HCl	3.5	2.7	3.5	−5.3	−2.7	0.0	1.1	2.9	4.0
KOH	3.5	5.7	2.8	−1.3	−3.0	0.0	−3.9	2.6	3.9
NaOH	1.7	1.7	2.9	−3.5	0.4	0.0	−2.3	3.8	5.3
NaCl	3.9	2.6	1.9	−2.1	7.8	−0.1	4.0	2.4	5.6
H$_2$O	4.1	4.8	3.8	0.9	3.9	0.0	0.7	1.4	2.8

cracks, causing irreversible changes such as chemical degradation and cracking. The presence of hydrophilic groups causes blistering. Cracking and blistering cause high water absorption, whereas degradation causes the leaching of small molecules.[39] Ester, hydroxyl, carboxyl, and methyl groups are polar groups and are responsible for surface solvolysis by the ions present in acidic, alkaline, and saline solutions. The ions of the acids, alkalis, and salt affect the water structure and hence the water-uptake tendency or enhance the hydrolysis tendency of the esters. Dipole–dipole interactions of opposite types favor solvolysis and hence weight gain. The absorbed water causes damage to mechanical properties, especially the tensile strength.[39] Because of a lack of facilities, this test was not performed.

Mechanical and electrical properties

For a plastic product designer, the knowledge of the thermomechanical and electrical properties of polymers is the foremost requirement. The tensile properties of polymers are most useful for engineering design and understanding the quality characteristics of the polymeric materials. In tensile testing, samples can be prepared by molding, compression molding, and punching. In this investigation, the samples were prepared by a punching technique according to the prescribed standard test. The mechanical and electrical properties of MHT films were not determined because of the brittle nature of MHT. The tensile strength, volume resistivity, and electrical strength of 30–45-μm-thick MET, MPT, and MBT films are reported in Table IV, from which it is clear that MET (12 MPa) and MBT (11 MPa) have comparable tensile strengths that are more than three times less than that of MPT (37.5 MPa). The low tensile strengths of MET and MBT versus that of MPT are mainly due to their low molecular weights and different molecular architectures. The comparable tensile strengths of MET and MBT are due to almost the same molecular weights according to the viscos-

ity data and almost the same molecular architectures. MET and MPT have comparable electric strengths, but MBT has an electric strength 2.3 times less than those of MET and MPT. All three copolyesters possess excellent volume resistivity. MET has 20.4 times more volume resistivity than MBT and 67.2 times more than MPT. The observed change in the volume resistivity is due to the different molecular architectures of the copolyesters. Poly(ethylene terephthalate) (PET) is the most useful commercial polyester, having a tensile strength of 58.6–72.4 MPa, an electric strength of 158 kV/mm, and a volume resistance of 10^{21} Ω. A comparison of the mechanical and electrical properties of the copolyesters and PET shows that PET is a superior polyester with respect to physical properties in comparison with the copolyesters under study. The mechanical properties of the copolymers are dependent not only on the structure but also on the types of the monomers in the copolyesters.[40] The copolyesters possess fairly good mechanical and electrical properties in comparison with PET. The mechanical and electrical properties of the polymers also depend on the temperature, humidity, time, loading conditions, rate of loading, morphology, molecular architecture, molecular weight, fillers, impurities, geometry of the electrodes, electrode material, sample thickness, structure and presence of polar groups in the polymer chains, and so forth.[41] In this case, the fairly good mechanical and excellent electrical properties are mainly due to the moderate molecular weights, compositions, and polar groups present in the monomers. The excellent

TABLE IV
Mechanical and Electrical Properties of the Copolyesters

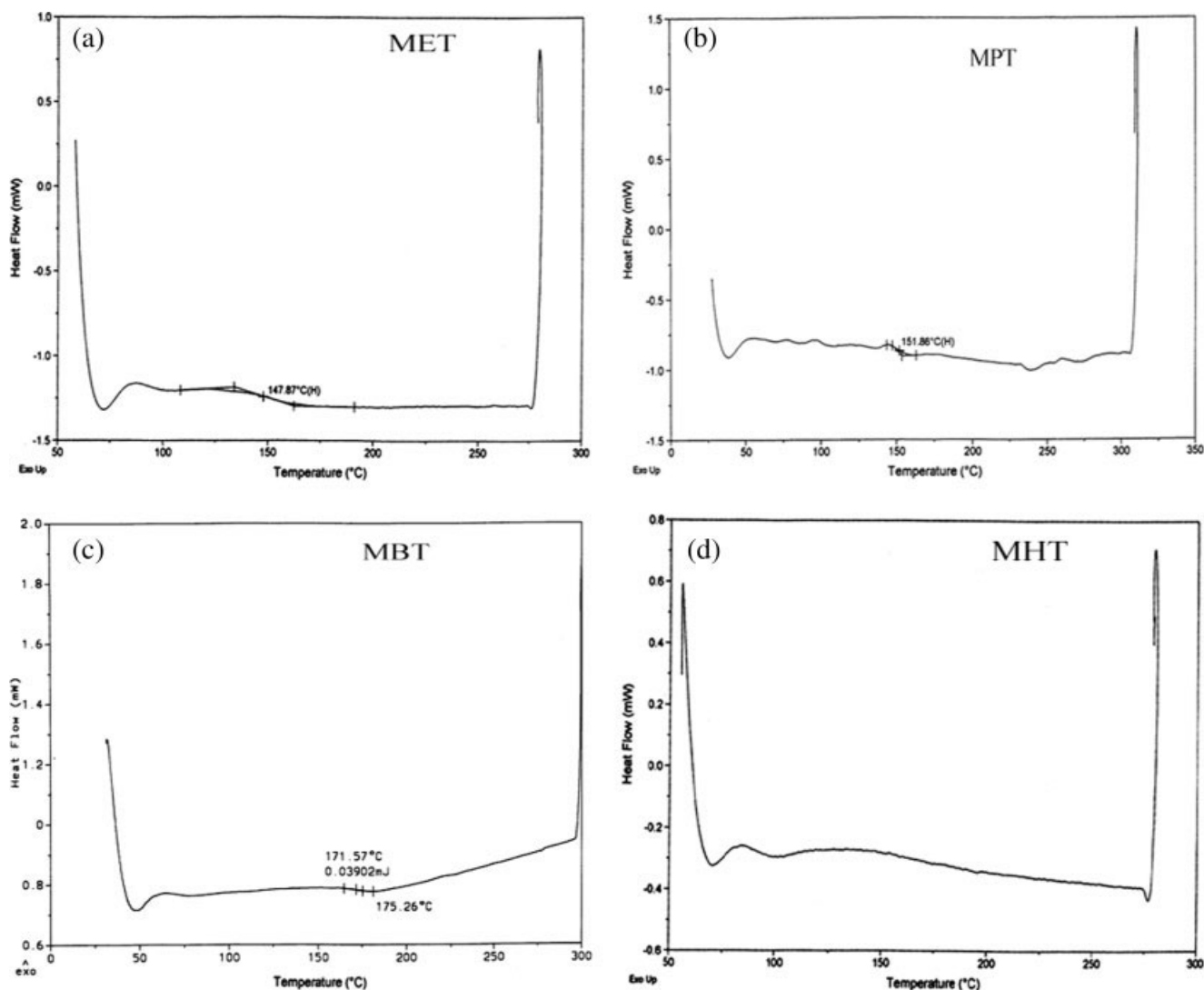| Copolyester	Thickness (μm)	Tensile strength (N/mm^2)	Volume resistivity (Ω cm)	Electric strength (kV/mm)
MET	42.1	12	2.56×10^{17}	45.65
MPT	45.0	37.5	3.81×10^{15}	44.44
MBT	30.5	11	1.26×10^{16}	19.35

Figure 3 DSC thermograms at a heating rate of 20°C in an N$_2$ atmosphere of (a) MET, (b) MPT, (c) MBT, and (d) MHT.

electrical properties of the copolyesters signify their usefulness as insulating materials.

Thermal analysis

Thermal analyses of polymers are of great importance, especially for the study of the degradation kinetics, degradation mechanism, bond strength, thermal stability, and molecular architecture. They are also useful in designing materials for high-temperature applications and for identification and processability. Thermogravimetric analysis (TGA) provides qualitative and semiquantitative rapid comparisons about the thermal stability and degradation fingerprint patterns of polymers.[42] The characteristic temperatures for the assessment of the relative thermal stability of polymers are the initial decomposition temperature (T_0), temperature of 10% weight loss (T_{10}), temperature of 50% weight loss (T_{50}), tem-

perature of maximum weight loss (T_{max}), and temperature of final decomposition (T_f). A differential thermal analysis or DSC technique provides much useful information about physicochemical changes occurring during the heating of polymeric materials. Thus, thermal analyses of polymers are quite useful in designing articles for specific applications.

In this investigation, DSC and TG thermograms of all four copolyesters were scanned at a heating rate of 20°C/min in a nitrogen atmosphere without a thermal treatment before their thermal analysis, and they are presented in Figures 3(a–d) and 4, respectively. The T_g, T_0, T_{10}, T_{50}, T_f, T_{max}, decomposition range, weight loss (%), and copolyester residue (%) values are reported in Table V, from which it is evident that T_g increases with an increase in the alkyl chain length of the diols, but little effect on T_0 and T_{max} is observed. In the case of MHT, T_g is determined from the slope change of the base line. The transition
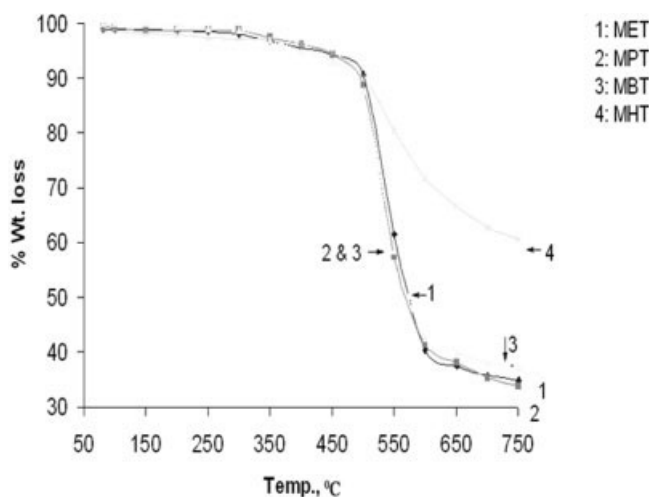
Figure 4 TG thermograms of MET, MPT, MBT, and MHT at a heating rate of 20°C in an N_2 atmosphere.

between 275 and 300°C is probably due to some physical change, and it is further supported by no weight change in the TG thermogram over the aforementioned temperature range. Other transitions below 100°C may be due to traces of moisture along with residual solvent. Because of the limitation of higher temperature ranges in DSC and TGA, thermograms were not scanned up to about 900°C, and so it is hard to judge the presence of crystallinity or completely amorphous nature of the samples. Compared with PET (67°C), the copolyesters possess high T_g's (148–195°C), but they are comparable or lower than those of some aromatic cardo copolyesters (185–300°C)[3,5,35,36] because of the presence of aliphatic diols of different structures. The copolyesters are thermally stable up to about 408–427°C and follow single-step degradation involving 38–58% weight losses with 34–59% residues. The observed T_{10} order for the copolyesters is MET > MPT > MBT > MHT. The higher T_{10} is, the greater the thermal stability is of the polymer.[43] Thus, the structure and alkyl chain length of the aliphatic diol affect the thermal stability. The thermal stability of MPT is slightly affected by a methyl pendant group. The copolyesters possess thermal stability comparable to that of some aromatic cardo copolyesters (408–484°C).[3,5,35,36]

Various kinetic parameters such as the energy of activation (E_a), frequency factor (A), order of reaction

TABLE VI
Kinetic Parameters of Cardo Copolyesters Derived According to the Anderson–Freeman Method

Copolyester	n	E_a (kJ)	A (S^{-1})	ΔS^* (J/K)	R^2
MET	2.6	396.3	5.2×10^{23}	200.7	0.995
MPT	2.8	454.3	3.4×10^{27}	273.8	0.986
MBT	2.9	408.9	5.1×10^{24}	219.8	0.971
MHT	2.8	132.5	2.6×10^{6}	−130.2	0.986

(n), and entropy change (ΔS^*) were determined according to the Anderson–Freeman method:[44]

$$\Delta \ln dW/dt = n\Delta \ln W - (E/R)\Delta(1/T) \quad (3)$$

$$A = E_a \beta / RT^2 e^{Ea/RT} \quad (4)$$

$$\Delta S^* = R \ln(Ah/kT) \quad (5)$$

where β is the rate of heating, R is the gas constant, h is Planck's constant, T is the temperature, and k is the Boltzmann constant. The other symbols have their usual meaning. The least-square values of the aforementioned parameters along with the regression coefficient (R^2) are reported in Table VI, from which it is clear that the copolyesters follow 2.6–2.9-order degradation kinetics. Both E_a and A are affected to some extent by the structure and alkyl chain length of the diol up to four carbons. For MHT, E_a and A are much lower than those of MET, MPT, and MBT, but it involves comparatively much lower weight loss and high residue. Comparatively, MPT has somewhat high E_a and A values in comparison with MET because of structural dissimilarities. It is presumed that a methyl pendant group may restrict free rotation about an ester bond and hence increase the rigidity of the copolyester chain. The higher E_a is, the higher A is. Similarly, ΔS^* of MPT is also higher than that of MET. The value of ΔS^* increases with the alkyl chain length up to four carbons, and beyond that, it decreases because of conformational changes. A large and positive magnitude of ΔS^* indicates a less ordered transition state, whereas a negative value of ΔS^* supports an ordered transition state.

The ester linkages are weak points in the copolyesters, and they degrade selectively to form free radicals. These radicals may further undergo recombination or rupture. The degradation is a complex process and

TABLE V
DSC and TG Data for the Cardo Copolyesters

Copolyester	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{50} (°C)	T_f (°C)	T_{max} (°C)	Decomposition range (°C)	Weight loss (%)	Residue (%)
MET	147.9	411.5	503.2	563.2	656.6	543.8	442–657	57.5	34.3
MPT	151.9	407.9	492.1	561.6	669.2	542.5	408–669	58.4	35.2
MBT	171.6	426.9	426.9	564.9	653.8	536.3	427–654	54.2	36.1
MHT	194.7	407.5	407.5	569.6	747.2	540.5	408–747	37.7	59.1

involves a variety of reactions, such as decomposition, crosslinking, branching, and rearrangement. A 34–59% residual weight above 650°C indicates the formation of crosslinked products. The thermal decomposition of polyesters usually starts with the scission of the polymer chain through a six-membered ring transition state. It is believed that this scission is mostly heterolytic and not a free-radical process.[18] However, this is not yet resolved. A kinetic analysis has shown that the thermal decomposition of polyesters is a complex process, with E_a varying from 100 to 250 kJ/mol. The observed E_a values (396–454 kJ/mol) for the copolyesters containing aliphatic diols with a chain up to four carbons long are much higher than the general range (100–250 kJ/mol), confirming the complex degradation process.

CONCLUSIONS

On the basis of the experimental findings, the following observations are made:

1. The copolyesters have moderate molecular weights on the basis of viscosity data and possess excellent solubility in common solvents.
2. The structure and alkyl chain length of the aliphatic diol affect the densities of the copolyesters.
3. The copolyesters possess moderate tensile strength but excellent electric strength and volume resistivity.
4. The copolyesters possess fairly good hydrolytic stability even in harsh acidic, alkaline, and saline environments.
5. The copolyesters possess high T_g values (148–195°C) and are thermally stable up to about 408–427°C with 34–59% residue, and they follow 2.6–2.9-order degradation kinetics.

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