Synthesis and Characterization of Polycarbonates by Melt-Phase Interchange Reactions with Alkylene and Arylene Diphenyl Dicarbonates

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ABSTRACT: Alkylene and arylene diphenyl dicarbonates were used as monomers for the preparation of polycarbonate polymers. The diphenyl dicarbonates were first prepared from dihydroxy compounds and phenyl chloroformate. The polycarbonates were then prepared by the melt-phase polycondensation of these diphenyl dicarbonates with dihydroxy compounds as monomers. The same polycarbonates were also synthesized by a different route involving the polycondensation of a different arylene or alkylene diphenyl dicarbonates with bisphenol A diphenyl dicarbonate to give another series of polycarbonates. The process involved precondensation under a stream of nitrogen and then melt polycondensation at a high temperature and low pressure. The prepared polycarbonates were characterized by inherent viscosity measurement, Fourier transform infrared spectroscopy, ^{1}H-NMR and ^{13}C-NMR spectroscopy, and powder X-ray diffraction. The thermal properties of the polycarbonates were studied with differential scanning calorimetry and thermogravimetric analysis. With alkylene or arylene diphenyl dicarbonates as monomers, the polycondensation reactions led to the formation of polycarbonates with inherent viscosities of up to 0.68 dL/g and with high thermal stability. The glass-transition temperature values of the polycarbonates were in the range 24–130°C. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3597–3609, 2006

Key words: degradation; esterification; polycarbonates; polycondensation; synthesis

INTRODUCTION

Polycarbonates are engineering thermoplastic polymers with outstanding mechanical, optical, and thermal properties and having a wide range of applications.[1–5] Bisphenol A (BPA) polycarbonate is a unique, supertough, heat-resistant, and transparent amorphous polymer.

Aromatic polycarbonates derived from BPA have been studied extensively and have been found to be the most important class of polycarbonates because of their rigid molecular structure, optical clarity, exceptional impact resistance, dimensional stability, toughness, and chemical stability.[6–8] They also offer excellent moldability and extrudability and good fire resistance, which has given this class of materials a wide range of applications.[9] Several modifications have been introduced into aromatic polycarbonates, such as aliphatic polycarbonates and aromatic–aliphatic polycarbonates.

Aliphatic polycarbonates have attracted less attention as structural materials than aromatic polycarbonates because of their poor mechanical properties. Nevertheless, they show potential as biodegradable and biocompatible materials for drug-delivery systems.[10–14]

Aromatic–aliphatic polycarbonates are a combination of aliphatic and aromatic components produced to mediate the properties of aliphatic and aromatic moieties of polycarbonates by increasing the flexibility and elasticity of aromatic polycarbonates and enhancing the poor physical properties of aliphatic polycarbonates.

Numerous studies have been conducted on the synthesis of polycarbonates. At first, both direct-reaction and melt-transesterification processes were employed. In the direct-reaction process, phosgene reacts directly with BPA to produce a polymer in a solution. In transesterification, diphenyl carbonate reacts with BPA to regenerate phenol for recycling and as a molten solvent for the polymer.

Recently, several studies have been carried out on the thermotropic properties of polycarbonates. Sun and coworkers[15–17] studied the thermotropic liquid-crystalline properties of polycarbonates prepared by the melt polycondensation of arylene diphenyl dicarbonates (e.g., 1,3-phenylene diphenyl dicarbonates) and aromatic dihydroxy compounds [e.g., hydroquinone (HQ) and 2,7-napthalene diol]. They also prepared polycarbonates from alkylene diphenyl dicarbonates {e.g., octamethylene and hexamethylene di-

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phenyl dicarbonates and bis[(hydroxyhexyl) benzyl-idene]phenylenediamine}. De Backer et al.[18,19] synthesized homopolycarbonates and copolycarbonates by the melt polycondensation of aromatic dihydroxy compounds [e.g., 1,5-bis(2-hydroxyethoxy)naphthalene] and alkylene diphenyl dicarbonates (e.g., pentamethylene diphenyl dicarbonate) with the aim of studying the effect of length of the alkylene part on the liquid-crystalline properties of these polycarbonates. Sato and coworkers[20–25] investigated the thermotropic liquid-crystalline properties of homopolycarbonates, copolycarbonates, and terpolycarbonates prepared from aromatic dihydroxy compounds [e.g., 6,6′-(4,4′-biphenylylenedioxy) dihexanol] and alkylene diphenyl dicarbonates [e.g., $PhOCO_2(CH_2)_nOCO_2Ph$, where $n = 2$–12].

Liaw and coworkers[6,26,27] prepared and characterized copolycarbonates via the melt polycondensation of various selected arylene and alkylene diphenyl dicarbonates (e.g., bisphenol AF diphenyl dicarbonate) with bisphenols (e.g., bisphenol S) and studied their thermal properties.

Numerous polycarbonates based on BPA and other assorted diphenols and aliphatic diols have been prepared to improve the physical properties of homopolycarbonates. Among the main variation on polycarbonates has been the synthesis of liquid-crystalline polycarbonates as poly(alkylene carbonate)s derived from aliphatic diols and BPA. Poly(alkylene carbonate)s show potential applications as biodegradable and biocompatible materials, which has encouraged researchers to develop synthetic methods and to introduce modifications to improve their poor physical properties. For example, in the field of biocompatible materials and with the aim of encapsulating pancreatic islets, Kessler et al.[28] treated a biocompatible polycarbonate membrane with plasma argon to improve its surface properties. The treatment decreased the hydrophobicity by fixing polyvinylpyrrolidone at the surface, increased the water permeability, preserved the structure and pore diameter, and allowed the installation of a uniform polyvinylpyrrolidone layer at the surface. Okada et al.[29] synthesized polytrimethylenecarbonates, which were hot-pressed into a film, sterilized, and transplanted to artificial defects in dog mandibles. The bone defects were reconstructed, and the film disappeared within approximately 12 weeks. In addition, polycarbonates and poly(ester carbonate)s of glycerol possessing a hydrolysable backbone, tunable hydrophobic/hydrophilic properties, and functionalizable pendent groups were also synthesized.[30] The free hydroxyl groups in these polymers were derivatized with a common nonsteroidal anti-inflammatory drug. Recently, Abramson et al.[31] reviewed bioresorbable-tyrosine-derived polycarbonates that offered a high degree of bone biocompatibility. Dhein et al.[32] discussed the blood compatibility and uses of

polycarbonates based on BPA in medical technology (e.g., membranes for hemodialysis).

The objective of this study was to synthesize and characterize a series of high-molecular-weight copolycarbonates based on BPA by interchange reactions of aliphatic and aromatic dihydroxy compounds or their diphenyl dicarbonates with arylene and alkylene diphenyl dicarbonates as monomers and to investigate the effect of structure on the physical properties and reactivity.

EXPERIMENTAL

Materials

The materials used were commercially available and were either analytical- or technical-grade reagents. They were used as received without any further purification except zinc acetate, chloroform, and tetrahydrofuran (THF). The chemicals were purchased from the following companies: ethylene glycol (EG), 1,4-butane diol (BuD), 1,6-hexane diol (HxD), hydroquinone (HQ), phenyl chloroformate (PCF), and zinc acetate dihydrate were purchased from Merck Schuchardt (Hohenbrunn, Germany); 4,4′-isopropylidene diphenol (BPA), 1,3-propane diol (PrD), and titanium(IV) n-butoxide were purchased from Across Organics (New Jersey, USA); 1,5-pentane diol (PeD) was purchased from Lancaster (Morecambe, England), diethylene glycol (DIGOL) was purchased from Cambrian Chemicals (Croydon, England), and Resorcinol (RESOL) was purchased from Riedel-de Haën (Seelze, Germany). Zinc acetate was heated at 100°C *in vacuo* for 8 h, and the chloroform and THF solvents were purified by refluxing and distillation over sodium wire and benzophenone.

Monomer and polymer synthesis

Monomer synthesis

The monomers were prepared by the reaction of the corresponding dihydroxy compound with PCF as shown in Scheme 1, according to a previously published procedure.[27]

A typical synthetic procedure for the preparation of bisphenol A diphenyl dicarbonate (BPA DPDC) follows: PCF (0.336 mol, 52.607 g) was added dropwise to a mixture of BPA (0.16 mol, 36.51 g) and pyridine (0.368 mol, 29.08 g) in THF (240 mL) below 5°C. The reaction mixture was stirred for 1 h at 0–5°C and overnight at room temperature and then poured onto distilled water (400 mL). The precipitate formed was collected and washed several times with a 10% aqueous sodium carbonate solution; the product was purified by recrystallization from ethyl acetate and dried at 50°C *in vacuo* overnight to give white crystals (yield = 92%).

The following diphenyl dicarbonates of the other dihydroxy compounds were prepared by the same proce-
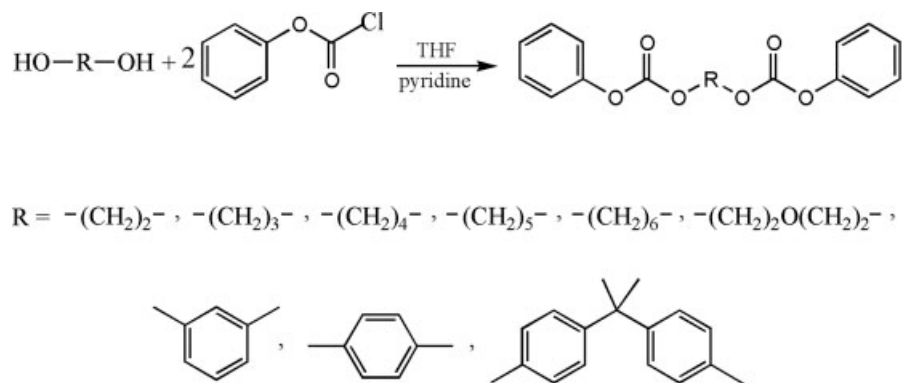
Scheme 1   Synthesis of alkylene and arylene diphenyl dicarbonate monomers.

dure: ethylene glycol diphenyl dicarbonate (EG DPDC), 1,3-propane diol diphenyl dicarbonate (PrD DPDC), 1,4-butane diol diphenyl dicarbonate (BuD DPDC), 1,5-pentane diol diphenyl dicarbonate (PeD DPDC), 1,6-hexane diol diphenyl dicarbonate (HxD DPDC), diethylene glycol diphenyl dicarbonate (DIGOL DPDC), hydroquinone diphenyl dicarbonate (HQ DPDC), and resorcinol diphenyl dicarbonate (RESOL DPDC).

The diphenyl dicarbonates of PrD and of DIGOL were obtained by extraction from the aqueous solution by chloroform and washed several times with 10% aqueous sodium carbonate solution; the chloroform layer was dried over anhydrous sodium sulfate and evaporated. PrD DPDC was recrystallized from ethyl acetate and dried at 50°C *in vacuo* overnight. DIGOL DPDC was obtained as a viscous liquid but was crystallized on long standing to give crystals with a melting temperature (T_m) of 44°C.

Polymer synthesis

The polymers were prepared according to the following general procedure: a glass reaction tube equipped with a Claisen distiller and a nitrogen gas inlet and outlet was filled with a homogeneous solid mixture composed of 10 mmol dicarbonate, 10 mmol diol, and anhydrous zinc acetate (2% mol of the dicarbonate). The reaction mixture was heated in a silicone oil bath at 145°C under a stream of nitrogen gas for 1 h. The temperature of the bath was increased to 175°C, and the reaction was kept at this temperature for 30 min. The reaction was then heated at 200°C for 30 min and at 230°C for another 30 min. The temperature was gradually increased to 260°C, and the pressure was reduced to 1 mmHg to remove the byproduct phenol in the polycondensation reaction. After 1 h, the glass reaction tube was cooled, and the formed polymer was dissolved in chloroform. The solution was filtered, and the polymer was precipitated by dropwise addition to methanol as a nonsolvent. The resulting polymer was filtered and dried in circulating air and *in vacuo* at 60°C for 24 h.

The same procedure was followed for the preparation of all of the following polycarbonates: BPA–EG polycarbonate, BPA–PrD polycarbonate, BPA–BuD polycarbonate, BPA–PeD polycarbonate, BPA–HxD polycarbonate, BPA–DIGOL polycarbonate, BPA–RESOL polycarbonate, BPA–HQ polycarbonate, and BPA–BPA homopolycarbonate.

Three series of polycarbonates were prepared by three reaction routes:

1. Series A was prepared from the reaction of BPA DPDC with the various dihydroxy compounds (Scheme 2).
2. Series B was prepared from the reaction of diphenyl dicarbonates of the various dihydroxy compounds with BPA as the dihydroxy compound (Scheme 3).
3. Series C was prepared by a developed method that involved the mixed melt polycondensation of two different diphenyl dicarbonates, one of them being BPA DPDC and the other being the diphenyl dicarbonate of the other various dihydroxy compounds (Scheme 4).

A typical procedure for the synthesis of polycarbonates by this mixed melt polycondensation method is described herein for BPA–HQ polycarbonate from BPA DPDC and HQ DPDC as follows:

BPA DPDC (10 mmol, 4.681 g), HQ DPDC (10 mmol, 3.5 g), and titanium(IV) *n*-butoxide (2% mol of the dicarbonate, 0.068 g) were placed in the glass reaction tube mentioned previously. The reaction mixture was heated in a silicone oil bath at 160°C under a stream of nitrogen gas for 1 h. The temperature was gradually increased to 210°C. After 1 h, the temperature was gradually increased to 260°C, and the pressure was reduced to 1 mmHg to remove the diphenyl carbonate byproduct produced by the polycondensation reaction. The reaction mixture was kept *in vacuo* for 1 h. Finally, the reaction temperature was decreased to ambient temperature, and the formed polymer was dissolved in chloroform. The
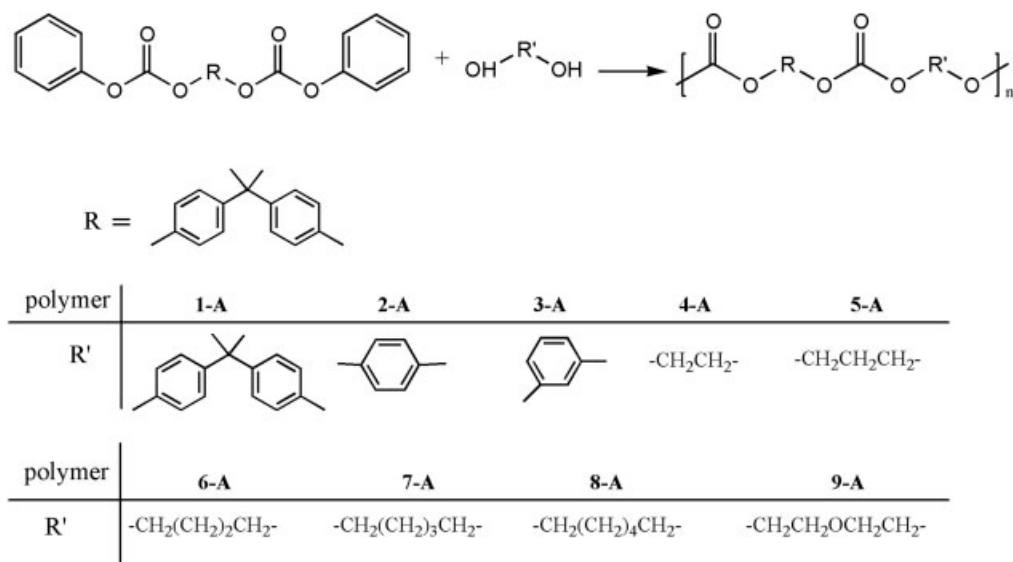
Scheme 2 Synthesis of the polycarbonates by melt polycondensation of BPA DPDC and dihydroxy compounds (series A).

solution was filtered, and the polymer was precipitated in methanol as a nonsolvent. The resulting polymer was dried in circulating air and *in vacuo* at 60°C for 24 h.

PrD DPDC and EG DPDC did not form the respective polycarbonates but instead formed cyclic trimethylene and cyclic ethylene carbonates.

Measurements

The inherent viscosity of the polymer solutions (0.5 g/dL) in chloroform were measured by an Ubbelohde glass capillary viscometer (Rheotek, Poulten Selfe & Lee Ltd., Essex, England) in a thermostated water bath temperature-controlled at 30 ± 0.1°C.

The solutions were temperature-equilibrated for approximately 15 min before viscosity was measured. Measurements were repeated several times until reproducible values were obtained. The Fourier transform infrared (FTIR) spectra (from 600 to 4000 cm^{-1}) of the monomers and polymers were recorded as neat films with a Thermo Nicolet 670 FTIR spectrophotometer (Madison, WI). The films were prepared by the cast solution of the purified monomer or polymer in chloroform over NaCl plates. The solvent was evaporated and further dried *in vacuo*. The ^{1}H-NMR and ^{13}C-NMR spectra of the monomers and polymers were recorded on a Bruker Avance DPX-300 spectrometer (300 MHz) (Wissembourg Cedex, France) in deuterated chloroform. Chemical shifts
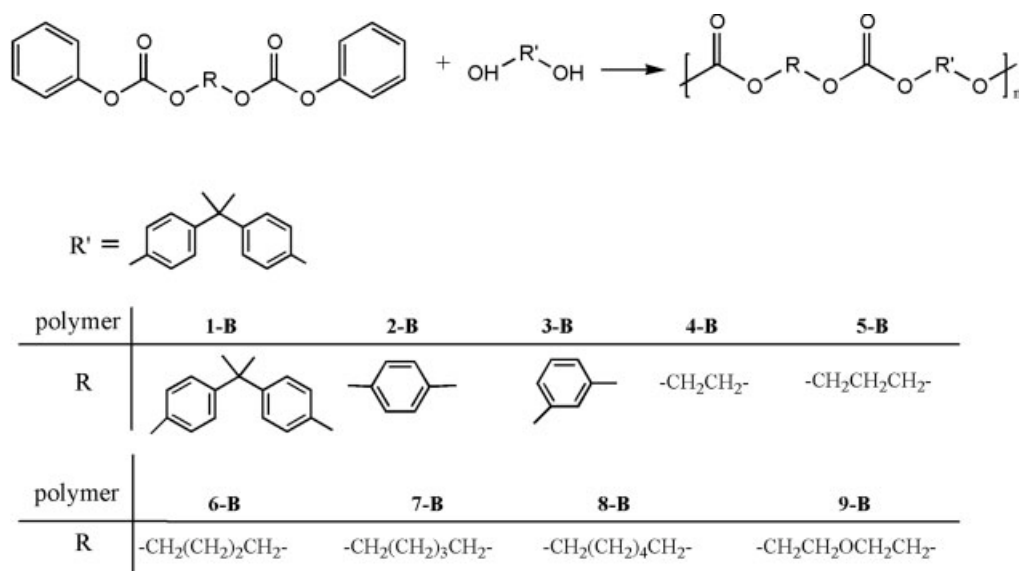
Scheme 3 Synthesis of the polycarbonates by melt polycondensation of diphenyl dicarbonates of dihydroxy compounds and BPA (series B).
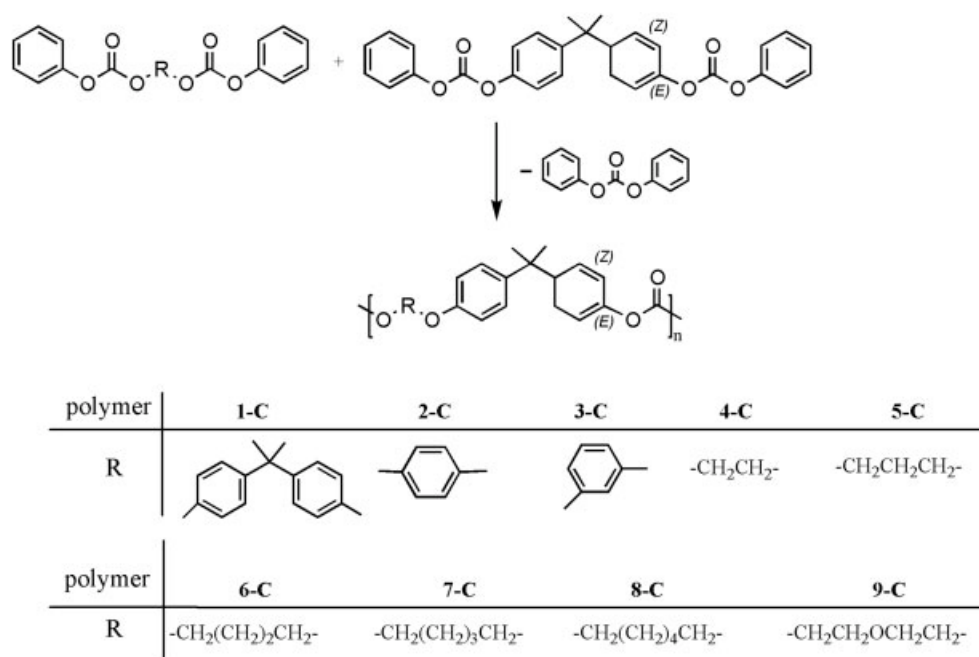
Scheme 4 Synthesis of the polycarbonates by melt polycondensation of mixed diphenyl dicarbonates (Series C).

(δ's) are given in parts per million with tetramethyl-silane as an internal standard. The glass-transition temperature (T_g) and the T_m values of the polymer samples were studied with a Netzsch 204 differential scanning calorimeter (Selb Bavaria, Germany). The T_g measurements done by differential scanning calorimetry (DSC) were performed on 10 ± 2 mg samples under a dry nitrogen atmosphere. The samples were first heated from ambient temperature to 150°C and maintained for 2 min before rapid quenching in liquid nitrogen. The thermal behaviors of the quenched samples were probed by heating to the molten state at a heating rate of 20°C/min for aromatic–aromatic polycarbonates and 10°C/min for aromatic–aliphatic polycarbonates. The T_g values were taken as the midpoint of the transition. To observe T_m, the samples were heated above T_g, kept at this temperature for 10 min in the DSC pan, cooled at 10°C/min to room temperature, and finally, heated at a rate of 20°C/min for aromatic–aromatic polycarbonates and 10°C/min for aromatic–aliphatic polycarbonates. T_m's for the various samples were taken as the maxima of the endothermic peaks. The thermal stabilities of the polymer samples were studied by thermogravimetric analysis (TGA) with a Netzch STA 409 PG/PC thermal analyzer (Selb Bavaria, Germany). Measurements were conducted at a heating rate of 20°C/min under a dry nitrogen atmosphere purging at a flow rate of 50 mL/min. For X-ray analysis, 0.5 g of each polycarbonate sample was frozen with liquid nitrogen, powder ground, and analyzed with a Philips PW 1840, compact powder X-ray Diffractometer System

(Eindhoven, The Netherlands) in a scanning range $2\theta = 2$–60° with a Cu Kα radiation filter with a receiving slit width of 0.2 mm.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The alkylene and arylene diphenyl dicarbonates were synthesized by the reaction of the various dihydroxy compounds with PCF.[27] The reaction proceeded by pyridine-catalyzed nucleophilic displacement of the chloride of PCF with the alcohol group of the dihydroxy compound (Scheme 1). The carbonate-forming reaction was reported to proceed via a colored pyridine–chloroformate adduct intermediate.[33,34] The structures of the diphenyl dicarbonates were confirmed by FTIR and NMR spectroscopy. The T_m values for odd-carbon-number alkylene diphenyl dicarbonates were lower than those of the neighboring even-carbon-number diphenyl dicarbonates. Even-carbon-number alkylenes diphenyl dicarbonates fit better in their crystal lattices than odd ones due to their structural symmetry and thus exhibited slightly higher T_m values. DIGOL DPDC was obtained as a viscous liquid that was crystallized into a solid on long standing; this may have been due to the effect of the presence of the ether linkage.

The IR spectra of the dicarbonates showed strong absorption bands due to C=O stretching vibrations from 1769 to 1787 cm^{-1} for arylene diphenyl dicarbonates and from 1754 to 1761 cm^{-1} for alkylene diphenyl dicarbonates. The FTIR spectra showed that the values

of the C=O stretching frequencies for arylene diphenyl dicarbonates (aromatic–aromatic dicarbonates) were higher than those for alkylene diphenyl dicarbonates (aromatic–aliphatic dicarbonates). The absorption bands due to the ether C—O—C stretching vibrations were observed in the region from 1230 to 1270 cm^{-1}. The IR data were typical for the carbonate group and thus suggest the formation of the various dicarbonates. Typical IR spectra for synthesized alkylene and arylene diphenyl dicarbonate monomers are presented in Figure 1.

The ^{1}H-NMR spectra of alkylene diphenyl dicarbonates showed singlet peaks at $\delta = 4.25$–4.53 ppm due to the protons of the terminal methylene groups (—OOCOCH_2—) attached to the carbonate group for the diphenyl dicarbonates of 1,2-ethane diol and BuD. The ^{1}H-NMR spectra of alkylene diphenyl dicarbonates showed triplets peaks in the same range due to the protons of the terminal methylene groups attached to the carbonate group for PrD, PeD, HxD, and DIGOL. The protons of the methylene groups next to the terminal methylene groups (—OOCOCH$_2$CH_2—) in all of the diphenyl dicarbonates showed multiplets at $\delta = 1.8$–2.2 ppm. The protons of the central methylene groups of PeD and HxD showed multiplets at $\delta = 1.5$–1.6 ppm. The signals for the aromatic protons of the phenyl rings of the alkylene diphenyl dicarbonates were observed at $\delta = 7.1$–7.3 ppm. These data confirm the formation of the alkylene diphenyl dicarbonates. The ^{1}H-NMR spectra of the arylene diphenyl dicarbonates showed peaks for the aromatic protons of both the arylene and phenyl parts in the same aromatic region at $\delta = 7.0$–7.5 ppm. In the case of BPA DPDC, the protons of the methyl groups of BPA showed a singlet peak at $\delta = 1.67$ ppm. The ^{1}H-NMR and ^{13}C-NMR data for the alkylene diphenyl dicarbonates are pre-

sented in Table I, and the ^{13}C-NMR data for the arylene diphenyl dicarbonates are presented in Table II.

Characterization of the polycarbonates

Solution viscosity measurements

The inherent viscosities of the polycarbonates synthesized were calculated from viscosity measurements of the dilute polymer solutions in chloroform. The polycarbonates had inherent viscosities in the range 0.08–0.68 dL/g. Table III summarizes the inherent viscosities (inh) of the various synthesized polycarbonates; $_{inh}$ is measured at a concentration of 0.5 g/dL in chloroform at 30°C.

The results showed that the polycarbonates prepared from the alkylene or arylene diphenyl dicarbonates and BPA as the dihydroxy compound (series B) had greater inherent viscosities than those synthesized from BPA DPDC and various dihydroxy compounds (series A); these viscosities were also greater than those synthesized from the mixed melt polycondensation of BPA DPDC and the other alkylene and arylene diphenyl dicarbonates (series C). This difference in inherent viscosity may have been due to the difference in the reactivity of the monomers involved in the polymerization reactions in the previous series. The higher reactivity of the dihydroxy compound used in the synthesis of the polymers in series B (BPA) than aliphatic diols, which have electron-releasing methyl groups that increase the nucleophilic properties of the phenolate anion,[27] may explain the formation of polymers with higher inherent viscosities.

The various structural differences that affected the polymer properties were attributed to other interchange reactions that could have taken place during polymerization. The principal and the most reactive interchange reaction taking place for polymer buildup was the nucleophilic attack of the hydroxyl group of the dihydroxy compound upon the carbonate group of the alkylene or arylene diphenyl dicarbonate monomer. This reaction gives linear polycarbonates in which the two monomer units are connected alternately along the entire length of the polymer chain. This reaction is appreciably influenced by the reactivity of the attacking dihydroxy compound.

A possible competing reaction that could have also occurred was the self-condensation of the diphenyl dicarbonate monomer. This reaction is less reactive and less likely to occur, but if it occurs, it can lead to minor structural irregularities represented by the occurrence of short sequences of only one monomer unit rather than alternating unit sequences in the polymer chain. Another possible intrachange reaction that may have occurred was the partial elimination of cyclic aliphatic carbonates from the alkylene diphenyl dicarbonate monomers or from the formed
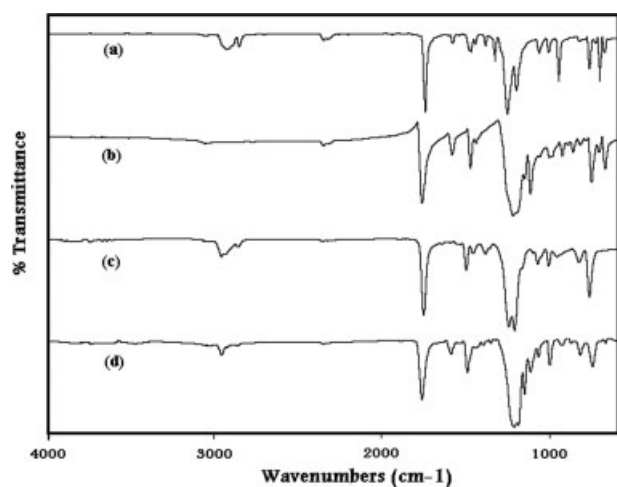

Figure 1 IR spectra of (a) HxD DPDC, (b) RESOL DPDC, (c) BPA–HxD polycarbonate, and (d) BPA–RESOL polycarbonate.

TABLE I
^{1}H-NMR and ^{13}C-NMR Data for the Alkylene Diphenyl Dicarbonates

Diphenyl dicarbonate		1	2	3	4	5	6	7	8	9	10	11
						δ (ppm)						
structure	H	4.53	4.53	—	—	a	a	a				
	^{13}C	65.9	65.9	153.6	151.1	121.1	129.6	126.3				
structure	H	4.40	2.18	4.40	—	—	a	a	a			
	^{13}C	65.0	28.0	65.0	153.7	151.1	121.1	129.6	126.2			
structure	H	4.30	1.89	1.89	4.30	—	—	a	a	a		
	^{13}C	68.1	25.2	25.2	68.1	153.8	151.1	121.1	129.6	126.1		
structure	H	4.26	1.79	1.60	1.79	4.26	—	—	a	a	a	
	^{13}C	68.5	28.3	22.2	28.3	68.5	153.8	151.2	121.1	129.5	126.1	
structure	H	4.24	1.76	1.48	1.48	1.76	4.26	—	—	a	a	a
	^{13}C	68.7	28.5	25.4	25.4	38.5	68.7	153.8	151.2	121.1	129.5	126.1
structure	H	4.41	3.81	3.81	4.41	—	—	a	a	a		
	^{13}C	68.9	67.6	67.6	68.9	153.8	151.1	121.1	129.6	126.1		

^{a} The signals of aromatic protons appeared in the range δ = 7.1–7.5.

polymer chains. This reaction would not only disturb the stoichiometric balance of the monomers in the reaction melt but would also lead to minor structural changes in the polymer backbone. Both effects would result in the formation of polycarbonates with smaller molecular masses and lower viscosities.

In this study, we observed that the diphenyl dicarbonates of ethylene and trimethylene moieties reacting with aliphatic and aromatic dihydroxy compounds did not afford the expected polycarbonates in both series B and series C but afforded instead cyclic ethylene and cyclic trimethylene carbonates. However, in series A, where EG and PrD were used as the attacking diols, the expected polymers were actually formed and isolated.

In addition to these complications and under our experimental conditions of high temperature and

TABLE II
^{13}C—NMR Data for Arylene Diphenyl Dicarbonates

Diphenyl dicarbonate	1	2	3	4	5	6	7	8	9	10	11
					Carbon δ (ppm)						
structure	151.4	130.2	151.4	118.9	114.4	118.9	151.7	150.9	122.9	129.7	126.5
structure	151.9	122.1	122.1	150.9	152.0	148.7	122.1	129.7	126.5	—	—
structure	31.0	42.7	148.4	128.1	120.5	149.0	152.5	151.1	120.5	129.7	126.4

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TABLE III
$_{inh}$**Values of the Polycarbonates**

Polymer	$\eta_{inh}{}^a$		
	Series A	Series B	Series C
BPA–ethane diol polycarbonate	0.10	—[b]	—[b]
BPA–PrD Polycarbonate	0.08	—[b]	—[b]
BPA–BuD polycarbonate	0.15	0.68	0.22
BPA–PeD polycarbonate	0.10	0.50	0.13
BPA–HxD polycarbonate	0.35	0.36	0.35
BPA–DIGOL polycarbonate	0.15	0.23	0.19
BPA–RESOL polycarbonate	0.28	0.21	0.14
BPA–HQ polycarbonate	0.26	—[b]	0.42
BPA–BPA polycarbonate	0.26	[c]	0.20

η_{inh} = inherent viscosity.
[a] Measured at a concentration of 0.5 g/dL in chloroform at 30°C.
[b] Polymer synthesis was complicated by the formation of side cyclic carbonate products.
[c] The method of preparation was the same as for series A.

low pressure, the formed polycarbonate chains may have also undergone polymer–polymer interchange reactions that led to molar mass changes. For example, the hydroxyl end groups of one polycarbonate chain could attack the carbonate group of another. The total number of polymer molecules does not change, but the average molecular mass of the polymer may change. This randomizing reaction would ultimately lead to the most probable molecular mass distribution. These minor structural variations would induce minor differences in the properties of the synthesized polycarbonates.

IR spectroscopy

The polycarbonates prepared were analyzed by FTIR. The FTIR spectra of polycarbonates showed strong absorption bands due to the C=O stretching vibration of the carbonate group from 1772 to 1775 cm^{-1} for aromatic–aromatic polycarbonates and from 1754 to 1761 cm^{-1} for aromatic–aliphatic polycarbonates. The values of the C=O stretching frequencies for aromatic–aromatic polycarbonates are generally higher than those for aromatic–aliphatic polycarbonates. Strong absorption bands due to the C—O—C stretching frequency for all of the polycarbonates were in the region from 1228 to 1256 cm^{-1}. These IR data, which are typical for the carbonate group, were in accordance with various data reported in the literature[33–38] and, therefore, confirm the formation of the various polycarbonates. On the other hand, the absorption bands due to the alcoholic groups of the dihydroxy compounds were absent in the FTIR spectra of the final polycarbonate. Typical IR spectra for the aromatic–aliphatic and aromatic–aromatic polycarbonates synthesized are presented in Figure 1.

The polymers BPA–ethane diol polycarbonate and BPA–PrD polycarbonate from series B and C did not

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form due to the occurrence of an important side reaction that led to the formation of cyclic ethylene and cyclic trimethylene carbonate, respectively, which were detected in the effluents of the reaction.

NMR spectroscopy

^{1}H-NMR spectra of polycarbonates. The polycarbonates were analyzed by NMR spectroscopy to elucidate their chemical structure and to support the formation of the expected polycarbonates. The ^{1}H-NMR spectra of the aromatic–aliphatic polycarbonates in deuterated chloroform confirmed the chemical structure of the polycarbonate series. In the ^{1}H-NMR spectra of the aromatic–aliphatic polycarbonates, which consisted essentially of a BPA unit linked via a carbonate group to an alkane moiety, the polycarbonates showed a similar pattern of peaks, except for the alkane moiety. The aromatic protons of the BPA unit were shown as an A–B splitting system ranging from δ = 6.8–7.2. The methyl protons were observed as a singlet, representing six protons at δ = 1.63–1.66. On the other hand, the signal of the protons of the terminal methylene groups ($-OOCOCH_2-$) of the alkane moiety attached to the carbonate group was observed at δ = 4.0–4.33. The signal of the methylene protons next to the terminal methylene groups ($-OOCOCH_2CH_2-$) was observed at δ = 1.75–2.25, whereas that of the protons of the central methylene groups of the 1,5-pentane and 1,6-hexane moieties was observed as at δ = 1.47–1.53 with the correct pattern of splitting for each polycarbonate. In the BPA–DIGOL polycarbonate, the signal of the protons of the methylene groups of the DIGOL moiety attached to the ethereal oxygen ($-CH_2OCH_2-$) was observed at δ = 3.75.

The signals of the protons of the terminal methylene groups attached to the carbonate group ($-OOCOCH_2-$) were highly indicative of the formation of polycarbonates. The attachment of the terminal methylene group to the carbonate oxygen atom led to a downfield shift in the position of the signal in the spectrum to δ = 4.0–4.33. This effect was highly indicative because the signal of the protons of the methylene groups attached to the ethereal oxygen ($-CH_2OCH_2-$), as in BPA–DIGOL polycarbonate, was observed below 4.0 δ.

The ^{1}H-NMR spectra of the aromatic–aromatic polycarbonates were generally not indicative in confirming the chemical structures of these polycarbonates. The signals of the protons of the two aromatic rings were collectively observed as asymmetric multiplets interfering with the symmetrical doublet signals of the BPA unit with δ's at δ = 7.1–7.3. Furthermore, the signal of the methyl groups of the BPA unit remained invariant in terms of form and multiplicity, as in the aromatic–aliphatic polycarbonates.

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From the integration of the signals of the aliphatic methylene protons, the BPA methyl protons and the BPA aromatic protons in the aromatic–aliphatic polycarbonates, we calculated that the ratio of the signals of the aliphatic methylene protons to the methyl protons of BPA and that of the aliphatic methylene protons to the BPA aromatic protons generally indicated that the polymer chains in these polycarbonates formed by the linkage of the two monomers in a 1:1 ratio. These data, deduced from the ^{1}H-NMR spectra, were a sufficient proof of the formation of the various polycarbonates.

^{13}C-NMR spectra of the polycarbonates. The ^{13}C-NMR spectra of the aromatic–aliphatic polycarbonates were quite informative and showed signals due to all of the aliphatic carbon types. Apart from the alkane moiety, the ^{13}C-NMR spectra of the aromatic–aliphatic polycarbonates were similar. The position of the carbon signals of the BPA unit were observed at about the same δ's in all spectra. The signal of the aliphatic quaternary carbon atom bearing the methyl groups appeared in the range 41–43 ppm, whereas the signal of the methyl carbon atoms appeared as a singlet at 31 ppm. The signals of all of the other aromatic carbon atoms of the BPA rings appeared beyond 120 ppm. In particular, the signal of the quaternary carbon atoms of the aromatic rings next to the aliphatic quaternary carbon, to which the methyl groups of BPA are attached, appeared as two doublets at about 149 ppm. The signal of the other quaternary carbon atoms of the aromatic rings next to the oxygen of the carbonate group appeared as two doublets at 148–148.5 ppm. The characteristic signal of the carbonyl carbon of the carbonate group appeared as three singlet peaks centered at about 154 ppm. The signals of the carbon atoms of the ring in the ortho position to the quaternary carbon atoms appeared at 113–128 ppm.

Regarding the aliphatic part, the terminal methylene carbons (—OOCOCH$_2$—) attached to the oxygen of the carbonate group showed downfield effects similar to those observed in the ^{1}H-NMR spectra, and their signals in all of the polycarbonates appeared in the spectra in the range 64–68 ppm. The signals of the methylene carbons next to the terminal methylene carbons (—OOCOCH$_2$CH$_2$—) appeared in the range 26–29 ppm. Finally, in the spectrum of BPA–DIGOL polycarbonate, the signal of the terminal methylene carbons attached to the oxygen atom of the carbonate group (—OOCOCH$_2$—O—) appeared at 69 ppm, whereas that of the methylene carbons attached to the ethereal oxygen (—CH$_2$OCH$_2$—) appeared at 67 ppm.

The ^{13}C-NMR spectra of the aromatic–aromatic polycarbonates also showed signals due to the carbon atoms of the carbonate at about 152 ppm. The signals of the carbon atoms of the aromatic rings of the BPA unit collectively appeared in the range 113–150 ppm. The signals of the aliphatic quaternary car-

bon atom of the BPA unit bearing the methyl groups and those of the carbon atoms of the methyl groups attached to it appeared in the same range as those of the aromatic–aliphatic polycarbonates.

The ^{13}C-NMR signals due to the carbon of the terminal methylene group attached to the carbonate group were highly indicative for the formation of the expected polycarbonates. The attachment of the terminal methylene group to the oxygen of the carbonate led to a downfield shift, which was reflected in the δ's of the carbon in the range 64–68 ppm. This effect was highly indicative because the signal of the methylene carbon attached to an ethereal oxygen (—CH$_2$OCH$_2$—) normally appears at a smaller δ value. This result was demonstrated by the ^{13}C-NMR spectrum of BPA–DIGOL polycarbonate, which showed two signals; one at 69 ppm for the methylene carbon attached to the carbonate and the other at 67 ppm for the methylene carbon attached to the ether oxygen.

Further spectral evidence for the existence of structural variations within the polymer backbone that affected the polymer properties was also observed. An interesting feature observed in the ^{13}C-NMR spectra of the polycarbonates containing aliphatic–aromatic moieties of the type
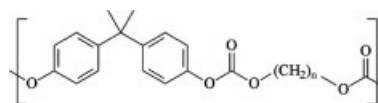
was the appearance of three small peaks from 152 to 156 ppm instead of one for the perfectly alternating sequence of monomer units. For example, the ^{13}C-NMR spectrum of BPA–HxD polycarbonate
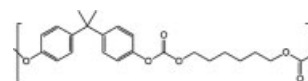
displayed three C=O peaks, as illustrated in Figure 2.

These peaks may be accounted for according to Figure 2. These three different peaks proved that the backbone of the polycarbonates synthesized under
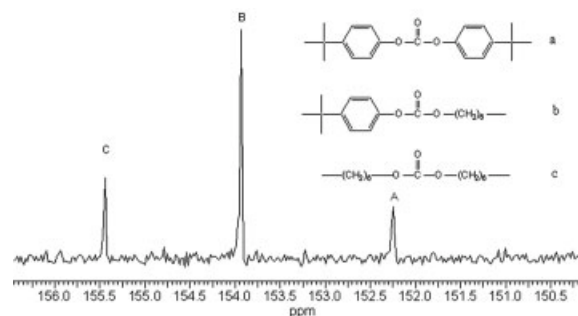

Figure 2 ^{13}C-NMR signals of C=O observed in the spectrum of BPA–HxD polycarbonate.

TABLE IV
T_g and T_m Values of the Polycarbonates

Polymer	Series A		Series B		Series C	
	T_g	T_m	T_g	T_m	T_g	T_m
BPA–ethane polycarbonate	36.4	—	—	—	—	—
BPA–1,3-propane polycarbonate	7.9	—	—	—	—	—
BPA–1,4-butane polycarbonate	32.3	—	49.2	109.7	44.1	—
BPA–1,5-pentane polycarbonate	14.7	—	33.4	—	17.6	142.3
BPA–1,6-hexane polycarbonate	38.5	115.9	54.0	—	48.4	—
BPA–DIGOL polycarbonate	32.6	—	60.9	—	47.6	—
BPA–RESOL polycarbonate	117.7	—	112.6	—	96.4	242.5
BPA–HQ polycarbonate	101.3	205.5	—	—	75.3	—
BPA polycarbonate	129.1	216.7	—	—	129.7	217.9

our experimental conditions by interchange reactions possessed, at least to a small extent, a random sequence of units in which all of these sequences coexisted. This same pattern was also observed in the ^{13}C-NMR spectra of the polycarbonates containing other alkylene units (e.g., —CH$_2$)$_n$— (where n = 2–5).

Thermal properties

The thermal properties of synthesized polycarbonates were investigated with DSC and TGA. The T_g and T_m values of the polycarbonates of the three prepared series are reported in Table IV. The T_g values of the aromatic–aromatic polycarbonates were generally higher than those of the aromatic–aliphatic polycarbonates. The aromatic–aromatic polycarbonates showed T_g values in the range 110–130°C, whereas the aromatic–aliphatic polycarbonates showed values from room temperature up to 55°C. The high T_g values of aromatic–aromatic polycarbonates were due to the existence of the stiffening aromatic groups, which restricted the movement of polymer segments and thus increased T_g, whereas the presence of aliphatic segments in the polymer imparted flexibility to the polymer chains. This ease of motion was reflected in the lower T_g values of the aromatic–aliphatic polycarbonates.

The polycarbonates prepared in series B generally had higher T_g values than those prepared in series A and C, which indicated that they possessed slightly higher molecular masses.

On the other hand, aromatic–aliphatic polycarbonates with odd-carbon-number aliphatic chains had lower T_g values than those with aliphatic chains with even carbon numbers. For example, as shown in Table IV, BPA–1,5-pentane polycarbonate, prepared by methods B and C, had a lower T_g than both BPA–1,4-butane polycarbonate and BPA–1,6-hexane polycarbonate. This may have been due to better packing of even-carbon-number chains and to symmetry. The presence of an ether bond in BPA–DIGOL polycarbonate induced extra flexibility, which was reflected

in a further decrease in the T_g value for this polycarbonate.[39]

In some cases, the T_g values of the polycarbonates prepared were low; this may have been due to the negative effect of several factors. At first, with a relatively moderate polycondensation temperature (260°C) for a relatively short reaction time at this temperature (1 h). This would not be enough for such condensation polymers, which require heating at high temperatures for long periods of time to achieve practically useful high-molecular-mass polymers. Moreover, the polymerization reactions may have also been complicated by the fact that alkylene and arylene diphenyl dicarbonates had higher volatility under our polycondensation conditions than the dihydroxy compounds and thus tended to escape from the reaction melt at an early stage, which caused the presence of unequal amounts of reacting monomers in the reaction melt. Furthermore, the polymerization may have also been complicated by the occurrence of other competing intrachange reactions, which led to the formation and subsequent elimination from the reaction medium of cyclic aliphatic carbonates from alkylene diphenyl dicarbonates. The occurrence of this intrachange reaction would also disturb the stoichiometric balance of monomers, which is a critical practical requirement for
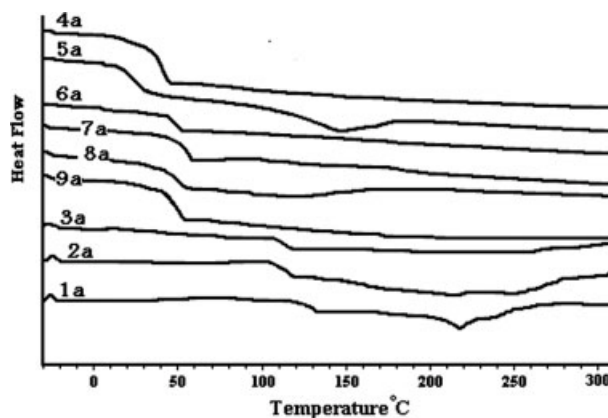

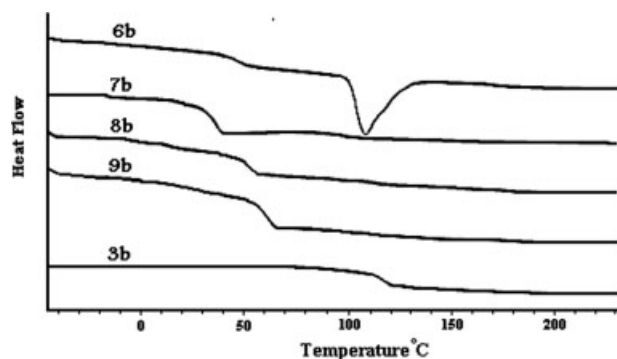**Figure 3** DSC thermograms of the series A polycarbonates.

Figure 4 DSC thermograms of the series B polycarbonates.

obtaining high-molecular-mass polymers. These effects influenced the molecular mass of the final polymers to variable extents and thus yielded polycarbonates with slightly lower molecular masses and lower T_g values. The DSC thermograms of the various polycarbonates synthesized in series A, B, and C are presented in Figures 3, 4, and 5, respectively.

The thermal stability of the polycarbonates synthesized was investigated by dynamic TGA under dry nitrogen. Table V summarizes the initial thermal decomposition temperatures ($T_d's$) that correspond to the temperatures at which 1% (T_d^i), 5% ($T_d^{5\%}$), and 10% ($T_d^{10\%}$) losses of mass of the polycarbonate samples occurred. Table V also shows the residual mass percentage after the polycarbonate samples were heated to 500°C. The T_d^i values of polycarbonates were in the range 214–374°C, $T_d^{5\%}$ was in the range 303–424°C, and $T_d^{10\%}$ was in the range 321–446°C. The residual mass percentage remaining at 500°C was from 3.9 to 42.5%. As shown in the values of the residual masses at 500°C, the aromatic–aliphatic polycarbonates had lower residual masses than the aromatic–aromatic polycarbonates. Among the polymers synthesized, the polycarbonates of series B showed higher thermal stabilities than those prepared in both series A and C, as indicated by their higher T_d values.
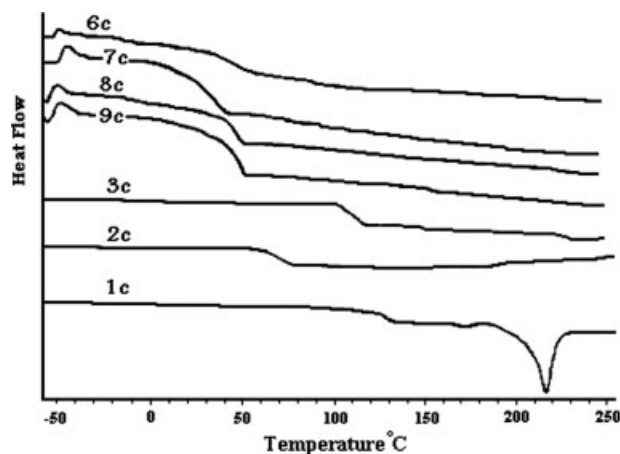
TABLE V
Thermal Stability Data of the Polycarbonates

Polymer code	T_d^i	$T_d^{5\%}$	$T_d^{10\%}$	Residual mass % at 500°C
1-a	374	424	446	42.5
2-a	225	400	414	32.9
3-a	249	313	346	37.6
4-a	253	353	378	15.5
5-a	312	355	372	15.3
6-a	260	350	361	9.2
7-a	300	345	358	5.8
8-a	314	354	366	3.9
9-a	214	346	364	14.2
1-b	—	—	—	—
2-b	—	—	—	—
3-b	324	335	374	36.9
4-b	—	—	—	—
5-b	—	—	—	—
6-b	278	303	321	24.9
7-b	318	350	361	5.2
8-b	314	343	357	6.1
9-b	328	363	377	17.3
1-c	308	385	408	34.3
2-c	337	400	414	32.9
3-c	324	371	394	35.4
4-c	—	—	—	—
5-c	—	—	—	—
6-c	320	331	364	18.9
7-c	271	350	361	5.2
8-c	263	343	357	6.1
9-c	229	357	375	12.0

The TGA curves of almost all of the polycarbonates displayed one-stage characteristics with a slow loss of mass starting from 200 to 300°C and a relatively fast loss of mass between 350 and 500°C. In particular, the thermogravimetric curves of the aromatic–aromatic polycarbonates showed that these polymers had good thermal stabilities. The thermograms of these polycarbonates displayed typical one-stage characteristics with a relatively fast mass loss occurring at temperatures higher than those of the aromatic–aliphatic polycarbonates.

The fast losses of all of the polycarbonates may have been due to further condensation of polymer
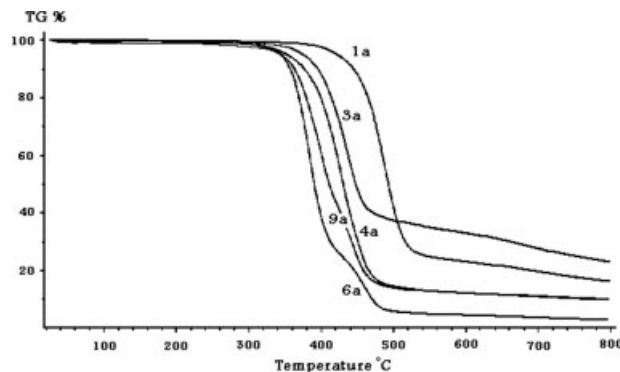

Figure 5 DSC thermograms of the series C polycarbonates.

Figure 6 TGA thermograms of the series A polycarbonates. TG % is the mass percentage of the polymer sample remaining after heating the polymer to a certain temperature.
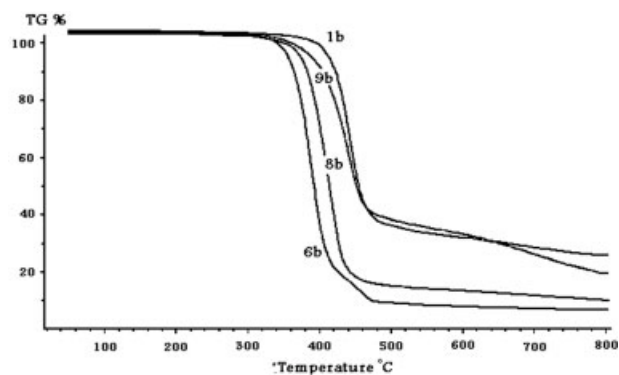
Figure 7 TGA thermograms of the series B polycarbonates. TG % is the mass percentage of the polymer sample remaining after heating the polymer to a certain temperature.

chains,[40] decarboxylation of carbonate groups, and elimination of cyclic aliphatic carbonates.[36,41–44] Figures 6, 7, and 8 present the TGA thermograms of the various polycarbonates prepared in series A, B, and C, respectively.

Powder X-ray diffraction

X-ray diffraction measurements of the polycarbonates synthesized indicated that the polycarbonates were generally amorphous, but the aromatic–aromatic ones contained a low degree of crystallinity. X-ray diffraction patterns of the aromatic–aromatic polycarbonates appear in Figure 9, and those of the aromatic–aliphatic polycarbonates appear in Figure 10 with intensity as a function of 2θ; θ is the angle of diffraction (Bragg angle).

Broadly speaking, in series A, B, and C, the aromatic–aromatic polycarbonates had higher crystallinities than the aromatic–aliphatic polycarbonates. Within the aromatic–aromatic polycarbonates and from the peaks at about $2\theta = 20°$, the highest diffraction intensity and thus highest crystallinity was observed for the BPA–HQ polycarbonate probably because it could fit better into crystalline form. As illustrated by the previous
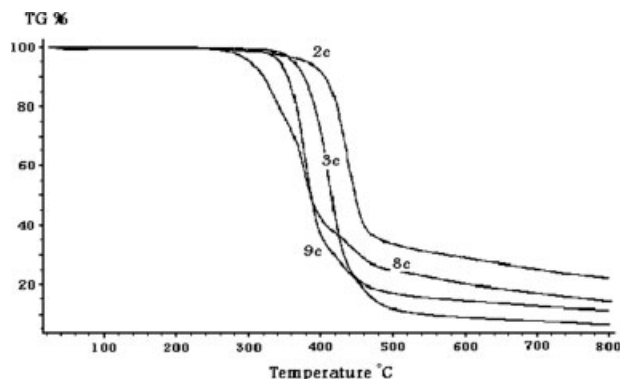

Figure 8 TGA thermograms of the series C polycarbonates. TG % is the mass percentage of the polymer sample remaining after heating the polymer to a certain temperature.
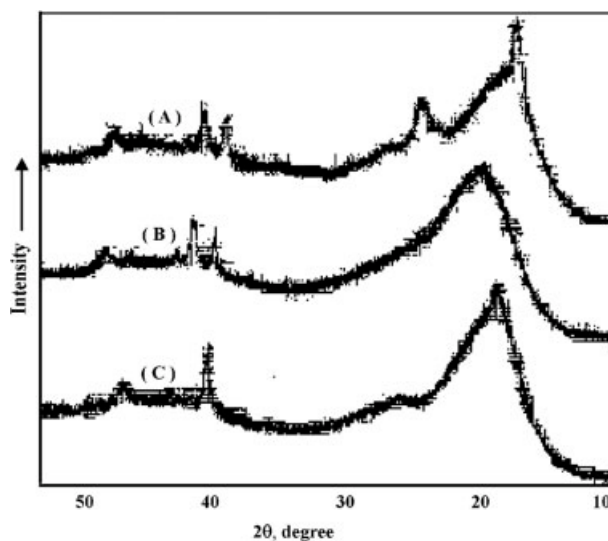

Figure 9 Powder X-ray diffraction patterns for aromatic–aromatic polycarbonates: (A) BPA–HQ polycarbonate, (B) BPA–RESOL polycarbonate, and (C) BPA–BPA polycarbonate homopolymer.

patterns, the polycarbonates that contained more than one type of monomer unit had more peaks in the X-ray pattern due to the reduction of symmetry in the polymer chains.

CONCLUSIONS

This study focused on the synthesis of linear polycarbonates based on BPA units from the reaction of alkylene or arylene diphenyl dicarbonates with dihydroxy compounds or from mixed diphenyl dicarbonates by a melt-phase polycondensation reaction.

The prepared polycarbonates, which should be useful industrial thermoplastic polymers, were character-
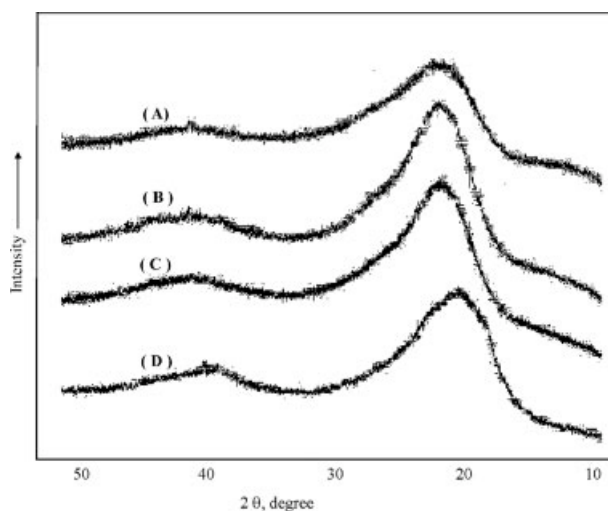

Figure 10 Powder X-ray diffraction patterns for aliphatic–aromatic polycarbonates: (A) BPA–DIGOL polycarbonate, (B) BPA–HxD polycarbonate, (C) BPA–PeD polycarbonate, and (D) BPA–BuD polycarbonate.

ized by IR spectroscopy, NMR spectroscopy, thermal analysis, X-ray diffraction, and inherent viscosity measurements. X-ray diffraction patterns indicated that the prepared polycarbonates were generally amorphous.

The highest inherent viscosity was observed for the polycarbonates in series B; this indicated that the polycarbonates in this series were formed with higher molecular masses than those in series A and C. The polycarbonates of series B also had higher T_g and T_d values, which indicated that these polycarbonates had higher molecular masses and higher thermal stabilities. Variations in T_g values also signified the occurrence of structural variations brought about by the partial elimination of cyclic aliphatic carbonates, decarboxylation of carbonate groups, and randomization reactions resulting from polymer–polymer interchange reactions.

In this study, alkylene and arylene diphenyl dicarbonate were used as monomers reacting with dihydroxy compounds in the molten state to give polycarbonates. The potential of this method was demonstrated by the successful synthesis of about 10 different aromatic–aliphatic and aromatic–aromatic polycarbonates in each of the three series of polycarbonates synthesized in this study. With this approach, it was possible to provide a flexible method of synthesis of polycarbonates whose properties could be varied by the variation of the structure of the alkylene or arylene diphenyl dicarbonate monomers. This approach is flexible in the sense that it may permit with alkylene and arylene diphenyl dicarbonates containing other organic functional groups and thus permit the synthesis of polycarbonates containing those organic groups. The introduction of these groups would allow the preparation of polycarbonates with widely varying structures and properties for variable applications. These studies are now being conducted in our laboratories.

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