EDITORIAL

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Synthesis and Characterization of Poly(ester carbonate)s by Melt-Phase Interchange Reactions of Dihydroxy Compounds with Alkylene and Arylene Diphenyl Dicarbonates Containing Ester Groups

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ABSTRACT: A new method of synthesis of poly(ester carbonate)s, based on the reaction of dihydroxy compounds with diphenyl dicarbonates containing ester groups was presented. The monomers utilized were diphenyl dicarbonates of cis/trans-1,4-cyclohexane dicarboxylate and of terephthalate units with butanediol or bisphenol A. The process consisted of a precondensation step under a stream of dry argon at atmospheric pressure with the elimination of phenol, followed by a melt polycondensation step at 225 or 250°C under vacuum. The prepared polymers consisted of linear chains containing partial random sequence distribution of monomer residues in the backbone. The inherent viscosities of polymers were from 0.23 to 0.48 dL/g and their T_g values were in the range −9 to 134°C. This method may open door to novel polycarbonates containing other organic functional groups. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39904.

INTRODUCTION

There is an increasing interest in the scientific community for the aliphatic and aromatic poly(ester carbonate)s in view of their favorable properties. Many poly(ester carbonate)s are liquid crystalline, transparent, heat and water resistant or dimensionally stable polymer.[1,2] Aliphatic poly(ester carbonate)s have been extensively studied and found to be potential biodegradable polymers[3–7] and therefore, they have found application in tissue engineering.[8,9] Poly(ester carbonate)s which contain 1,4-cyclohexylene ring in the backbone were found to be mechanically robust polymers having high T_g values.[10] The incorporation of increasing amounts of 1,4-cyclohexylene dicarboxylate linkages was found to enhance the segmental mobility and plastic yielding in poly(ester carbonate)s glasses.[10–12]

Numerous studies have been performed on the synthesis of poly(ester carbonate)s for various applications. The methods used for preparing biodegradable aliphatic poly(ester carbonate)s for biomaterials applications reported in the literature comprise ring opening polymerization of cyclic carbonates with various reagents,[13–19] polycondensation of diesters,

diphenyl carbonates, and diols,[6] polycondensation of diacids with diols[7] and reaction of bisphenols and hydroxy phenyl alkylates with triphosgene.[1] Poly(ester carbonate)s were also prepared from the reaction of cyclic esters with cyclic carbonates,[20] solid state polymerization or interchange reaction of polyester and polycarbonate oligomers,[21,22] solution polymerization of monomethyl carbonate of bisphenols with diacid chlorides[23] solution polymerization of bisphenols and diacid chlorides with phosgene[24] and by phase-transfer catalysis and modified interfacial polymerization via interfacial phosgenation of aromatic dicarboxylic acids and bisphenols under controlled pH, elevated temperature (70°C) and using potassium carbonate base.[25]

The purpose of this work is to study a new step growth polymerization route to poly(ester carbonate)s by melt-phase interchange reactions of alkylene and arylene diphenyl dicarbonates containing ester groups with dihydroxy compounds as monomers without using phosgene or other environmentally unfriendly materials. This study is an effort toward the development of green preparation methods to poly(ester carbonate)s and polycarbonates. This work presents the results of this study.
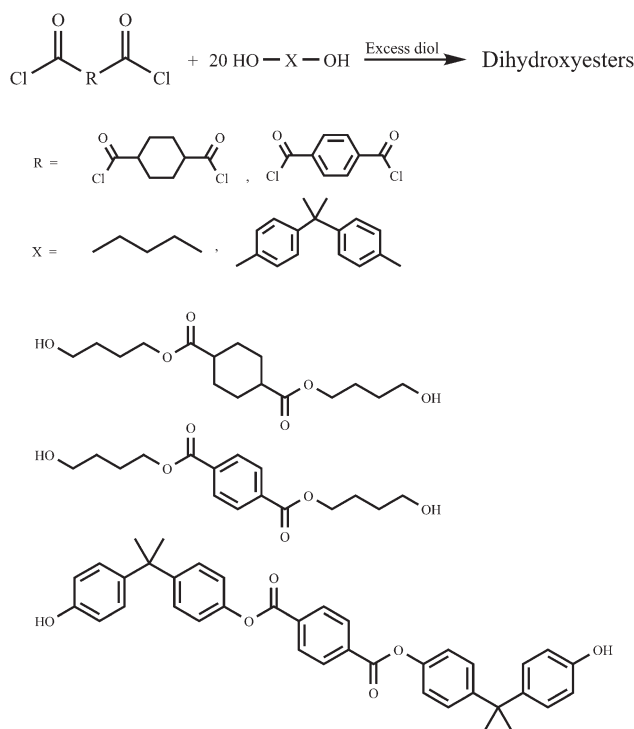
Scheme 1. Synthesis of aliphatic and aromatic dihydroxy compounds containing ester groups based on terephthalate and cis/trans-1,4-cyclohexanedicarboxylate units.

EXPERIMENTAL

Materials

The materials used were commercially available analytical grade reagents and were used as received except zinc acetate, chloroform and tetrahydrofuran (THF). The chemicals were purchased from the following companies: 1,4-butane diol (BuD), hydroquinone (HQ), phenyl chloroformate (PCF), and zinc acetate dihydrate from Merck (Schuchardt, Germany); 4,4′-isopropylidene diphenol (bisphenol A, BPA), bisphenol A bischloroformate (BPABCF), biphenol (BIPH), terephthaloyl dichloride, thionyl chloride, titanium(IV) n-butoxide, 4-dimethylamino pyridine (4-DMAP), and cis/trans-1,4-cyclohexane dicarboxylic acid from Across Organics (Geel, Belgium); diethylene glycol (DIGOL) from Cambrian Chemicals (Beddington, UK); resorcinol (RESOL) and pyridine from Riedel-de Haën (Seelze, Germany); anhydrous sodium sulphate, and anhydrous sodium carbonate from S.D. fine chemicals (Mumbai, India); Zinc acetate was heated at 100°C under vacuum for 24 h while chloroform, THF, and dichloromethane solvents were purified by refluxing and distillation over sodium wire and benzophenone.

Synthesis of Aliphatic Dihydroxy Compounds Containing Ester Groups

Aliphatic dihydroxy compounds were prepared by solution reaction of the diacid chloride with large excess amounts (10 folds of the stoichiometric quantity) of 1,4-butane diol as shown in Scheme 1. A typical procedure for the preparation of bis(4-hydroxybutyl) terephthalate (t-PHTH–BuD) follows: terephthaloyl dichloride (12.18 g, 0.06 mol) in THF (60 mL) was added dropwise under nitrogen from a pressure equalizing

funnel to a stirred solution of 1,4-butanediol (1.2 mol, 108 g), pyridine (0.18 mol, 14.2 g), and a catalytic amount of 4-DMAP in THF (300 mL) in 500 mL round-bottomed flask below 5°C. The reaction mixture was stirred for 1 h at 0–5°C and over night at room temperature. THF was evaporated and chloroform (300 mL) was added to the formed solid product, the chloroform solution was transferred to a 1 L separatory funnel, washed with water, acidified with aqueous HCl solution (8% v/v, 100 mL) and then washed with distilled water until a neutral washing was obtained. The chloroform layer was dried over anhydrous sodium sulfate, filtered and evaporated (Rotatory evaporator). The product was dried at 50°C under vacuum over night to give a white solid. The crude product was crystallized from water to white crystals in 86% yield, melting point: 80°C (lit. value 79–80°C,[26] and also 81°C).[27] The other aliphatic dihydroxy compound: bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate (CH–BuD) was prepared by the same way as a viscous liquid from cis/trans-1,4-cyclohexanedicarboxylic acid dichloride (CHAC) and excess 1,4-butanediol. CHAC was prepared from the reaction of cis/trans-1,4-cyclohexane dicarboxylic acid with large excess of thionyl chloride as described in the literature.[28]

Synthesis of Aromatic Dihydroxy Compounds Containing Ester Groups

The aromatic dihydroxy compound, 1,4-[di-(4-hydroxydiphenyl-2,2′-propane)]-terephthalate (t-PHTH–BPA), was obtained by the reaction of the terephthaloyl chloride with an excess amount (25% folds of the stoichiometric quantity) of BPA in the presence of pyridine according to a previously published procedure.[29,30] In brief, Pyridine (43.5 g, 0.55 mol) was added dropwise to a stirred solution of BPA (141.5 g, 0.62 mol) in chloroform (150 mL) at 0°C. A solution of terephthaloyl chloride (50.76 g, 0.25 mol) in chloroform (100 mL) was then added dropwise to the reaction mixture at 0°C. The reaction mixture was stirred for 2 h at 0°C and 1 h at room temperature. Chloroform solvent was distilled off and the residue was poured into excess cold water (500 mL), a white solid was precipitated, filtered, dried under reduced pressure and recrystallized from methanol/water mixture (1/1, v/v), yield 73%, melting point 197–199°C (literature value is 199–201°C).[30]

Monomer Synthesis

The diphenyl dicarbonate monomers were prepared by the reaction of the various dihydroxy compounds with PCF (Scheme 2) following previously published procedures.[31–33] A typical procedure for the preparation of bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate diphenyl dicarbonate (CH−Bu DPDC) follows: PCF (26.62 g, 0.17 mol) in dry chloroform solution (30 mL) was added dropwise to a stirred solution of cis/trans-1,4-cyclohexanebis(4-hydroxybutyl ester) (CH–Bu) (25.31 g, 0.08 mol), pyridine (15.82 g, 0.20 mol), and a catalytic amount of 4-DMAP in chloroform (125 mL) below 5°C. The reaction mixture was stirred for 1 h at 0−5°C and over night at room temperature. The chloroform solution was washed several times with water and 10% aqueous sodium carbonate solution, dried over anhydrous sodium sulfate, filtered and chloroform was evaporated under reduced pressure. The product was dried at 50°C under vacuum over night to give a colorless solid, yield = 94%.
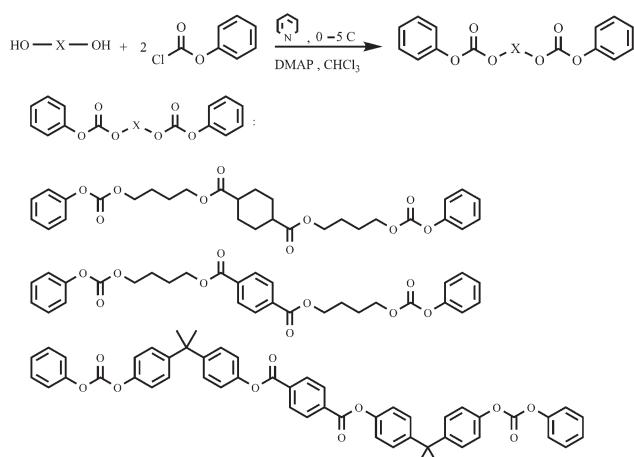
Scheme 2. Synthesis of diphenyl dicarbonates of dihydroxy compounds containing ester groups.

Scheme 3. Synthesis of poly(ester carbonate)s by melt polycondensation of bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate diphenyl dicarbonate with dihydroxy compounds (Series A).
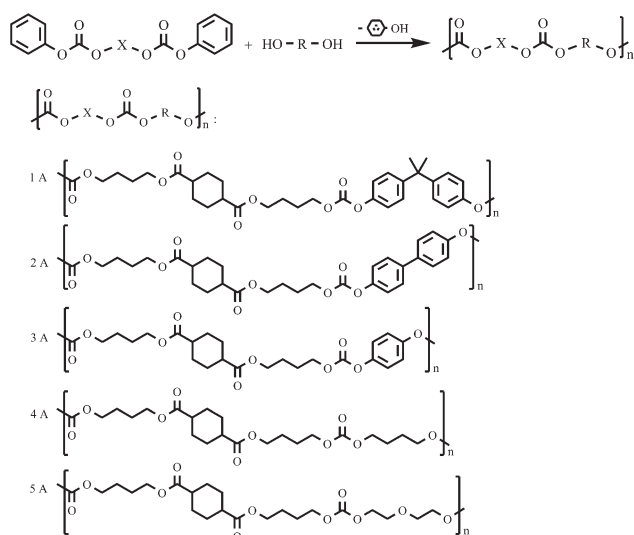
The other two monomers were prepared by the same way: bis(4-hydroxybutyl) terephthalate diphenyl dicarbonate (*t*-PHTH–Bu DPDC) and 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate diphenyl dicarbonate (*t*-PHTH–BPA DPDC).

Polymer Synthesis

The various poly(ester carbonate)s were synthesized according to the following general procedures:

a. Aliphatic–aliphatic polycarbonates: A glass reaction tube (30 × 150 mm) equipped with an inert gas inlet and outlet was filled with a homogeneous solid mixture composed of 10 mmol dicarbonate, 10 mmol dihydroxy compound and anhydrous zinc acetate (2% mol of the dicarbonate). The reaction mixture was heated in a silicone oil bath and stirred with a magnetic follower at 150°C under a stream of argon gas for 30 min. The reaction mixture was heated at 170°C for 1 h, at 190°C for 1 h, and at 210°C for 1 h. The temperature was increased to 225°C and the pressure was gradually reduced to 1 mmHg to remove the by-produced phenol and heating was maintained for 2 h. Finally, the reaction tube was cooled, the polymer synthesized at the bottom was dissolved in chloroform, the solution was filtered and the polymer was precipitated by dropwise addition to methanol. The resulting polymer was filtered and dried in a drying pistol at 60°C *in vacuo* over night. The following aliphatic–aliphatic poly(ester carbonate)s were prepared by the same procedure: bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate-1,4-butylene (CH–Bu–Bu) polycarbonate, bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate–diethylene glycol (CH–Bu–DIGOL) polycarbonate, bis(4-hydroxybutyl) terephthalate–1,4-butylene (*t*-PHTH–Bu–Bu) polycarbonate, and bis(4-hydroxybutyl) terephthalate–diethylene glycol (*t*-PHTH–Bu–DIGOL) polycarbonate.

b. Aliphatic-aromatic and aromatic-aromatic polycarbonates: The same procedure as that in above was followed except that the reaction mixture was heated at 210°C for 1 h, at 230°C for 1 h, and that the temperature was increased to 250°C and the pressure gradually reduced to 1 mmHg and heating was maintained for 2 h. The following aliphatic-aromatic polycarbonates were prepared by this procedure: bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate–bisphenol A (CH–Bu–BPA)

polycarbonate, bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate–biphenol (CH–Bu–BIPH) polycarbonate, bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate–hydroquinone (CH–Bu–HQ) polycarbonate, bis(4-hydroxybutyl) terephthalate–bisphenol A (*t*-PHTH–Bu–BPA) polycarbonate, bis(4-hydroxybutyl) terephthalate–biphenol (*t*-PHTH–Bu–BIPH) polycarbonate, bis(4-hydroxybutyl) terephthalate–hydroquinone (*t*-PHTH–Bu–HQ) polycarbonate, 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate–1,4-butylene (*t*-PHTH–BPA–Bu) polycarbonate, 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate–diethylene glycol (*t*-PHTH–BPA–DIGOL) polycarbonate. The following aromatic–aromatic poly(ester carbonate)s were also prepared by the same procedure: 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate–biphenol (*t*-PHTH–BPA–BIPH) polycarbonate and 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate–hydroquinone (*t*-PHTH–BPA–HQ) polycarbonate.

Three series of poly(ester carbonate)s were synthesized by the reaction of diphenyl dicarbonate monomers with various dihydroxy compounds: Series A was based on CH–Bu DPDC (Scheme 3), Series B was based on *t*-PHTH–Bu DPDC (Scheme 4), and Series C was based on *t*-PHTH–BPA DPDC (Scheme 5).

Measurements

The inherent viscosity of polymer solutions in dichloromethane (0.5 g/dL) were measured by a dilution Ubbelhode glass capillary viscometer (Rheotek, Poulten Selfe & Lee, Essex, England) in a thermostated water bath temperature controlled at 25°C. The infrared (IR) spectra (from 400 to 4000 cm^{-1}) of the dihydroxy compounds, monomers and polymers were recorded as neat films on Thermo Nicolet Nexus 670 FT-IR spectrometer (Madison, WI). The films were prepared by the cast solutions in chloroform on NaCl plates. The ^{1}H-NMR and ^{13}C-NMR spectra of the dihydroxy compounds, monomers and polymers in deuterated chloroform were recorded on a Bruker Avance DPX 300 Spectrometer at 300 MHz (Wissembourg Cedex, France). Chemical shifts (δ's) for ^{1}H and of 75
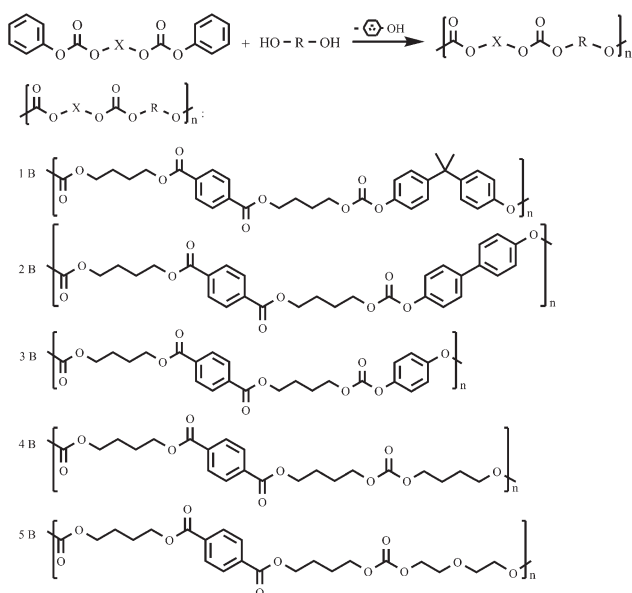
Scheme 4. Synthesis of poly(ester carbonate)s by melt polycondensation of bis(4-hydroxybutyl) terephthalate diphenyl dicarbonate with dihydroxy compounds (Series B).

MHz for ^{13}C are given in ppm with tetramethylsilane (TMS) as the internal standard. The glass transition temperature (T_g) of polymer samples was studied with a Netzsch 204 F 1 differential scanning calorimeter (DSC) (Selb Bavaria, Germany). The T_g measurements were performed on 10 ± 2 mg samples under a dry nitrogen atmosphere by heating to the molten state at a heating rate of 10°C /min. The T_g values were taken as the mid point of the step transition. The thermal stability of the polymer samples were studied by thermogravimetric analysis (TGA) with NETZCH STA 409 PG/PC Thermal Analyzer (Selb Bavaria, Germany). Measurements were conducted at a heating rate of 20°C /min under dry nitrogen purging at a flow rate of 50 mL/min.
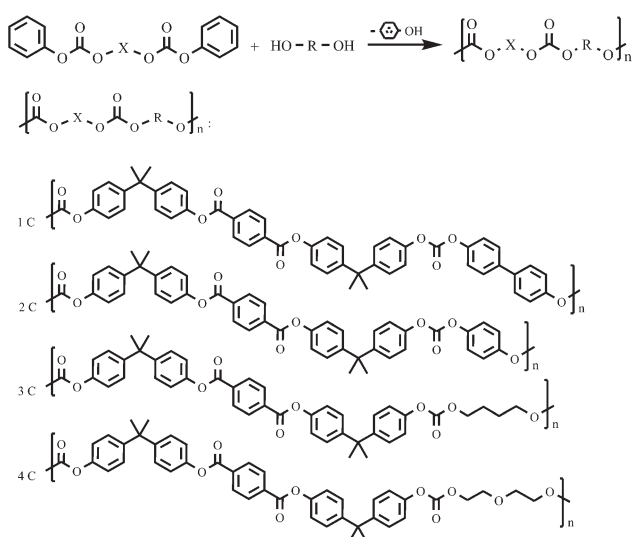
Scheme 5. Synthesis of poly(ester carbonate)s by melt polycondensation of 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate diphenyl dicarbonate with dihydroxy compounds (Series C).

RESULTS AND DISCUSSION

Synthesis and Characterization of Dihydroxy Compounds Containing Ester Groups

In this study, three types of dihydroxy compounds each containing two ester groups were utilized, a dihydroxy compound containing aliphatic–aliphatic ester group, bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate (CH-Bu), a dihydroxy compound containing aromatic–aliphatic ester group, bis(4-hydroxybutyl) terephthalate (*t*-PHTH-Bu), and a dihydroxy compound containing aromatic-aromatic ester group, 1,4-[di-(4-hydroxydiphenyl-2,2′-propane)] terephthalate (*t*-PHTH-BPA). CH-Bu and *t*-PHTH-Bu were synthesized from the reaction of CHAC and terephthaloyl chloride (*t*-PHTHC) with a 10-fold excess of 1,4-butanediol, respectively, (Scheme 1). The aromatic-aromatic dihydroxy compound (*t*-PHTH–BPA) was prepared by the reaction of terephthaloyl chloride with a 25% excess amount of the stoichiometric quantity of BPA according to a previously published procedure.[29,30] The excess quantity of the diols was used to ensure forming the monomeric dihydroxy compound rather than the corresponding polyester. Bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate (CH–BuD) is a new compound and was obtained in high yield as a light yellow viscous liquid. The other two dihydroxy compounds, *t*-PHTH–BuD[26,27,34–39] and *t*-PHTH–BPA[29,30,40] were already known in the literature and were obtained in high yields as white solids. These compounds were characterized by melting point, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The spectroscopic details were discussed, tabulated, and interpreted in the electronic Supporting Information (ESI) part. The solid nature of *t*-PHTH–BuD may have been due to the effect of the linear geometry of the terephthalate unit and linear BuD alkane chain which provide large surface area through which intermolecular interaction can take effect. The solid nature of *t*-PHTH–BPA may be attributed to the linear geometry of the terephthalate unit and the extensive aromatic character of BPA unit. The melting point (T_m) of *t*-PHTH–BPA diol is 197–199°C (literature value is 199–201°C[30]) and the melting point of *t*-PHTH–BuD is 80°C (literature value is 79–80°C[26,27]). The melting point of *t*-PHTH–BPA diol was much higher than that of *t*-PHTH–BuD; this may be due to the extensive aromatic character of *t*-PHTH–BPA diol.

Synthesis and Characterization of Monomers

The prepared dihydroxy compounds containing ester groups were reacted with PCF[30–33] (Scheme 2) to obtain the following diphenyl dicarbonate monomers: bis(4-hydroxybutyl) cis/trans-1,4-cyclohexanedicarboxylate diphenyl dicarbonate (CH–Bu DPDC), bis(4-hydroxybutyl) terephthalate diphenyl dicarbonate (*t*-PHTH−Bu DPDC), and 1,4-[di-(4-hydroxy-diphenyl-2,2′-propane)] terephthalate diphenyl dicarbonate (*t*-PHTH−BPA DPDC). Mechanistically, the reaction proceeds by the pyridine-catalyzed nucleophilic displacement of the chloride of PCF with the alcoholic group of the dihydroxy compound.[41–44] To our knowledge, all these monomers are completely novel compounds; therefore, they were characterized by melting point, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy to confirm their structures. The spectroscopic details were discussed, tabulated, and interpreted in the ESI part. CH−Bu DPDC was obtained as a light yellow viscous liquid, while *t*-PHTH−Bu DPDC and

Table I. Yield, IR Data, Inherent Viscosity and T_g Values of Poly(ester carbonate)s

Polymer code	Polycarbonate	Yield (%)	v C=O (cm^{-1}) (ester)	v C=O (cm^{-1}) (carbonate)	v C—O—C (cm^{-1})	η_{inh} (dL/g)	T_g (°C)
Series A							
1 A	CH—Bu—BPA	14	1730	1758	1255, 1224, 1168	0.42	4.1
2 A	CH—Bu—BIPh	16	1729	1759	1166, 1215, 1253	0.42	11.7
3 A	CH—Bu—HQ	28	1730	1759	1257,1191	0.48	1.6
4 A	CH——Bu—Bu	20	1729	1745	1250, 1166	0.27	−2.1
5 A	CH—Bu—DIGOL	22	1729	1747	1254, 1168	0.26	−9.8
Series B							
1 B	t-PHTH—Bu—BPA	21	1720	1761	1259	0.29	54.9
2 B	t-PHTH—Bu—BIPh	62	1717	1761	1266, 1214	0.39	37.3
3 B	t-PHTH—Bu—HQ	50	1720	1762	1263, 1189	0.34	24.5
4 B	t-PHTH—Bu—Bu	60	1718	1744	1264	0.44	−2.6
5 B	t-PHTH—Bu—DIGOL	32	1720	1746	1270	0.41	8.6
Series C							
1 C	t-PHTH—BPA—BIPH	31	1738	1773	1240, 1195, 1164	0.23	134.1
2 C	t-PHTH—BPA—HQ	52	1739	1774	1242, 1199, 1165	0.25	121.5
3 C	t-PHTH—BPA—Bu	73	1740	1761	1249, 1202, 1168	0.29	108
4 C	t-PHTH—BPA—DIGOL	54	1739	1763	1262, 1202, 1169	0.39	92.4

t-PHTH−BPA DPDC were white solids. The fact that CH−Bu DPDC is a liquid may have been due to the extensive aliphatic nature of the CH−Bu moiety, and the low coplanarity level and the irregularity of the sections of the CH−Bu DPDC monomer which render it have low tendency to fit well in the crystal lattice. The melting point of t-PHTH−Bu DPDC (81°C) is reasonable due to the presence of flexible linear butane chain. For the t-PHTH−BPA DPDC molecule, it seems that although the two phenylene rings of BPA are not coplanar (i.e., enhance liquid), the molecule is not a liquid but a solid due to the extensive aromatic character of the molecule. The high melting point of t-PHTH−BPA DPDC (156°C) compared with that of t-PHTH−Bu DPDC (81°C) may have been due to the fact that apart from the noncoplanarity of BPA p-phenylene rings, the molecule contains a number of molecular planar sections (i.e., phenylene ring of terephthalate, the planar ester group, the planar carbonate group, and the planar phenyl ring), which can fit well to the corresponding planar sections of another molecule, and therefore, they can stack easily in the crystal lattice.

Synthesis and Characterization of Poly(ester carbonate)s

This study was based on the melt-phase polycondensation of diphenyl dicarbonates containing ester groups with dihydroxy compounds. This approach was shown, in the course of this work, to be a convenient method of synthesis of poly(ester carbonate)s. The polycondensation reaction proceeds by zinc acetate catalyzed nucleophilic displacement of the phenoxy group of the diphenyl dicarbonate with the alcoholic group of the dihydroxy compound. All polymerization reactions afforded the postulated poly(ester carbonate)s. This result was deduced from viscosity measurements and the spectroscopic analysis of the synthesized polymers, especially the ^{1}H-NMR and ^{13}C-NMR spectra of the alkylene, and arylene groups attached to the carbonate group.

The synthesized polymers were characterized by; inherent viscosity, IR spectroscopy, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, DSC, and TGA. Three series of poly(ester carbonate)s were synthesized (Series A–C) as illustrated in Schemes 3–5.

As can be seen in Table I, the yield of series A polycarbonates was low compared to those of series B or C. This is because; series A polycarbonates were prepared at lower polycondensation temperature (225°C) than those of series B and C polycarbonates (250°C). A lower polycondensation temperature was used for series A polycarbonates to keep the formed aliphatic–aliphatic carbonate groups from partial decarboxylation at higher temperatures. If decarboxylation occurs; it would lead to the formation of aliphatic-aliphatic ether groups which would alter the properties of the final poly(ester carbonate)s. Using lower temperature, however, resulted in the formation of a lower proportion of high molecular mass polycarbonates which when isolated by precipitation in methanol during purification gave rise to smaller amount of product and thus to a lower polycarbonate yield. On the other hand, since the aromatic–aliphatic polymers of series B and the aromatic–aromatic polymers of series C are more thermally stable under polycondensation temperature, they were synthesized at 250°C. Apparently higher yields of large polycarbonate chains were obtained.

Solution Viscosity Measurements

The inherent viscosities of the poly(ester carbonate)s synthesized were calculated from viscosity measurements of dilute polymer solutions (Concentration 0.5 g/dL) in chloroform at 25°C. The results of viscosity, together with yield, physical data and T_g values, are summarized in Table I. The synthesized polymers had inherent viscosities in the range from 0.23 to 0.48 dL/g. This implies that the polymers had low to fair inherent viscosities (i.e., low to fair molecular masses).[42]

Small variations in inherent viscosities were observed among the three series. These variations may be attributed to the difference in the chemical structure of the polymers and to the occurrence of competing interchange reactions during polymerization. At first, series A polymers based on CH–Bu unit and series B polymers based on *t*-PHTH–Bu unit generally have slightly higher inherent viscosities than series C polymers based on *t*-PHTH–BPA unit. For example, the effect of monomer structure on inherent viscosities of three polymers having the same dihydroxy compound, HQ, linked to the three monomer units may be elucidated. The inherent viscosity (η_{inh}) values of CH–Bu–HQ, *t*-PHTH–Bu–HQ, and *t*-PHTH–BPA–HQ polycarbonates are 0.48, 0.34, and 0.25 dL/g, respectively. The corresponding η_{inh} values of the same monomers linked to BIPH instead of HQ are 0.42, 0.39, and 0.23 dL/g, respectively which show almost similar trend. The observed trend may have been due to that the 1,4-butylene chain in series A and B being more flexible than the aromatic BPA unit in series C made the reaction melt less viscous and thus would have facilitated the removal of the by-produced phenol and have push the equilibrium polycondensation reaction toward the products side to a greater extent. This would lead to the formation of higher molecular mass polymers and higher viscosity. The higher inherent viscosity of CH–Bu–HQ than *t*-PHTH–Bu–HQ may have been due to the higher flexibility of the cis/trans nature of the cyclohexylene ring than the terephthalate unit. Apparently, poly(ester carbonate)s involving Bu unit show higher inherent viscosity than those involving BPA. Furthermore, the higher viscosity of *t*-PHTH–BPA–DIGOL than the polycarbonates of series C may have been due to the greater flexibility effect imparted by the DIGOL unit for probably the same reason. Second, the occurrence of competing interchange reactions during polymerization is also another factor of variation. The principal interchange reaction taking place and leading to polymer chain build up is the nucleophilic attack of the hydroxyl group of the dihydroxy compound on the carbonate group of the monomer. This reaction gives linear polymers in which the two monomer residues are connected alternately along the entire polymer chain. A part from this reaction, a possible competing reaction is the interchange reaction that leads to randomization of reactants residues or intrachange reaction that leads to the formation and subsequent elimination of cyclic aliphatic carbonates from the oligomers or the preformed polymers. The occurrence of this reaction would lead to the formation of shorter polymer chains and lower viscosity.

FT-IR and NMR Spectroscopy

The poly(ester carbonate)s prepared were analyzed by FT-IR and NMR spectroscopy. The structures of these polymers and their spectroscopic details including yield, FT-IR, ^{1}H-NMR spectra, ^{13}C-NMR spectra were discussed, tabulated, and interpreted in the ESI part.

Comparing the proton and carbon NMR spectra and the chemical shifts of all proton and carbon peaks of the reactant monomers and the synthesized polymers, it may be possible to disclose the following observations:

i. The disappearance and appearance of some proton and carbon peaks as well as the transformation of proton peaks from symmetric peaks in the spectra of monomers to asymmetric peaks in the spectra of polymers indicate connection of two different monomer units, which implicitly suggest reaction of the two monomers and the synthesis of the postulated poly(ester carbonate)s.

ii. The ^{1}H-NMR and ^{13}C-NMR signals of the terminal methylene groups attached to the carbonate group appeared at higher δ values than those attached to the ester which is in turn appeared at higher δ values than those attached to the ether groups. This order was found and repeatedly observed in the NMR spectra of all aromatic–aliphatic and aliphatic–aliphatic polycarbonates.

iii. The aromatic proton signals of the *t*-PHTH unit appeared as singlet at $\delta = 8.30$ ppm a way from those of both BPA unit which appeared at $\delta = 7.0$–7.7 ppm and Bu unit which appeared at or less than $\delta = 4.4$ ppm and is distinguishable in its form. The *t*-PHTH peak appeared as singlet while those of Bu or BPA were displaced as a triplet or as an AB system.

iv. When DIGOL was used as the diol a poly(ester carbonate) containing ether linkage was obtained. This reaction constitutes a means of synthesis of poly(ester ether carbonate)s by interchange reaction of monomers with diols containing ether bond.

v. In the C=O peak region, the ^{13}C-NMR signal of the carbonyl carbon of the carbonate group appeared at slightly variable position depending on the chemical nature of the moieties connected to it. The spectra showed that the characteristic signal of C=O occurred at about $\delta = 152$ ppm in aromatic–aromatic polymers, at about $\delta = 153.7$ ppm in aromatic–aliphatic polymers and at about $\delta = 155$ ppm in aliphatic–aliphatic polymers. Furthermore, the ^{13}C-NMR signal of the carbonyl carbon of the ester group showed parallel dependence on the chemical nature of the moieties attached to it. For example, the spectra showed that the characteristic signal of C=O occurred at about $\delta = 164$ ppm in aromatic–aromatic ester, at about $\delta = 166$ ppm in aromatic–aliphatic ester and at about $\delta = 175$ ppm for aliphatic–aliphatic ester.

^{13}C-NMR Spectral Evidence of Monomer Sequence Randomization

Another spectral evidence for the existence of structural variations in polymer backbone of the synthesized poly(ester carbonate)s was also observed. The synthesized polymers, under polycondensation conditions, may also undergo polymer–polymer or polymer–monomer interchange reactions causing molar mass alterations. For example, the monomer alkylene and arylene residues may be exchanged and subsequently become partially randomly distributed throughout a polymer chain. The reaction may involve two end-groups, an end-group with a mid-chain group, or two mid-chain groups. These reactions would lead to the formation of randomized short sequences of one monomer unit and would ultimately lead to polymers with complete randomization of monomer residues and statistical molecular mass distribution. In this work, the occurrence of these randomizing reactions was confirmed by analysis of the ^{13}C-NMR signal of the carbonyl carbon of the carbonate group (Figure 1).
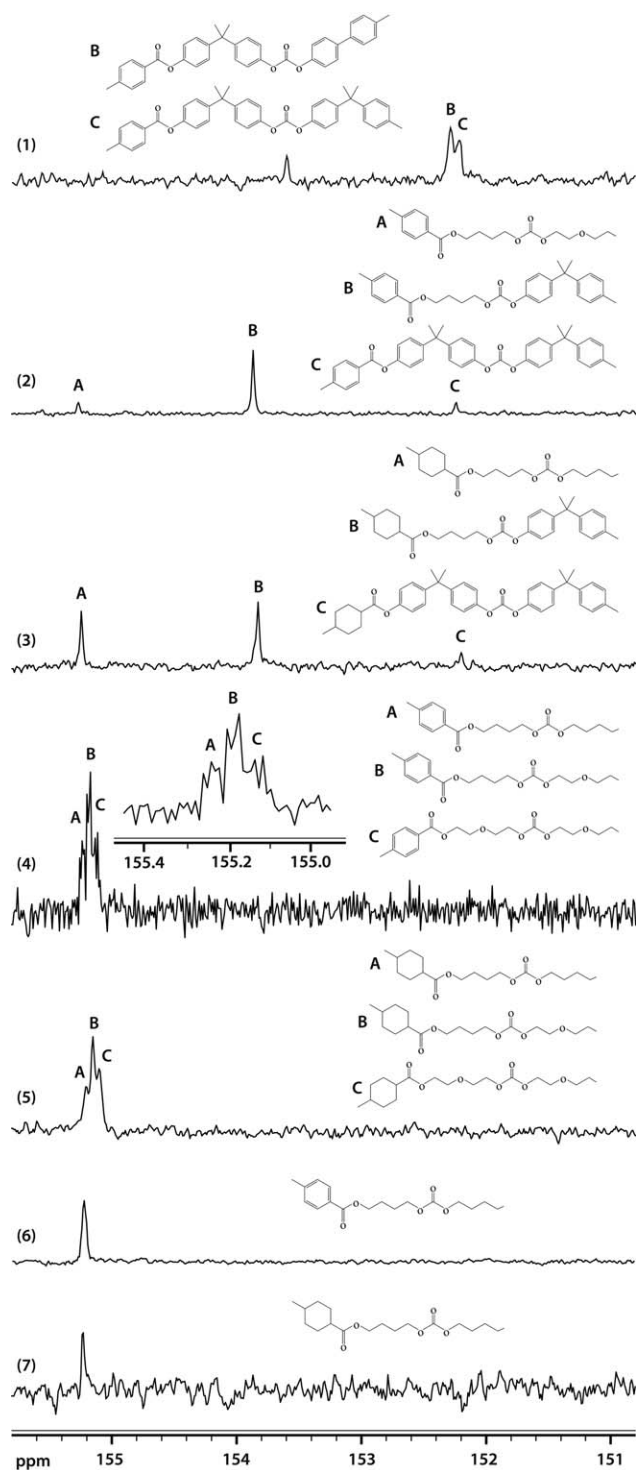
Figure 1. ^{13}C-NMR signals of C=O observed in the spectra of selected poly(ester carbonate)s: (1) poly(t-PHTH-BPA-BIPH carbonate), (2) poly(t-PHTH-Bu-BPA carbonate), (3) poly(CH-Bu-BPA carbonate), (4) poly(t-PHTH-Bu-DIGOL carbonate), and (5) poly(CH-Bu-DIGOL carbonate), (6) poly(t-PHTH-Bu-Bu carbonate), and (7) poly(CH-Bu-Bu carbonate).

Based on the observed ^{13}C-NMR spectra of all series of poly(ester carbonate)s synthesized, most polymer types, whether aromatic–aromatic aliphatic–aromatic, and aliphatic–aliphatic polymers, underwent partial randomization of monomer residues about the

carbonate group (Spectra 1 to 5). As can be seen from Figure 1, the aromatic-aromatic poly(t-PHTH–BPA–BIPH carbonate) underwent partial randomization and the signal of the C=O group in its ^{13}C NMR spectrum (Figure 1, Spectrum 1) displayed two very close partially resolved signals out of three expected within the aromatic region of the spectrum at about 152 ppm. Similarly, the aromatic-aliphatic (e.g., poly(t-PHTH–Bu–BPA carbonate) and poly(CH–Bu–BPA carbonate)) underwent randomization and the signal of the C=O group in its ^{13}C NMR spectrum (Figure 1, Spectra 2 and 3) displayed three completely separated signals over the aliphatic and aromatic δ values of C=O in the range from 152 to 155. The aliphatic-aliphatic polymers [e.g., Poly(t-PHTH–Bu–DIGOL carbonate) and poly(CH–Bu–DIGOL carbonate)] also underwent randomization and the signal of the C=O group in their ^{13}C NMR spectra (Figure 1, Spectra 4 and 5) displayed three very close partially resolved signals within the aliphatic region of the C=O group at about 155 ppm. The C=O pattern of peaks of poly(t-PHTH–Bu–DIGOL carbonate) was displayed as three peaks each one is constituted of two sub peaks, this form has never been observed in our previous works. Interestingly, the ^{13}C-NMR spectrum of aliphatic-aliphatic polymers involving the same aliphatic alkane chains about the carbonate group (e.g., Poly(CH–Bu–Bu carbonate) and poly(t-PHTH–Bu–Bu carbonate) displayed one peak constituted of only a single line (Figure 1, Spectrum 6 and 7) within the aliphatic region of the C=O group at about 155 ppm. The randomization patterns represented in Spectra 1–5 of Figure 1 imply that the two different monomer residues were randomized about the carbonate group. The polymers whose carbon spectra did not show randomization patterns are those involving the same alkyl group on both sides of the carbonate group (Spectra 6 and 7). Therefore, the patterns represented in Spectra 6 and 7 imply that the monomer residues was not randomized about the carbonate group and that the C=O group is always surrounded from both sides with two Bu alkane units. In fact, even if these units have been actually interchanged, no randomized signals would be observed due to their exact chemical identity. On the other hand, the signals designated as B in Spectra 1–5 represent the alternate sequence of monomer residues in the polymers backbones. These peaks arise from the direct interchange reaction of alkylene or arylene diphenyl dicarbonate monomers with the various dihydroxy compounds. Apparently, the peaks assigned B in Spectra 2 and 3 refer to the sequence t-PHTH–CO–Bu–OCOO–BPA which have been abbreviated in the caption of Figure 1 as t-PHTH–Bu–BPA and its carbon signal was displayed at the same position. The occurrence of the random sequences A and C are due to other interchange reactions such as polymer–polymer and polymer–monomer interchange reactions. This pattern of peaks confirms that the backbone of a typical poly(ester carbonate) molecule possessed a partial random sequence of units in which all of these sequences coexisted. Based on the randomization patterns in our earlier publications[45–47] and comparing the spectra of Figure 1, the peaks of all polycarbonates have been accounted for according to Figure 1. In this figure were displayed aromatic and aliphatic spectra of polymers representative of all series which showed randomization of units about the carbonate group.

Apparently, signal C in Spectra 2 and 3 are the same as signal C in Spectrum 1, they occur at the same δ value. In addition,

Peak B in Spectra 2 and 3 refer to the sequence (i.e., *t*-PHTH–CO–Bu–OCOO–BPA) and occurred at the same position. Furthermore, the peaks assigned A in Spectra 3 to 7 refer to the sequence –Bu–OCOO–Bu– and they occur at the same position in all spectra. It may be deduced that Peak A in Spectrum 1 was not detected, so the sequence *t*-PHTH–CO–BIPH–OCOO–BIPH was not formed. These comparisons imply that our interpretation of the pattern of signals should be correct.

Thermal Properties

The thermal properties of poly(ester carbonate)s synthesized were also investigated with DSC and their stability were evaluated by TGA. The T_g values of the poly(ester carbonate)s (Table I) showed a wide range of variation from -9.8 to $134.1°C$. The T_g values are dependent on the variation of the chemical structure of the poly(ester carbonate)s, i.e., the stiffening effect of the aromatic moieties and the flexibility effect of the alkylene and ether groups. The experimentally observed values are the net effect of these factors. The T_g values of the polycarbonates containing aromatic–aromatic carbonate and ester groups (e.g., *t*-PHTH–BPA–BIPH and *t*-PHTH–BPA–HQ) generally have highest values, and that those containing aliphatic–aliphatic carbonate and ester groups (e.g., CH–Bu–Bu and CH–Bu–DIGOL) have lowest values. The polymers with mixed aromatic and aliphatic carbonate and ester groups generally have intermediate values. The introduction of aliphatic moieties containing ether groups to poly(ester carbonate) chains yields poly(ester ether carbonate)s with lowest T_g values (e.g., CH–Bu–DIGOL and *t*-PHTH–BPA–DIGOL) compared with the corresponding poly(ester carbonate)s of series B and C that do not contain ether groups (e.g., CH–Bu–Bu and *t*-PHTH–BPA–Bu). The DSC thermograms of poly(ester carbonate)s synthesized in Series A are presented in Figure 2.

The thermal stability of poly(ester carbonate)s was also investigated by TGA under dry nitrogen atmosphere. Table II reports the $T_d^{1\%}$, $T_d^{5\%}$, $T_d^{10\%}$, $T_d^{50\%}$ decomposition temperatures, which correspond to the temperatures at which 1, 5, 10, and 50% loss of mass of poly(ester carbonate) occurred, respectively.
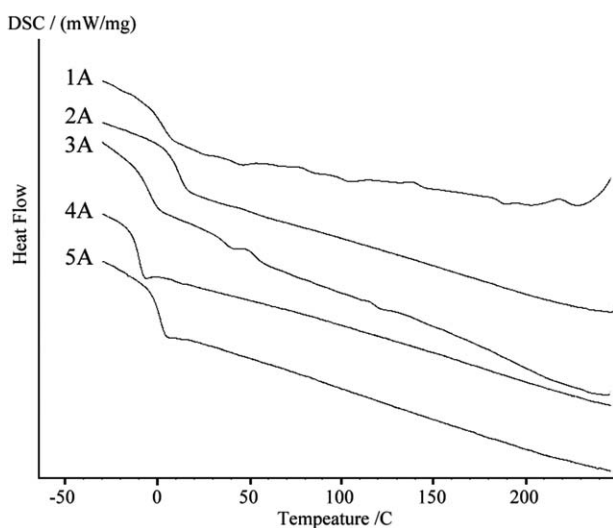
Table II. Thermal Stability Data of Poly(ester carbonate)s

Polymer	T_d^i	$T^{5\%}$	$T^{10\%}$	$T^{50\%}$	Residual mass % at 500°C
1 A	106	252	305	399	13.2
2 A	241	338	355	416	13.1
3 A	314	348	361	412	6.1
4 A	290	346	381	421	13.8
5 A	287	320	347	428	8.3
1 B	172	343	361	414	19.1
2 B	326	349	361	397	16.3
3 B	335	350	359	395	13.2
4 B	157	282	304	383	0.0
5 B	298	322	339	425	1.7
1 C	371	442	468	517	68.7
2 C	342	407	430	498	49.2
3 C	276	351	369	451	26.5
4 C	98	334	377	440	21.4

The table also shows the residual mass percent remaining upon heating the polymer samples to 500°C.

The data in Table II generally show that the thermal decomposition temperatures (T_d) of the poly(ester carbonate)s depend of their chemical structure. It has been found that the fully aromatic polymers (e.g., *t*-PHTH–BPA–BIPH and *t*-PHTH–BPA–HQ) have highest T_d values, and that the slightly aromatic polymers (e.g., CH–Bu–BPA and *t*-PHTH-BPA-DIGOL) have lowest values. It has also been found that the fully aromatic polymers have higher residual mass percentage values at 500°C and that slightly aromatic polymers (e.g., *t*-PHTH–Bu–Bu and *t*-PHTH–Bu–DIGOL) have the lowest values. Furthermore, the aromatic-aromatic carbonate and ester polymers have higher T_d and higher residual mass percentage values at 500°C than the rest of the polymers in any series. These facts may be explained by considering that the thermal stability of a selected polymer depends on the combination of the particular chemical structure and the aromatic or aliphatic nature of the organic

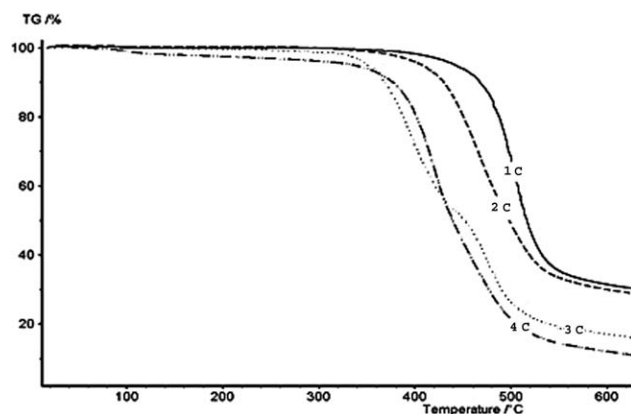**Figure 2.** DSC thermogram of poly(ester carbonate)s (Series A).

Figure 3. TGA thermograms of poly(ester carbonate)s (Series C). TG % is the mass percentage of the polymer sample remaining after heating the polymer to a certain temperature.

moieties attached to the ester and the carbonate groups. The thermograms of poly(ester carbonate)s displayed typical one-stage characteristics with a slow mass loss starting from 200 to 300°C and a relatively fast mass loss between 350 and 500°C. The fast mass losses may be attributed to further condensation of polymer chains,[48] decarboxylation of carbonate groups and elimination of cyclic aliphatic carbonates.[49–53] A typical TGA thermograms of series C poly(ester carbonate)s are presented in Figure 3.

CONCLUSIONS

A new method of synthesis of linear poly(ester carbonate)s by melt polycondensation of dihydroxy compounds with diphenyl dicarbonates containing ester groups was developed. All reactions without exception afforded methanol insoluble polycarbonates. In the synthesized polymer chains, monomer residues were partially randomized about the carbonate group, and therefore, aliphatic and aromatic carbonate groups coexist in a typical polymer backbone. The synthesized polycarbonates had intermediate to high inherent viscosities. A wide variation in T_g values was observed which reflects the effect of variations in the structure of the polymers. This approach may be used to synthesize poly(ester carbonate)s whose properties could be varied by varying the structure of the monomers and dihydroxy compound. This approach may permit synthesis of polycarbonates containing other organic groups for variable industrial applications.

ACKNOWLEDGMENTS

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