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

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ABSTRACT: A new method of synthesis of poly(ether carbonate)s based on interchange reactions of dihydroxy compounds with alkylene and arylene diphenyl dicarbonates containing ether group was presented. The diphenyl dicarbonate monomers were prepared from phenyl chloroformate and dihydroxy compounds containing ether group (e.g., diethylene glycol, bis(2-hydroxyethyl ether) of bisphenol A, and 4,4'-oxydiphenol). The process consisted of a precondensation step under a stream of dry argon followed by a melt polycondensation at 230 or at 250°C under vacuum. Four series of poly(ether carbonate)s were prepared using this approach. Using alkylene and arylene diphenyl dicarbonate-containing ether groups as monomers, the polycondensation reaction with dihydroxy compounds led to the formation of poly(ether carbonate)s having inherent viscosity values up to 0.56 dL/g and high thermal stability. The glass transition temperature values of polycarbonates were in the range 7–122°C. The polymers were characterized by inherent viscosity and spectroscopic (Fourier transform infrared spectroscopy and ^{1}H-NMR and ^{13}C-NMR) and thermal (differential scanning calorimeteric and thermogravimetric) methods. This approach may permit the use of diphenyl dicarbonates containing other organic functional groups for the synthesis of polycarbonates containing those groups. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polycarbonates; diphenyl dicarbonates; melt-phase polycondensation; interchange reactions; poly(ether carbonate)s; bisphenol A; synthesis

INTRODUCTION

Poly(ether carbonate)s derived from bisphenol A (BPA) are an important class of polycarbonates. Poly(ether carbonate)s have attracted attention because of their desirable properties such as high tensile elongation and excellent low-temperature characteristics, liquid crystallinity, biodegradability, and transparency.[1–5] Many poly(ether carbonate)s have characteristics such as high breaking strength and high elongation at break.[6]

An interesting reported advance of some poly(ether carbonate)s is the development of injectable polymers suitable to be implanted in the human body without requiring a surgical procedure. Novel reverse thermoresponsive injectable poly(ether carbonate)s were synthesized from poly(ethylene glycol) (PEG) dichloroformate with poly(propylene glycol) (PPG) oligomers (molecular mass = 3000) to produce PEG/PPG block copolymer.[7,8] In a recent report on the potential of using poly(ether carbonate)s as reverse thermoresponsive gelation materials, Yang et al.[9] reported that poly(ether carbonate)s water solutions have better reverse thermoresponsive gelation characteristics than the best investigated materials, poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide) triblocks (PEO-PPO-PEO). Poly(ether carbonate)s showed combined low viscosity at the injection stage, with viscosity developed to a higher value *in situ* for gel or semisolid consistency as their water solutions heat up to body temperature after injection.

A number of studies have been conducted on the synthesis of poly(ether carbonate)s. Poly(ether carbonate)s, with controlled composition, were prepared from oligomeric PPG diols with carbonyldiimidazole or diglycoyl chloride.[10] A polycarbonate block with a polyether block containing appropriate reactive end groups leads to a block poly(ether carbonate). The preparation of a poly(ether carbonate) composed of a poly(BPA carbonate) block and a polyether block derived from poly(tetramethyleneglycol) and poly(3-methyltetramethylene glycol) was described.[6] Other poly(ether carbonate)s were prepared by melt polycondensation of BPA and the bis(2-hydroxyethyl ether) of various bisphenols with diphenyl carbonate[11,12]

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from the reaction of oxiranes with cyclic and linear aromatic and aliphatic carbonates[13,14] and from diphenolates, cyclic carbonates, and dihalo compounds.[15]

Step-growth polymerization is a method that can be used to prepare polymers with well-defined chemical compositions. In many cases, the composition of step-growth polymers reflects the composition of the monomers feed. The alkylene or arylene diphenyl dicarbonates containing ether groups may be used, via step-growth polymerization, to introduce alkylene or arylene units containing ether groups into polymeric chains. The advantage of this approach is that it would produce linear polycarbonates containing controlled proportions of ether groups in the polymer backbone. Varying the structures of the monomers would lead to polymers with varying properties (e.g., thermal properties such as T_g). The introduction of the aliphatic ether groups would also increase the mobility and thus the flexibility of the polycarbonate chains. This effect would be reflected in a considerable lowering of the glass transition temperatures of otherwise rigid polymers. Furthermore, the controlled introduction of flexible ether groups may improve the processability of polycarbonates derived from rigid bisphenols and help preparing polycarbonates with tailored properties.

The purpose of this work was to introduce a new synthetic method to poly(ether carbonate)s by melt-phase interchange reactions of alkylene and arylene diphenyl dicarbonates containing ether groups with dihydroxy compounds as monomers. To our knowledge, the synthesis of poly(ether carbonate)s from these monomers is completely novel, and no article on the preparation of poly(ether carbonate)s using these reactants appeared in the literature.

EXPERIMENTAL

Materials

The materials used were of analytical grade reagents and were used as received, except for zinc acetate, chloroform, dichloromethane, and tetrahydrofuran (THF). The chemicals were obtained from the following sources: 1,4-butanediol, ethylene glycol (EG), hydroquinone (HQ), phenyl chloroformate (PCF), and zinc acetate dihydrate from Merck (Schuchardt, Germany); 4,4′-isopropylidene diphenol (BPA), biphenol (BiPh), 1,4-cyclohexanedimethanol (CHDM, mixture of cis- and trans-isomers), 4,4′-oxydiphenol (OxDiPh), titanium(IV) n-butoxide, and 4-dimethylaminopyridine (4-DMAP) from Acros Organics (Geel, Belgium); diethylene glycol (DIGOL) from Cambrian Chemicals (Beddington, UK); resorcinol (RESOL) from Riedel–de Haën (Seelze, Germany); potassium iodide from S. D. Fine Chemicals (Mumbai, India); and cyclic ethylene carbonate (EC) from Scharlau (Barcelona, Spain). Bis(2-hydroxyethyl ether) of BPA (BHEEBPA) has been synthesized in our laboratories. Anhydrous

chloroform was purchased from VWR (Souchez, France) and used as received. Zinc acetate was heated at 100°C under vacuum overnight, whereas dichloromethane was distilled from calcium hydride before use, and THF was purified by refluxing and distillation over sodium wire and benzophenone.

Synthesis of BHEEBPA

This diol was prepared according to an already published procedure[16] with minor modification. In brief, BPA (0.20 mol, 45.7 g), EC (0.42 mol, 37.0 g), and potassium iodide (2.4 mmol, 0.4 g) were introduced into a 250-mL three-necked round-bottomed flask equipped with a nitrogen inlet and outlet, a thermometer, and a condenser. The flask was flushed with dry argon and heated between 80 and 120°C for 1 h, and then the temperature was raised to 170°C and maintained at this temperature until CO_2 evolution subsided (5 h). On cooling to room temperature, a viscous liquid was obtained, which was converted on standing to an off-white solid. The crude product was purified by recrystallization from water/N,N-dimethylformamide mixture (H_2O : DMF; 2 : 1) and dried at 50°C in vacuo overnight. A white solid of melting point of 108–110°C (literature value = 110°C) was obtained (48.03 g, yield = 76%).

Monomer synthesis

The monomers were prepared by the reaction of the various dihydroxy compounds with PCF as demonstrated in Scheme 1, following literature procedures.[17–19] A typical synthetic procedure for the preparation of oxydiphenol diphenyl dicarbonate (OxDiPh DPDC) is as follows: PCF (0.17 mol, 26.3 g) in anhydrous chloroform solution was added dropwise to a stirred solution of OxDiPh (0.08 mol, 16.18 g), pyridine (0.18 mol, 14.55 g), and a catalytic amount of 4-DMAP in chloroform below 5°C. The reaction mixture was stirred for 1 h at 0–5°C and overnight at room temperature and then poured into distilled water. The precipitate formed was collected and washed several times with 10% aqueous sodium carbonate; the product was purified by crystallization from ethyl acetate and dried at 50°C in vacuo for 8 h to give white crystals with a melting point of 80°C (33.2 g, yield = 96%).

The DIGOL DPDC and BHEEBPA DPDC were synthesized by the same procedure; however, they were obtained as viscous liquids. They were purified by extraction from the aqueous solution with chloroform and washed with water and then several times with 10% aqueous sodium carbonate solution; the chloroform layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The DIGOL DPDC, which was initially obtained as a
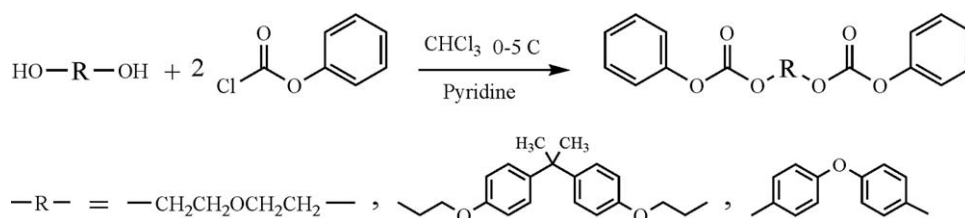
Scheme 1 Synthesis of alkylene and arylene diphenyl dicarbonate monomers containing ether groups from dihydroxy compounds.

viscous liquid, was crystallized on long standing of the melt in the storage flask on the bench to give white crystals with a melting temperature (T_m) of 44°C. The BHEEBPA DPDC remained as a liquid.

Polymer synthesis

The polymers were prepared according to the following two general procedures.

a. Aliphatic–aliphatic polycarbonates: A glass reaction tube equipped with an inert gas inlet and outlet was filled with a solid mixture composed of 10 mmol dicarbonate, 10 mmol diol, and zinc acetate (2% mol of the dicarbonate). The reaction mixture was heated and stirred in a silicone oil bath at 150°C under a stream of argon gas for 30 min. The reaction mixture was heated at 170°C for 1 h, 190°C for 1 h, and at 210°C for 2 h. The temperature was then increased to 230°C, and the pressure was gradually reduced to 1 mmHg to remove the by-produced phenol. After 1.5 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. The resulting polymer was filtered and dried at 60°C *in vacuo* for 8 h.
The other aliphatic–aliphatic polycarbonates were prepared following the same procedure: DIGOL–CHDM polycarbonate, DIGOL–BHEEBPA polycarbonate, BHEEBPA–CHDM polycarbonate, and BHEEBPA–Bu polycarbonate.

b. Aliphatic–aromatic and aromatic–aromatic polycarbonates: The same procedure was followed except that after heating at 210°C for 2 h, the reaction mixture was also heated at 230°C for 1 h, the temperature was increased to 250°C, and the pressure gradually reduced to 1 mmHg, and this condition was maintained for 1.5 h.

This procedure was followed to prepare the following aliphatic–aromatic polycarbonates: DIGOL–BPA polycarbonate, DIGOL–BiPh polycarbonate, DIGOL–HQ polycarbonate, BHEEBPA–BiPh polycarbonate, BHEEBPA–RESOL polycarbonate, OxDiPh–CHDM polycarbonate, OxDiPh–Bu polycarbonate, OxDiPh–

BHEEBPA polycarbonate, and OxDiPh–DIGOL polycarbonate; the following aromatic–aromatic polycarbonates were also prepared by this procedure: OxDiPh–BPA polycarbonate and OxDiPh–RESOL polycarbonate.

The preparation procedures for these series of polycarbonates were according to either procedure (a) or (b) depending on the aliphatic or aromatic nature of the two reacting DPDC monomers. Four series of poly(ether carbonate)s (Series A–D) were synthesized by four reaction routes:

1. Series A was prepared from the melt polycondensation of DIGOL DPDC with the various dihydroxy compounds (Scheme 2).
2. Series B was prepared from the melt polycondensation of BHEEBPA DPDC with the various dihydroxy compounds (Scheme 3).
3. Series C was prepared from the melt polycondensation of OxDiPh DPDC with the various dihydroxy compounds (Scheme 4).
4. Series D was prepared by melt polycondensation of diphenyl dicarbonate monomers with dihydroxy compound each containing ether group (Scheme 5).

Measurements

The measurement of inherent viscosity was conducted on polymer solutions (0.5 g/dL) in chloroform
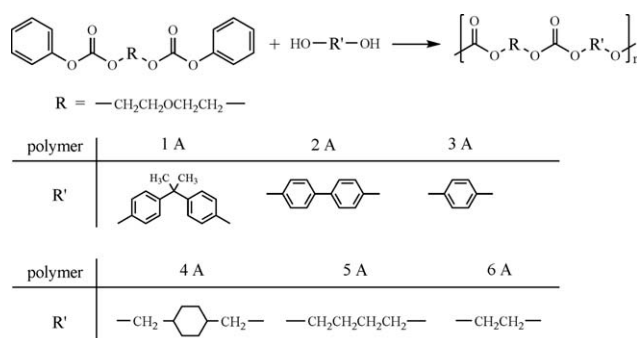
Scheme 2 Synthesis of poly(ether carbonate)s by melt polycondensation of DIGOL DPDC with dihydroxy compounds (Series A).
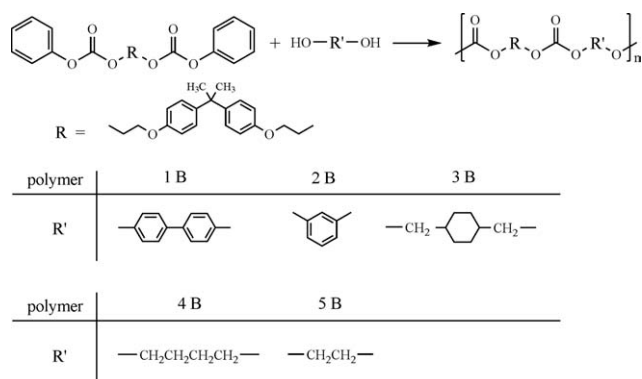
Scheme 3 Synthesis of poly(ether carbonate)s by melt polycondensation of BHEEBPA DPDC with dihydroxy compounds (Series B).

by a dilution Ubbelohde glass capillary viscometer (Rheotek, Poulten Selfe & Lee, Essex, England) in a thermostated water bath with temperature controlled at 25°C. The solutions were temperature equilibrated for ~ 10 min before viscosity was measured. The Fourier transform infrared (FTIR) spectra (from 400 to 4000 cm^{-1}) for neat films were recorded with a Thermo Nicolet 670 Nexus FTIR spectrophotometer (Madison, WI). The films were prepared by the cast solution of the purified monomer or polymer in chloroform over NaCl plates. Single-beam spectra of the samples were obtained after averaging 48 scans with a resolution of 4 cm^{-1}. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra of monomers and polymers were recorded in deuterated chloroform with a Bruker Avance DPX 300 Spectrometer (Wissembourg Cedex, France). Chemical shifts (δ) are given in ppm using tetramethylsilane as the internal standard. The glass transition temperature (T_g) of polymers were 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. The samples were first heated from ambient temperature to 150°C and maintained for 2 min before rapid quenching in liquid nitrogen to ambient temperature or subambient temperature. The thermal behaviors of the samples were probed by heating at a heating rate of 20°C/min for
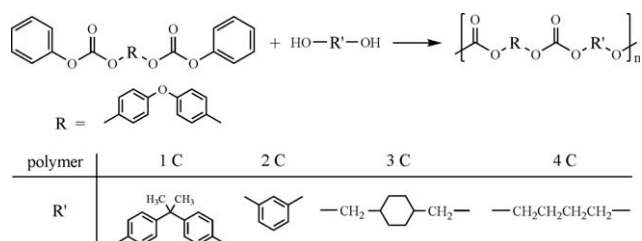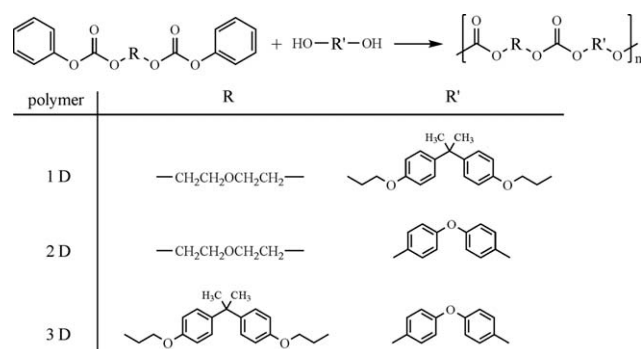
aromatic–aromatic polycarbonates and 10°C/min for aromatic–aliphatic and aliphatic–aliphatic polycarbonates. The thermal stabilities of the polymers were studied by thermogravimetric analysis (TGA) with a Netzsch STA 409 PG/PC Thermal Analyzer (Selb Bavaria). Measurements were conducted at a heating rate of 20°C/min under a dry nitrogen atmosphere purging at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

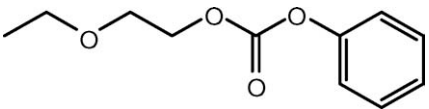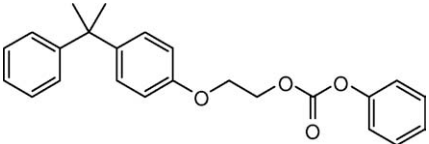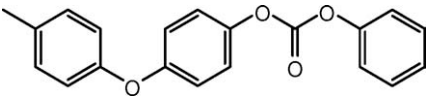### Synthesis and characterization of BHEEBPA

BHEEBPA may be conveniently prepared, in terms of yield and purity, by the reaction of BPA with EC in the presence of potassium iodide or potassium carbonate.[11,12,16,20,21] BHEEBPA was synthesized, in this work, by melt-phase interchange reaction of BPA with EC according to literature procedure.[16] The structure of the resulting dihydroxy compound was confirmed by FTIR and ^{1}H-NMR and ^{13}C-NMR spectroscopy.

The FTIR spectrum of BHEEBPA showed a strong and broad absorption band at 3356 cm^{-1} due to the stretching vibration of the alcoholic group and strong bands at 1180 and at 1248 cm^{-1} due to the stretching vibration of C—O—C. These IR data are conformed to the reported literature.[11,16] The ^{1}H-NMR spectrum of BHEEBPA showed a singlet peak at $\delta = 2.54$ ppm for the proton of the hydroxyl group and two triplets at $\delta = 3.92$ and at 4.03 ppm attributed to the methylene protons next to hydroxyl group (—CH$_2$OH) and next to the ethereal oxygen atom (—OCH$_2$CH$_2$OH), respectively. The protons of the methyl groups of BPA were observed as singlet peak at $\delta = 1.67$ ppm. The signals of the aromatic protons of BPA unit were collectively observed in the range $\delta = 6.7$–7.5 ppm. In the ^{13}C-NMR spectrum of BHEEBPA, the signal for the methylene carbon atom attached to the hydroxyl group (—CH$_2$OH) was observed at $\delta = 61.5$, whereas that of the methylene carbon atom next to it, which is attached to

Scheme 4 Synthesis of poly(ether carbonate)s by melt polycondensation of OxDiPh DPDC with dihydroxy compounds (Series C).

Scheme 5 Synthesis of poly(ether ether carbonate)s by melt polycondensation of diphenyl dicarbonates and dihydroxy compounds each containing ether group (Series D).

TABLE I
Structure, Yield, and Physical Properties of Alkylene and Arylene Diphenyl Dicarbonate Monomers

Monomer	Yield (%)	T_m (°C)	ν C=O (cm⁻¹)	ν C—O—C (cm⁻¹)
	93	44	1762	1260, 1212
	91	Viscous liquid	1762	1236, 1213
	96	80	1777	1232, 1173

the ethereal oxygen atom (—OCH$_2$CH$_2$OH), was observed at δ = 69.2 ppm. Concerning the carbon signals of the BPA unit, the signal of the aliphatic quaternary carbon atom bearing the methyl groups appeared at δ = 41.8 ppm and that of the methyl carbon atoms appeared as singlet at δ = 31.1 ppm. The signal of the quaternary carbon atom of the aromatic rings linked to the aliphatic quaternary carbon appeared at δ = 144 ppm and, interestingly, that of the aromatic quaternary carbon atom attached to the oxygen of the ether appeared at δ = 156 ppm. The signals of the carbon atoms of the ring in ortho- and meta-positions to the ether group appeared in the range δ = 114–128 ppm. The proton and carbon spectra of BHEEBPA are in accordance with the reported literature.[11]
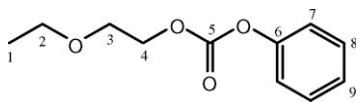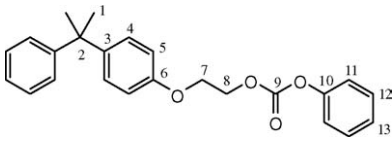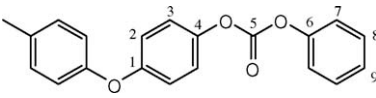
Monomer synthesis and characterization

The monomers were synthesized in solution as shown in Scheme 1.[17–19] The reaction proceeds via a colored pyridine–chloroformate adduct intermediate,[22–24] which depends on the concentration and the stability of the adduct and the concentration and nucleophilicity of the attacking dihydroxy compound.[25] The structures of the diphenyl dicarbonates, which were obtained in high yields as colorless solids or liquids, were confirmed by melting point and FTIR and NMR spectroscopies. The structures, yield, and physical properties of the monomers are presented in Table I. The BHEEBPA DPDC was obtained as a viscous liquid. The melting point of DIGOL DPDC was low due to the presence of flexible linear aliphatic alkane chain of the ether. The melting point of OxDiPh DPDC was high because it is aromatic ether. The high melting point of OxDiPh DPDC may have been due to the fact that the mole-

cule contains a number of molecular planar sections (i.e., phenylene ring of OxDiPh, the carbonate group, and the phenyl ring), which can fit very well to the corresponding planes of another molecule, and therefore, they can stack easily in their crystal lattice. The fact that BHEEBPA DPDC was a liquid may be due to the fact that the two aromatic rings of BPA in the molecule are not coplanar. The molecule also contains two ether groups. This noncoplanarity and irregularity of the various sections of the molecule makes the monomer have much less tendency to orient itself to fit well into the crystal lattice.

The FTIR spectra of diphenyl dicarbonates showed strong absorption bands due to the C=O stretching vibration of the carbonate group at 1762 and 1777 cm⁻¹. The FTIR spectra showed that the C=O stretching frequency of the carbonate group of aromatic–aromatic DPDC (e.g., OxDiPh DPDC) was higher than that of aromatic–aliphatic DPDC (e.g., BHEEBPA DPDC), which is in turn higher than that of aliphatic–aliphatic DPDC (e.g., DIGOL DPDC). The bands in the range of 1173–1260 cm⁻¹ were assigned to the asymmetric stretching of C—O—C. The IR data in Table I were typical for the carbonate group[17,26,27] and thus suggest the formation of the postulated monomers.

The ^{1}H-NMR data of monomers (Table II) showed that the signals of methylene protons attached to the carbonate group (—OCOO**C**H$_2$—) were observed at a higher δ value than those attached to the ethereal (—**C**H$_2$OCH$_2$—) oxygen atom. The ^{1}H-NMR signals of both the arylene and the phenyl moieties for all monomers were collectively observed in the same region at 6.6–7.5 ppm. Similarly, the ^{13}C-NMR spectra of monomers (Table II) showed that the signals of methylene carbon atoms attached to the carbonate group (—OCOO**C**H$_2$—) were also observed at a

TABLE II
^{1}H-NMR and ^{13}C-NMR Data for Diphenyl Dicarbonate Monomers Containing Ether Groups

Diphenyl dicarbonates		Chemical shift δ(ppm)												
		1	2	3	4	5	6	7	8	9	10	11	12	13
	^{1}H	4.40	3.80	3.80	4.40	–	–	a	a	a				
	^{13}C	68.9	67.5	67.5	68.9	154	151	121	129	126				
	^{1}H	1.65	–	–	a	a	–	4.24	4.58	–	–	a	a	a
	^{13}C	31.1	41.8	143.8	127.9	114	156.2	65.6	67.0	153.7	151	121	129.6	126.2
	^{1}H	–	a	a	–	–	–	a	a	a				
	^{13}C	155	119	121.1	146.7	152.4	151	121	129.7	126.5				

a The signals of aromatic protons appear in the range δ = 6.6–7.5 ppm.

slightly higher δ value than those attached to the ethereal oxygen atom (—CH₂OCH₂—). It was observed that the difference in the above peak positions is smaller for carbon peaks than for proton peaks. The positions of the ^{13}C-NMR signals of the BPA unit in BPA DPDC are close to the values already observed in our previous articles.[26,27] Interestingly, the ^{13}C-NMR signal of the quaternary aromatic carbon atom of the BPA rings and that of OxDiPh rings attached to the ether oxygen appeared at a higher δ value (δ = 155–156.2 ppm) than those attached to the carbonate group (δ = 151 ppm). Apparently, these signals (Table II, entry 2, carbon 6 and entry 3, carbon 1) lie in the carbonyl carbon signal region of the aliphatic carbonate group and mask with them. Furthermore, the signal of the C=O of the aromatic–aromatic carbonate was observed at a slightly lower δ value (δ = 152.4 ppm) than that of the aromatic–aliphatic carbonate (153.7 ppm), which are the correct positions for these types of carbonyl carbons.

Synthesis and characterization of poly(ether carbonate)s

The synthetic approach used in this work was based on the reaction of alkylene and arylene diphenyl dicarbonates containing ether groups with aliphatic and aromatic dihydroxy compounds. The melt polycondensation reaction proceeded by the nucleophilic displacement of the phenoxy group of the diphenyl dicarbonate with the alcoholic group of the dihydroxy compound using zinc acetate as the transesterification catalyst. This approach was shown, in the course of this work, to be a convenient method for the synthesis of poly(ether carbonate)s. Most of the polymerization reactions afforded the postulated polycarbonates; however, in only a few cases, the polymers were not formed. This assertion follows from the spectroscopic analysis of the formed polycarbonates, especially the ^{1}H-NMR and ^{13}C-NMR spectra of the alkylene and arylene groups attached to the carbonate group and the analysis of the ^{13}C-NMR spectra of the carbonyl carbon atom of the carbonate group. Four series of poly(ether carbonate)s were synthesized (Series A–D) as illustrated in Schemes 2–5.

Solution viscosity measurements

The inherent viscosities of the polymers synthesized were calculated from viscosity measurements of dilute polymer solutions (0.5 g/dL) in chloroform at 25°C. The results of viscosity, together with yield, physical data, and T_g values, are presented in Table III. The obtained polymers had inherent viscosities in the range from 0.20 to 0.56 dL/g. This implies that the polycarbonates had low to fair inherent viscosity (i.e., low to fair molecular mass).

The variation observed in inherent viscosities 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 DIGOL unit generally have the lowest inherent viscosities of all polycarbonate series. This may have been due to the aliphatic structure of the DIGOL ether chain, which is apparently more flexible than the aromatic–aliphatic ether (BHEEBPA) structure and the aromatic–aromatic ether (OxDiPh) structure. For example, the effect of monomer structure on inherent viscosity of three polycarbonates having the same dihydroxy compound linked to the DIGOL unit may be elucidated. The η$_{inh}$ values of DIGOL–CHDM, BHEEBPA–CHDM, and OxDiPh–CHDM polycarbonates are 0.22, 0.32, and 0.51 dL/g, respectively. Second, the T_g

TABLE III
Yield, Inherent Viscosity, IR Data, and T_g Values of Poly(ether carbonate)s

Polymer code	Polycarbonate	Yield (%)	ν C=O (cm^{-1})	ν C—O—C (cm^{-1})	η_{inh} (dL/g)	T_g (°C)
Series A						
1 A	DIGOL–BPA	40	1753	1241	0.20	47
2 A	DIGOL–BiPh	33	1763	1260	0.26	56
3 A	DIGOL–HQ	27	1760	1260	0.23	32
4 A	DIGOL–CHDM	21	1744	1256	0.22	7
5 A	DIGOL–Bu	–[a]	–	–	–[a]	–[a]
6 A	DIGOL–EG	–[a]	–	–	–[a]	–[a]
Series B						
1 B	BHEEBPA–BiPh	81	1762	1228	0.37	82
2 B	BHEEBPA–RESOL	18	1762	1227	0.34	62
3 B	BHEEBPA–CHDM	58	1746	1244	0.32	51
4 B	BHEEBPA–Bu	24	1749	1233	0.30	53
5 B	BHEEBPA–EG	-a	–	–	–[a]	–[a]
Series C						
1 C	OxDiPh–BPA	75	1774	1229, 1163	0.34	122
2 C	OxDiPh–RESOL	32	1778	1222	0.33	47
3 C	OxDiPh–CHDM	62	1760	1249, 1194	0.51	66
4 C	OxDiPh–Bu	51	1760	1247, 1167	0.43	34
Series D						
1 D	DIGOL–BHEEBPA	63	1749	1267, 1239	0.35	32
2 D	DIGOL–OxDiPh	54	1757	1230	0.56	66
3 D	BHEEBPA–OxDiPh	64	1760	1260, 1195	0.32	36

[a] Polymer was not formed.

values also accord largely to the above trend, and thus, Series A polymers based on DIGOL unit generally have the lowest T_g values of all polycarbonate series. The T_g values of the polycarbonates based on aliphatic–aliphatic ether (DIGOL) units are lower than those based on aromatic–aliphatic ether (BHEEBPA) units, which are in turn lower than those based on aromatic–aromatic ether (OxDiPh) units. Thus, introducing aromatic–aliphatic or aromatic–aromatic ether structures in the place of aliphatic–aliphatic ether structures in the polymer backbone would increase the T_g values of the resulting polymers. For example, the T_g values of DIGOL–CHDM, BHEEBPA–CHDM, and OxDiPh–CHDM polycarbonates are 7, 51, and 66°C, respectively. Similarly, the effect of the monomer structure on the T_g values of the polymers with the same dihydroxy compounds follows a similar trend. For example, the T_g value of DIGOL–BPA (47°C) was lower than that of OxDiPh–BPA (122°C), and the T_g value of DIGOL–BiPh (56°C) was lower than that of BHEEBPA–BiPh (82°C). Therefore, it may be concluded that varying the structure of the polymers by varying the proportions of aromatic–aromatic and aromatic–aliphatic ether units in a polymer chain would variably raise its T_g value. Third, the occurrence of competing interchange reactions during polymerization is also another factor. The principal interchange reaction taking place and leading to polymer chain buildup 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 units are connected alternately along the entire length of the polymer chain. Apart from this reaction, a possible competing reaction is the intrachange reaction that leads to the formation and the 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. These effects would naturally influence the yield and the molecular mass of the final polymers to variable extents. For example, the yields of the various polycarbonates varied from 18 to 81%. Furthermore, in this work, it was observed that DIGOL DPDC reacting with 1,2-ethanediol did not also afford the postulated polymer most probably due to the elimination of EC.

FTIR spectroscopy

The poly(ether carbonate)s prepared were analyzed by FTIR. The IR spectra showed that the C=O stretching frequencies of aromatic–aromatic polycarbonates were higher than those of aromatic–aliphatic polymers, which is in turn higher than those of aliphatic–aliphatic polymers. The IR data (Table III), which are typical for the carbonate group, are in accordance with the data reported in literature[17,18,26,28–31] and, therefore, suggest the formation of the various poly(ether carbonate)s.

NMR spectroscopy

^{1}H-NMR spectra

The chemical structures of the various polycarbonates essentially consisted of a DIGOL and a BHEEBPA unit linked to different dihydroxy compounds by a carbonate group. In their ^{1}H-NMR data (Tables IV–VI), the polycarbonates of each series showed similar pattern of peaks for each of the ether units, except for the dihydroxy compounds attached to them. In the case of aromatic–aromatic OxDiPh polycarbonates, the proton signals of the aromatic OxDiPh unit were observed in the same region as asymmetric multiples masked with those of aromatic dihydroxy compounds (e.g., BPA and RESOL). The spectra of aromatic–aromatic polycarbonates were not generally indicative in confirming the chemical structures of these polymers. The signals of all protons were collectively observed as asymmetric multiplets in the aromatic region of the spectra.

^{13}C-NMR spectra

The ^{13}C-NMR data (Tables IV–VI) of the polycarbonates synthesized exhibit a close proximity in the core structure, derived from the monomers, but differs in the alkylene or the arylene parts of the various dihydroxy compounds. Therefore, the change in the pattern of ^{13}C-NMR spectra of polymers could be correlated with the structure of the dihydroxy compounds. With the exception of the dihydroxy compounds, the pattern of the ^{13}C-NMR spectra for the DIGOL unit, BHEEBPA unit, and OxDiPh unit, in all polycarbonates series was similar to their monomers. The positions of the aliphatic carbon signals in the spectra of all poly(ether carbonate)s containing these unit, were observed at chemical shifts close to those in the monomers.[26–28,32]

By comparing the NMR spectra and the chemical shifts of all proton and carbon peaks, it was possible to disclose the following observations:

i. The ^{1}H-NMR and ^{13}C-NMR data of the terminal methylene groups of the dihydroxy compounds attached to the carbonate group were highly indicative for the formation of the postulated polycarbonates. The attachment of the terminal methylene group to the carbonate led to a downfield shift in the positions of the signals of these terminals, which was reflected in the chemical shifts in the hydrogen spectra of the polycarbonates in the range δ = 3.92–4.22 ppm and carbon spectra in the range δ = 67.8–73.6 ppm.

ii. The disappearance and appearance of some proton and carbon peaks as well as the transformation of some 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 suggest the formation of the postulated poly(ether carbonate)s.

iii. The peaks for aliphatic methylene protons and carbons attached to carbonate group occur at higher δ values than those attached to ethereal oxygen.

iv. The ^{13}C-NMR signal of the quaternary aromatic carbon atoms of the aromatic rings of BHEEBPA unit and those of OxDiPh unit attached to the ether oxygen appeared in the range δ = 155–156.2 ppm. Apparently, the positions of these signals lie in the carbonyl carbon signal region of the aliphatic carbonate group and interfere with it. These signals, however, make no problem as they are distinguished by their different form displayed in the spectrum. The C=O peak is normally displayed as three equally spaced subpeaks, whereas the peak of the aromatic quaternary carbon is displayed as an overlapped multiplet of peaks (Fig. 1, Spectrum 2).

v. Within the C=O peak region, the ^{13}C-NMR signal of the carbonyl carbon of the carbonate group appears at slightly variable positions depending on the chemical structure of the units attached to it. The spectra showed that this signal occurred at about δ = 152 ppm for aromatic–aromatic polycarbonates, at about 153.7 ppm for aromatic–aliphatic polycarbonates, and at about 155 ppm for aliphatic–aliphatic polycarbonates.

A further spectral evidence for the existence of structural variations within the polymer backbone that affected the polymer properties was also observed. The ^{13}C-NMR signal of the C=O group appeared as a set of three small peaks from 152 to 156 ppm instead of one for the perfectly alternating sequence of monomer residues. During polymerization, the already formed polycarbonate chains may also undergo polymer–polymer or polymer–monomer interchange reactions causing molar mass alterations. The reaction may involve two chain 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 within the polymer chain and would ultimately lead to statistical molecular mass distribution. In this work, the occurrence of these randomizing reactions was confirmed by the analysis of ^{13}C-NMR signal of the carbonyl carbon of the carbonate group (Fig. 1).

For example, the ^{13}C-NMR spectrum of the aromatic–aliphatic DIGOL–BPA polycarbonate displayed

TABLE IV
^{1}H-NMR and ^{13}C-NMR Data for Poly(ether carbonate)s Based on DIGOL Unit (Series A)

Polymer Code	Polycarbonate structure		Chemical shift δ(ppm)												
			1	2	3	4	5	6	7	8	9	10	11	12	13
1 A		^{1}H	4.33	4.33	3.75	3.75	4.33	–	–	a	a	–	–	1.64	
		^{13}C	68.9	68.9	67.0	67.0	68.9	153.8	149	120.5	128	148.2	42.6	31.0	
2 A		^{1}H	4.35	4.35	3.76	3.76	4.35	–	–	a	a	–	–		
		^{13}C	69.0	69.0	67.6	67.6	69.0	153.7	150.6	121.5	128.2	138.2	138.2		
3 A		^{1}H	4.28	4.28	3.74	3.74	4.28	–	–	a	a	–			
		^{13}C	69.0	69.0	67.1	67.1	69.0	153.5	148.6	122	122	148.6			
4 A		^{1}H	4.25	4.25	3.69	3.69	4.25	–	3.92	1.81	1–1.7	1–1.7	1.81	3.92	
		^{13}C	68.9	68.9	66.9	66.9	68.9	155.3	72.9	37.0	25.1, 28.6	25.1, 28.6	37.0	72.9	

a The signals of aromatic protons of BPA unit appear in the range δ = 6.7–7.6 ppm.

TABLE V
¹H-NMR and ¹³C-NMR Data for Poly(ether carbonate)s Based on BHEEBPA Unit (Series B)

Polymer code	Polymer structure			1	2	3	4	5	6	7	8	9	10	11	12	13
													Chemical shifts δ (ppm)			
1 B		¹H		1.55	–	–	a	a	–	4.18	4.51	–	–	a	a	–
		¹³C		31.1	41.8	143.7	128	114	156.2	65.6	67.0	153.7	150	121.3	128.3	138.3
2 B		¹H		1.59	–	–	a	a	–	4.18	4.50	–	–	a	a	a
		¹³C		31.1	41.8	143.7	128	114.4	156.2	65.6	66.4	153.2	151.4	120.3	130	114.4
3 B		¹H		1.6	–	–	a	a	–	4.14	4.45	–	3.94	1.82	1–1.6	1–1.6
		¹³C		31.1	41.8	143.7	127.8	114	156.2	65.6	66.3	155.3	73.0	37.0	28.6	28.6
4 B		¹H		1.59	–	–	a	a	–	4.14	4.46	–	4.21	1.82		
		¹³C		31.1	41.8	143.7	127.8	115	156.2	65.6	66.3	155.1	67.8	25.2		

ª The signals of aromatic protons of BPA unit appear in the range δ = 6.7-7.6 ppm.

TABLE VI
^{1}H-NMR and ^{13}C-NMR Data for Poly(ether carbonate)s Based on OxDiPh Unit (Series C)

Polymer code	Polycarbonate structure		Chemical shifts δ (ppm)										
			1	2	3	4	5	6	7	8	9	10	11
1 C		^{1}H	–	a	a	–	–	–	a	a	–	–	1.66
		^{13}C	155	119.7	122.3	146.6	152.3	149	120.4	128	148.3	42.6	31.0
2 C		^{1}H	–	a	a	–	–	–	a	a	–	a	
		^{13}C	155	119.8	122.3	146.6	152.4	151.2	118	130	151.2	114	
3 C		^{1}H	–	a	a	–	–	4.06	1.86	0.9–1.8	0.9–1.8	1.86	4.06
		^{13}C	154.8	119.6	122.4	146.7	154	73.6	37	28.5	28.5	37	72.8
4 C		^{1}H	–	a	a	–	–	4.22	1.82	1.82	4.22	–	
		^{13}C	155.1	119.7	122.4	146.7	153.9	67.8	25.2	25.2	67.8	153.9	

^{a} The signals of aromatic protons of BPA unit appear in the range δ = 6.7–7.6 ppm.
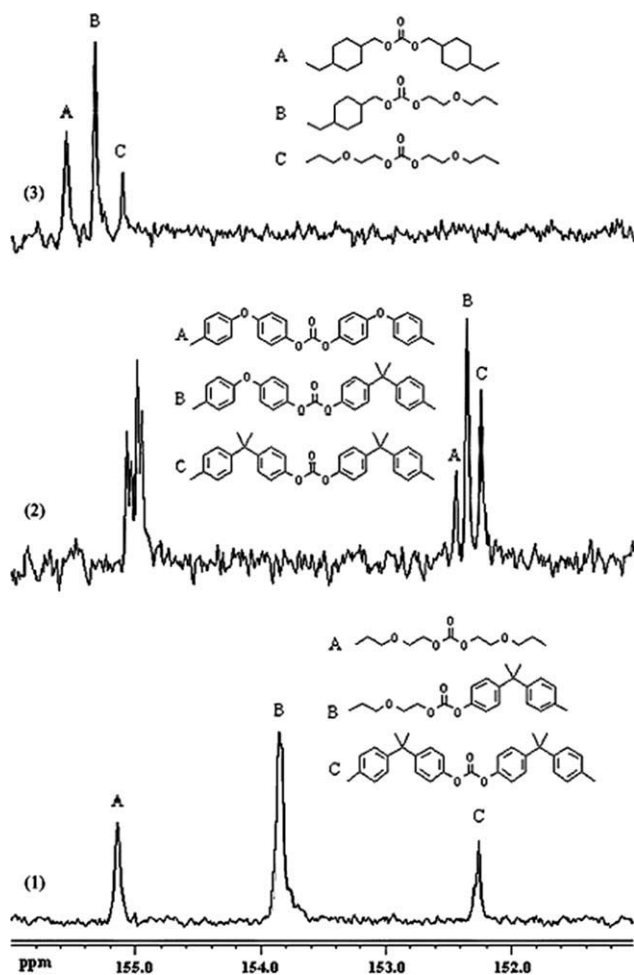
Figure 1 ^{13}C-NMR signals of C=O observed in the spectra of selected poly(ether carbonate)s.

three close peaks for the C=O of the carbonate group (Fig. 1, Spectrum 1). The positions of these peaks are dependent on the aromatic and aliphatic nature of the groups attached to the carbonate group. These peaks may be accounted for according to Figure 1.[26,27] Peak B in Spectrum 1 represents the alternate sequence of monomer residues in the polymer backbone. This peak should be due to the sequence resulting from the direct reaction of the BPA with DIGOL DPDC monomers. The occurrence of the random sequences A and C may have been due to other interchange reactions such as elimination of EC from polymer chains and to polymer–polymer reactions. These three peaks proved that the backbone of a polycarbonate molecule synthesized by interchange reactions possessed a partial random sequence of units in which all of these sequences coexist.

Similar patterns of peaks were also observed in the ^{13}C-NMR spectra of other poly(ether carbonates). For example, the signal of the C=O group in the aromatic–aromatic OxDiPh–BPA polycarbonate in Spectrum 2 at about 152.2 ppm was split into three very close signals within the aromatic region. Appa-

rently, signal C in Spectrum 2 is the same as signal C in Spectrum 1, and therefore, the three aromatic signals were explained as depicted in Spectrum 2 of Figure 1. In addition, another set of overlapping signals was also observed in the aliphatic region of Spectrum 2; this set of signals should not be due to a carbonyl carbon of an aliphatic group because such groups are not present in the fully aromatic BPA–OxDiPh polycarbonate. It was attributed to the already mentioned (Point iv) quaternary carbon atom(s) of the aromatic rings of OxDiPh units attached to the ether group (e.g., Table II, entry 3, peak 1). The signal has a different form from that observed for aromatic–aromatic C=O peak splitting. Furthermore, another similar pattern of peak splitting was also observed for the C=O of the aliphatic–aliphatic DIGOL–CHDM polycarbonate. To explain these peaks, poly(CHDM carbonate) homopolymer was prepared and its ^{13}C-NMR spectrum was recorded. The position of the C=O peak, which appeared as a single line, was observed in the spectrum at 155.52 ppm. The peaks were, therefore, accounted for as in Spectrum 3 of Figure 1. In fact, this interpretation should be correct, because Peak A of Spectrum 1 should be the same as Peak C of Spectrum 3. These comparisons imply that our interpretation of the pattern of signals should be correct.

Thermal properties

The thermal properties of poly(ether carbonate)s were also investigated with DSC and TGA. The T_g values of the polycarbonates (Table III) were in the range 7–122°C. The higher T_g values of aromatic–aromatic polycarbonates may have been due to the stiffening effect of the aromatic moieties, which restricted the movement of polymer chain segments. The lower T_g values of aromatic–aliphatic or aliphatic–aliphatic polycarbonates than aromatic–aromatic polycarbonates may have been due to the imparted flexibility effects of the aliphatic moieties. In particular, the presence of aliphatic moieties containing ether linkages in the polymer backbone imparted extra flexibility to polymer segments to move under the effect of temperature. This ease of motion is reflected in the extra lower T_g values of poly(ether ether carbonate)s of Series D than those of Series A, B, or C.

The thermal stability of the poly(ether carbonate)s was investigated by TGA under dry nitrogen. Table VII summarizes the initial thermal decomposition (onset) temperature T_d^i, $T_d^{5\%}$, $T_d^{10\%}$, and $T_d^{50\%}$ decomposition temperatures, which correspond to the temperatures at which 1, 5, 10, and 50% loss of mass of poly(ether carbonate) occurred, respectively. The table also shows the residual mass percent remaining after heating the polycarbonates to 500°C.

TABLE VII
Thermal Stability Data of Poly(ether carbonate)s

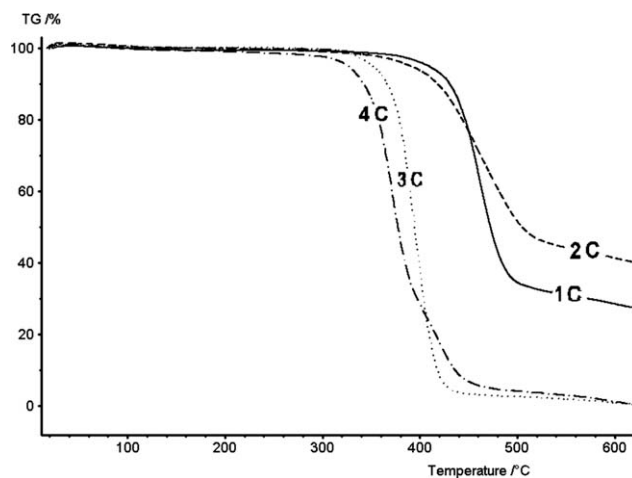| Polymer	T_d^i	$T_d^{5\%}$	$T_d^{10\%}$	$T_d^{50\%}$	Residual mass % at 500°C
1 A	327	360	374	407	13.1
2 A	328	358	372	405	18.9
3 A	285	343	358	396	13.4
4 A	227	342	362	393	6.5
5 A	–[a]	–	–	–	–
6 A	–[a]	–	–	–	–
1 B	330	376	391	427	16.2
2 B	357	385	397	428	19.5
3 B	339	361	373	409	11.1
4 B	299	344	362	400	20.4
5 B	–[a]	–	–	–	–
1 C	315	409	431	473	34.4
2 C	295	390	418	505	51.7
3 C	320	351	367	395	2.5
4 C	196	326	342	378	4.0
1 D	272	354	373	410	7.5
2 D	348	378	394	441	21.0
3 D	315	346	360	397	17.9

[a] Polymer was not formed.

Figure 2 TGA thermograms of poly(ether carbonate)s (Series C). TG% is the mass percentage of the polymer sample remaining after heating the polymer to a certain temperature.

The data in Table VII show that aromatic–aromatic poly(ether carbonate)s had higher thermal decomposition temperatures (T_d) than aromatic–aliphatic poly(ether carbonate)s, which are in turn higher than aliphatic–aliphatic poly(ether carbonate)s. The data also indicate that aromatic–aromatic polymers have higher residual mass percentages at 500°C. The thermograms of aromatic–aromatic poly(ether carbonate)s display typical one-stage characteristics with a relatively fast mass loss occurring at temperatures higher than those of aromatic–aliphatic and aliphatic–aliphatic polycarbonates. The fast mass losses may have been due to further condensation of polymer chains,[33] decarboxylation of carbonate groups, and elimination of cyclic aliphatic carbonates.[30,34–37] The collective TGA thermogram of

poly(ether carbonate)s synthesized in Series C is presented in Figure 2.

To expand the discussion of the thermal properties of poly(ether carbonate)s, it may be useful to compare their T_g values with those of the corresponding polycarbonates to elucidate the effect of the ether group on T_g. The T_g values of poly(ether carbonate)s prepared in this work were compared with those of polycarbonates prepared in our previous works. The results are presented in Table VIII. In this table, BPA-containing polycarbonates were compared with OxDiPh-containing poly(ether carbonate)s, and the alkylene moieties of dihydroxy compound containing ether group were compared with the alkylene moieties that do not contain ether group. Apparently, the T_g values indicated that the effect of the ether group was generally to lower the T_g values of poly(ether carbonate)s below those of the corresponding polycarbonates. In some cases,

TABLE VIII
Comparison of T_g Values of Poly(ether carbonate)s to Polycarbonates

Serial	Poly (ether carbonate)	T_g (°C)	Polycarbonate[a]	T_g (°C)
1	OxDiPh–BPA	122	BPA–BPA[b]	129.1
2	OxDiPh–Bu	34	BPA–Bu[b]	32.3, 49.2
3	OxDiPh–DIGOL	66	BPA–DIGOL[b]	32.6, 60.9
4	OxDiPh–RESOL	47	BPA–RESOL[b]	117.7, 112.6
5	OxDiPh–Bu	34	BPA–Bu[c]	56.5
6	DIGOL–BPA	47	BPA–Pe[c]	49.5
7	OxDiPh–RESOL	47	BPA–RESOL[c]	83.1
8	OxDiPh–CHDM	66	CHDM–BPA[c]	90.4

[a] The T_g values were taken from our previous works (Refs. 26 and 27).
[b] Prepared by interchange reactions of diphenyl dicarbonates with dihydroxy compounds.
[c] Prepared by interchange reactions of diphenyl dicarbonates with diacetate compounds.

the T_g values of poly(ether carbonate)s were comparable to those of polycarbonates; however, the T_g lowering observed must have been, at least in part, due to the presence of the ether group in the monomers which is known for imparting flexibility. The difference in the reported T_g values may have also been affected by other factors such as the experimental conditions used and the nature of the polymerization reaction conducted. For example, the reaction of alkylene and arylene diphenyl dicarbonates with dihydroxy compounds was not always conducted at the same temperature, and some polycarbonates have been prepared by the reaction of alkylene and arylene diphenyl dicarbonates with alkylene and arylene diacetates. These differences would produce polycarbonates with variable chain length and thus slightly different T_g values.

CONCLUSIONS

In this study, a new method of synthesis of poly (ether carbonate)s based on melt-phase interchange reactions of dihydroxy compounds with alkylene and arylene diphenyl dicarbonates containing ether linkages was developed. The potential of this method was demonstrated by the successful synthesis of four series of poly(ether carbonate)s containing aromatic and aliphatic ether groups. The formed polymers consist of chains in which the alkylene and the arylene moieties are partially randomized about the carbonate function, and therefore, aliphatic–aliphatic, aromatic–aliphatic, and aromatic–aromatic carbonate groups coexist in the polymers backbone. The polymers obtained had low to fair inherent viscosities; however, they generally had low to fair molecular masses. The prepared polycarbonates have good thermal stability and widely varying T_g and, thus, may fit for a wide range of application. The variation in T_g values signifies the effect of variations in the structure of the polymers. Using this approach, it was possible to provide a flexible method of synthesis of polycarbonates containing ether groups whose properties could be varied by varying the structure of the alkylene or arylene unit of the monomer and the dihydroxy compound. This approach is flexible in the sense that it may permit reaction of dihydroxy compounds with diphenyl dicarbonates containing other organic groups and thus would allow the synthesis of polycarbonates containing those groups.

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