# A New, Nonphosgene Route to Poly(bisphenol A Carbonate) by Melt-Phase Interchange Reactions of Alkylene Diphenyl Dicarbonates with Bisphenol A

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**ABSTRACT:** This article describes a new, nonphosgene method for the synthesis of poly(bisphenol A carbonate) (PC). The method involves three steps: the reaction of an aliphatic diol with phenyl chloroformate to form an alkylene diphenyl dicarbonate, the reaction of the alkylene diphenyl dicarbonate with bisphenol A to produce an aromatic–aliphatic polycarbonate, and the thermal treatment of the polycarbonate at 180–210°C under a stream of nitrogen with Ti(OBu)$_4$ to give PC and a cyclic alkylene carbonate. The method furnished low to moderate molecular masses of PC upon the complete elimination of the aliphatic moieties. The approach may be considered a new method, based on polycarbonate thermochemical degradation, for the synthesis of cyclic aliphatic carbonates. The obtained polymers were characterized by intrinsic viscosity and IR, $^1$H-NMR, and $^{13}$C-NMR spectroscopy. The thermal treatment step was conducted in a glass reaction tube at 180–210°C under a stream of nitrogen, and the reaction was completed by heating to 250°C. In the thermal treatment step, semisolid effluents composed of cyclic alkylene carbonates were formed and subsequently eliminated from the reaction mixture. Heating to 250°C under nitrogen or under a dynamic vacuum furnished the pure aromatic PC residue. This intrachange reaction provides a flexible method for the synthesis of polycarbonates with alkylene diols containing two or three methylene groups, from which the pure PC homopolymer can be prepared. The potential of this approach was demonstrated by the successful synthesis of PC homopolymer from five different polycarbonates with a bisphenol A unit linked to 1,2-propylene, 1,3-propylene, 2-methyl-1,3-propylene, 2,2-dimethyl-1,3-propylene, and 1,3-butylene as the alkane chains. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2278–2292, 2008

**Key words:** linear; melt; polycarbonates; polycondensation; synthesis

## INTRODUCTION

Polycarbonates are a class of thermoplastics that offer excellent physical and chemical properties and have the potential for wide application. Poly(bisphenol A carbonate) (PC) is one of the most widely used engineering thermoplastics because of its excellent properties, including a high impact strength, heat resistance, flame retardancy, dimensional stability, high optical transparency, and outstanding toughness.[1] The industrial processes used for PC manufacturing include an interfacial process that uses phosgene and a phase-transfer catalyst, a melt-phase interchange reaction with diphenyl carbonate (DPC) and 4,4′-isopropylidene diphenol [bisphenol A (BPA)] as starting materials, and a solution process that involves phosgene and BPA in dichlorome-

thane.[1–4] Each process has its own advantages and disadvantages; the first and the third processes use phosgene, which is known for its high toxicity, and dichloromethane is suspected to be a carcinogen and a source of chlorine in the production of dioxin.[5] Phosgene is also a corrosive and expensive substance, and the method produces wasted sodium chloride contaminated with organic substances.[6] Because there is increasing pressure to avoid the use of chlorinated organic solvents in the chemical industry, the search for a safer and an environmentally benign processing route to PC that does not involve phosgene and chlorinated solvents is required.[5,7,8]

The second process uses DPC, prepared initially from phosgene and phenol,[2,9,10] as a carbonate-providing compound for BPA transesterification. To avoid the use of DPC generated from phosgene, the direct synthesis of DPC from phenol and carbon dioxide has been given considerable attention.[11–18] Nonphosgene methods of preparing DPC to overcome the drawbacks have been reported, and the subject has been reviewed.[3,19–21]

The synthesis of PC via a melt-phase process based on BPA and the readily available dimethyl carbonate (DMC) was investigated as a desirable alternative route. DMC is industrially produced from methanol and carbon monoxide with copper catalysts,[3,20–22] but the use of DMC to prepare DPC by the interchange reaction of phenol with DMC is slow and unfavorable from the equilibrium and thermodynamic viewpoints.[21,23] The other reason why high-molecular-mass PCs are not attained is that DMC or diethyl carbonate evaporates in vacuo and at high temperatures from the reaction mixture parallel with the byproduct (methanol) before high-molecular-mass PC is obtained.[5] Another method, which is analogous to transesterification with BPA diacetate and DMC, was also reported.[3] The process has not been commercialized, however, because of the problem of recycling methyl acetate back to BPA diacetate.[3]

Many researchers have considered the self-poly-condensation of BPA dimethyl dicarbonate to PC, but the occurrence, in the bulk of the reaction, of BPA mono(methyl carbonate), which bears a terminal hydroxyl group, tends to give low-molecular-mass PC.[24] Furthermore, it has been observed that the synthesis of BPA dimethyl dicarbonate from BPA and DMC is slow at atmospheric pressure, and the yield is not high.[25] Even if the process is conducted under pressure, the reaction remains slow because the continual addition of DMC and the evaporation of the starting material happens simultaneously with the removal of the byproduct (methanol).[24] In an improvement to this process,[5] a binary catalyst system composed of distanoxane, (Bu$_2$SnCl)$_2$O, and 4-N,N-dimethylaminopyridine was used to promote the slow interchange reaction of BPA with DMC and remove the byproduced methanol with 4A molecular sieves.[26] The subsequent melt polymerization of the BPA dimethyl dicarbonate intermediate for 120 h gave a final polymer with a relatively high number-average molecular mass of 20,000.[5] Although a high-molar-mass PC was obtained, a very long reaction time was required.

In most of the previous studies, researchers have considered varying the carbonate-providing compound with the aim of synthesizing BPA dimethyl dicarbonate and its subsequent self-polycondensation to PC. The disadvantage of these procedures is the difficulty of synthesizing high-molecular-mass PC in a reasonable period of time because of thermodynamically unfavorable reaction and because DMC is more volatile than BPA and, therefore, eventually evaporates under the experimental vacuum and high temperatures necessary to remove the low-molecular-mass byproduct before the high-molecular-mass PC is attained. To overcome the problem, a less volatile carbonate-providing compound was used in this study to lessen the thermodynamic unfavorability of the interchange reaction. This method is based on the use of a DPC group instead of DMC in the carbonate-providing compound. This compound, which has a high molecular mass, should be less volatile than DMC. Therefore, the reaction that may be suggested is the interchange reaction between BPA and alkylene diphenyl dicarbonates as a carbonate-providing compound, such as ethylene glycol diphenyl dicarbonate (EG DPDC), 1,3-propane diol diphenyl dicarbonate (Pr-1,3-D DPDC), or 1,4-butane diol diphenyl dicarbonate (Bu-1,4-D DPDC):
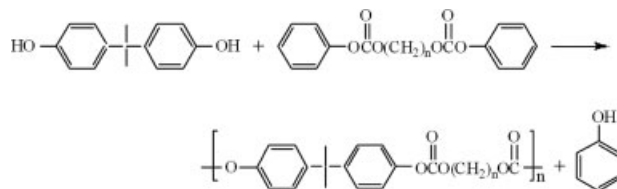


The subsequent thermal treatment of the aliphatic–aromatic polycarbonate polymer, in the presence of a proper interchange reaction catalyst, would eliminate the aliphatic moieties as cyclic carbonate and leave only the target aromatic PCs as the residue. The byproduct, phenol, even though it is less volatile than methanol, could be removed completely from the reaction mixture under the experimental vacuum and high-temperature conditions and, thus, would not cause any serious problems in the synthesis of the aromatic–aliphatic polycarbonates nor disturb the position of the equilibrium reaction. The strategy of this approach was to prepare a product beyond the target product (aromatic–aliphatic polycarbonate) and then to return back to the target product (PC). The net result of the interchange reaction leading to the formation of aromatic–aliphatic polycarbonates and the intrachange reaction leading to the elimination of the aliphatic moieties as cyclic carbonates was the introduction of the carbonyl linking group to BPA and, thus, the production of the PC homopolymer. The use of diphenyl dicarbonate derivatives of alkanes diols instead of dimethyl or diethylcarbonate should eliminate the thermodynamic unfavorability of the reaction with BPA and drastically reduce the volatility of the carbonate-group-providing compound so that it will not leave the reaction mixture at an early stage of reaction when the molecular mass of the PC is still low. With these modifications, we expected to obtain a high-molecular-mass PC. The set of reactions that we suggest in this project is presented in Scheme 1. To our knowledge, a nonphosgene process based on an interchange reaction for the preparation of alkylene diphenyl dicarbonates from alkane diols and a carbonate-providing compound has not yet been reported. Therefore, the preparation of alkylene diphenyl dicarbonate monomers may be achieved by the reaction of alkane diols with phenyl chloroformate (PCF; step 1 in Scheme 1). The preparation of the aromatic–aliphatic polycarbonates may be performed by
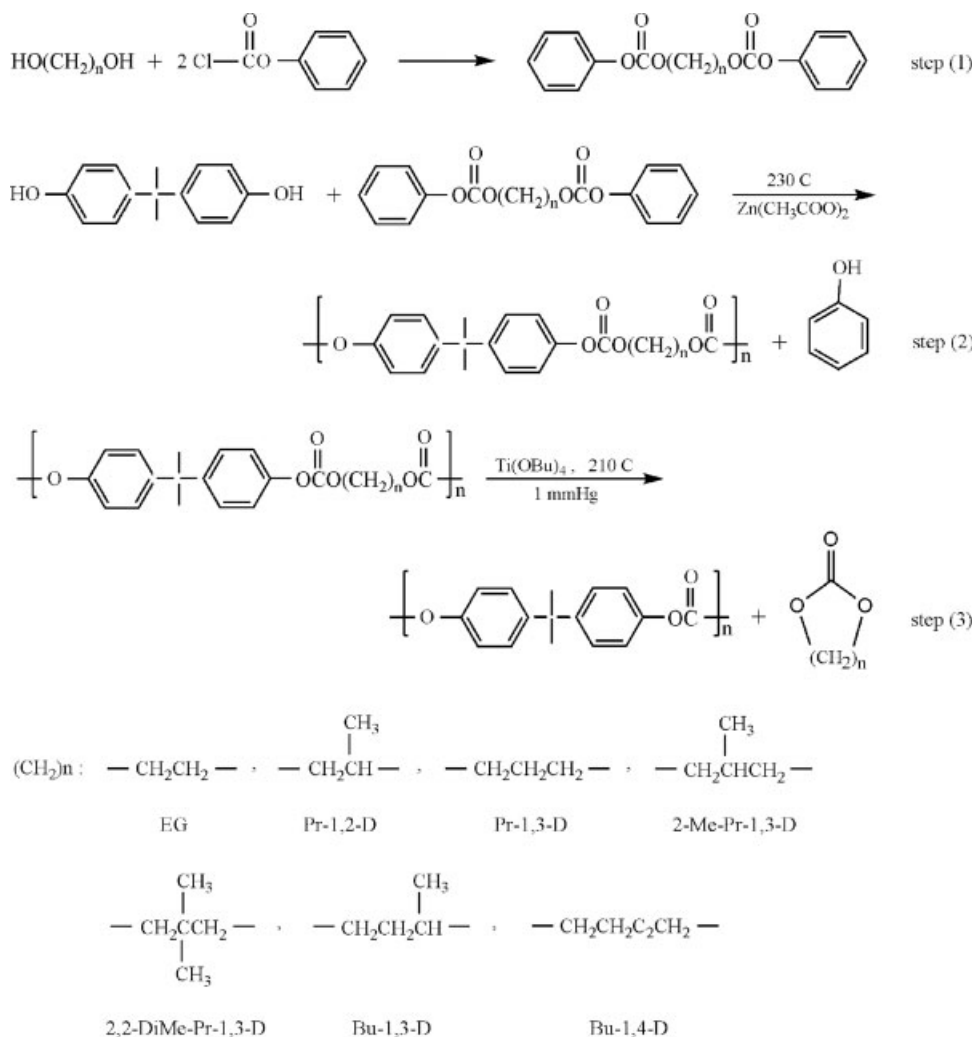
**Scheme 1** Synthesis of the PC homopolymer by the three-step reaction sequence.

the melt-phase interchange reaction between BPA and alkylene diphenyl dicarbonates (step 2 in Scheme 1). The thermal treatment of polycarbonates (step 3 in Scheme 1) may be conducted at high temperatures under a dynamic vacuum or under a stream of dry nitrogen gas in the presence of a catalyst. To our knowledge, a study of the synthesis of PC by the interchange reaction of BPA and alkane diol diphenyl dicarbonate derivatives has not yet been reported. In this article, we present the results of this study.

## EXPERIMENTAL

### Materials

The materials used were commercially available, were either analytical reagents or technical-grade reagents, and were used as received, except for zinc acetate, chloroform, and tetrahydrofuran. The chemicals were purchased from the following commercial sources: BPA, 2,2-dimethyl-1,3-propane diol (2,2-DiMe-Pr-1,3-D), and titanium (IV) butoxide were purchased from Acros (USA); PCF, ethylene glycol (EG), 1,4-butane diol (Bu-1,4-D), and zinc acetate dihydrate were purchased from Merck (Darmstadt, Germany); 1,3-propane diol (Pr-1,3-D) was purchased from Analyt (Sandycroft, UK); 1,2-propane diol (Pr-1,2-D) was purchased from Reidel-De-Haën (Seelze, Germany); 1,3-butane diol (Bu-1,3-D) was purchased from BDH (Poole, UK); and 2-methyl-1,3-propane diol (2-Me-Pr-1,3-D) was purchased from Aldrich (Steinheim, Germany). Zinc acetate was heated at 100°C in vacuo for 8 h. The dichloromethane solvent was purified by refluxing and distillation over sodium hydride. Tetrahydrofuran was dried over sodium metal and bezophenone and was then distilled.

### Monomer and polymer synthesis

#### Monomer synthesis

The various alkylene diphenyl dicarbonate monomers were synthesized by the reaction of the corresponding alkane diol with PCF (step 1 in Scheme 1),

according to a previously published procedure.[27] The preparation of the various alkylene diphenyl dicarbonates were conducted with either dichloromethane or tetrahydrofuran as the solvent. A typical procedure is described here for the synthesis of Bu-1,4-D DPDC.

PCF (0.22 mol, 34.45 g) was added dropwise over a period of 2 h to a mixture of Bu-1,4-D (0.10 mol, 9.01 g), pyridine (0.24 mol, 18.98 g), and a catalytic amount of 4-(dimethylamino)pyridine dissolved in dichloromethane (240 mL) at 0–5°C. The reaction mixture was left under stirring for 1 h at 0–5°C and overnight at room temperature and then poured into distilled water (400 mL). The precipitate formed was collected by suction filtration and washed several times with a 10% aqueous sodium carbonate solution; the product was purified by recrystallization from ethyl acetate and dried at 40°C in vacuo overnight to give white crystals (mp = 82°C, yield = 66.1 g or 91%).

The following diphenyl dicarbonates of all of the other dihydroxyl compounds were prepared by following the same procedure: ethylene glycol diphenyl dicarbonate (EG DPDC), 1,2-propane diol diphenyl dicarbonate (Pr-1,2-D DPDC), 1,3-propane diol dyphenyl dicarbonate (Pr-1,3-D DPDC), 2-methyl-1,3-propane diol diphenyl dicarbonate (2-Me-Pr-1,3-D DPDC)), 2,2-dimethyl-1,3-propane diol diphenyl dicarbonate (2,2-DiMe-Pr-1,3-D DPDC), and 1,3-butane diol diphenyl dicarbonate (Bu-1,3-D DPDC).

The diphenyl dicarbonates of Pr-1,3-D and Pr-1,2-D formed viscous liquids when the reaction mixture was poured into water. Therefore, they were obtained by extraction from the aqueous solution by chloroform and washed several times with a 10% aqueous sodium carbonate solution; the chloroform layer was dried over anhydrous sodium sulfate and evaporated.

Polymer synthesis

The polycarbonates were prepared by the following procedure: a homogeneous solid mixture composed of 10 mmol BPA, 10 mmol diphenyl dicarbonate, and anhydrous zinc acetate (2% mol of the dicarbonate) were introduced into a glass reaction tube equipped with a Claisen distiller and a nitrogen gas inlet and outlet. The reaction mixture was immersed to its half height in a silicone oil bath and heated under a stream of nitrogen gas at 150°C for 30 min. The temperature of the oil bath was increased to 170°C for 1 h, 190°C for 1 h, 210°C for 2 h, and 230°C for 1 h. The pressure was gradually reduced to 1 mmHg to remove the byproduced phenol of the polycondensation reaction. After 1.5 h, the glass reaction tube was cooled, and the formed polymer was dissolved in dichloromethane. The solution was

filtered, and the product was precipitated by dropwise addition to methanol as a nonsolvent. The obtained polymer was filtered and dried in vacuo at 60°C overnight.

The same procedure was followed for the preparation of all of the following polycarbonates: bisphenol A–ethylene glycol polycarbonate (BPA–EG), bisphenol A–1,2-propane diol polycarbonate (BPA–Pr-1,2-D), bisphenol A–1,3-propane diol polycarbonate (BPA–Pr-1,3-D), bisphenol A–2-methyl-1,3-propane diol polycarbonate (BPA–2-Me-Pr-1,3-D), bisphenol A–2,2-dimethyl-1,3-propane diol polycarbonate (BPA–2,2-DiMe-Pr-1,3-D), and bisphenol A–1,3-butane diol polycarbonate (BPA–Bu-1,3-D).

Thermal treatment of the polycarbonates

The polymer samples were subjected to thermal treatment according to the following general procedure. The aromatic aliphatic polycarbonate polymer (1.0 g) and titanium(IV) butoxide (catalyst, 2% mol, calculated on the basis of the molecular mass of the repeating unit of the polymer) were added to the glass reaction tube. The reaction mixture was heated in a silicone oil bath at 180°C under a stream of nitrogen gas for 30 min. The temperature was increased to 210°C over a period of 1 h; after 30 min, the glass reaction tube was removed from the oil bath and cooled. The formed semisolid effluents were separated by dissolution in dichloromethane, and the solution was filtered. To complete the reaction, the glass tube was returned to the oil bath, and the temperature of the reaction mixture was gradually increased over a period of 1 h to 250°C, and the pressure was reduced to 1 mmHg. After 1 h, the glass reaction tube was cooled to ambient temperature. The polymer residue remaining in the bottom of the tube was dissolved in dichloromethane. The solution was filtered, and the polymer was precipitated in methanol as a nonsolvent. The resulting polymer was dried in vacuo at 60°C overnight.

Measurements

The intrinsic viscosities of the polymer solutions at four different concentrations in chloroform were measured by a dilution Ubbelohde glass capillary viscometer (Rheotek, Poulten Selfe & Lee, Ltd., Essex, England) in a thermostated water bath that was temperature-controlled at 30 ± 0.1°C. The solutions were temperature-equilibrated for approximately 15 min before the viscosity was measured. Fourier transform infrared (FTIR) spectra (from 500 to 4000 cm$^{-1}$) of the monomers and polymers were recorded as neat films with a Thermo Nicolet 670 FTIR spectrometer (Madison, WI). The films were prepared by the cast solution of purified monomer

TABLE I
Physical Properties of the Alkylene Diphenyl Dicarbonate Monomers

| Sample | Alkylene diphenyl dicarbonate[a] | Yield (%) | IR [$v$ (cm$^{-1}$)] C=O | C—O | mp (°C) |
|---|---|---|---|---|---|
| 1 | EG | 93 | 1757 | 1257, 1209 | 94 |
| 2 | Pr-1,2-D | 92 | 1763 | 1268, 1238, 1210 | Liquid |
| 3 | Pr-1,3-D | 88 | 1759 | 1242, 1210 | 52 |
| 4 | 2-Me-Pr-1,3-D | 92 | 1762 | 1239, 1210 | Liqiud |
| 5 | 2,2-DiMe-Pr-1,3-D | 91 | 1761 | 1264, 1209 | 47 |
| 6 | Bu-1,3-D | 89 | 1760 | 1261, 1211 | 66 |
| 7 | Bu-1,4-D | 90 | 1759 | 1263, 1209 | 82 |

or polymer in chloroform over NaCl plates. The solvent was evaporated and dried in vacuo. The $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer (300 MHz; Wissemburg, Cedex, France) in deuterated chloroform. The chemical shift ($\delta$) values are given in parts per million with tetramethylsilane as an internal standard. The melting points of the alkylene diphenyl dicarbonate monomers were determined in open capillary tubes with an electrothermal MelTemp (Rochford, Essex, UK) apparatus, and they were uncorrected.

## RESULTS AND DISCUSSION

### Monomer synthesis and characterization

This study was based on the melt-phase interchange reaction of BPA with alkylene diphenyl dicarbonate to form the aromatic–aliphatic polycarbonate followed by a melt-phase intrachange reaction involving the elimination of the aliphatic moieties as cyclic alkylene carbonates and the production of the PC homopolymer. To our knowledge, a viable industrial method for the preparation of alkylene diphenyl dicarbonates from alkane diols and a carbonate-providing compound has not been previously developed. Therefore, the alkylene diphenyl dicarbonates were synthesized (step 1 in Scheme 1) in a solution of alkane diols and PCF in the presence of excess pyridine, according to previously published procedure.[27] Pyridine acted as an acid acceptor and reacted with PCF to form an ionic adduct that was more reactive than PCF.[21] The reaction proceeded via pyridine-catalyzed nucleophilic displacement of the chloride of PCF with the alcohol group of the alkane diol. The reactivity depended on the concentration and stability of the ionic adduct and the concentration and nucleophilicity of the attacking diol.[28,29] The structures of the alkylene diphenyl dicarbonates, which were obtained as white crystalline materials or slightly viscous liquids, were characterized by melting point data and IR, $^{1}$H-NMR, and $^{13}$C-NMR spectroscopy. The physical properties of the alkylene diphenyl dicarbonates of the various diols are presented in Table I.

Table I shows that high yields of the alkylene diphenyl dicarbonates were obtained. The melting point values of the alkylene diphenyl dicarbonates were in the range 47–94°C. The diphenyl dicarbonates of Pr-1,2-D and 2-Me-Pr-1,3-D were obtained as viscous liquids. The diphenyl dicarbonate of 2,2-DiMe-Pr-1,3-D, which had two methyls substituted on the alkane chain, was obtained as a solid but showed the lowest melting point value of all of the synthesized diphenyl dicarbonates. This may have been due to the effect of the methyl substituent groups on the alkane chain, which tends to hinder close packing of molecules in a crystal.

The IR spectra of the alkylene diphenyl dicarbonates showed strong absorption bands due to the stretching vibrations of the C=O of carbonate groups in the range 1757–1763 cm$^{-1}$. The range of values of the C=O stretching frequencies of all of the diphenyl dicarbonates was narrow because they were all aromatic–aliphatic diphenyl dicarbonates. The absorption bands due to the C—O stretching vibrations were observed in the region from 1239 to 1268 and at 1210 cm$^{-1}$. The absorption bands due to the alcoholic groups of the alkane diols were completely absent in the IR spectra of the alkylene diphenyl dicarbonates. On the other hand, the band due to the C=O stretching vibration of the chloroformate group of PCF, which was observed at 1787 cm$^{-1}$, was shifted to 1757 to 1763 cm$^{-1}$ in the various diphenyl dicarbonates. These IR data, which are typical for the carbonate group, conformed to the reported literature[27,30–37] and thus confirmed the formation of the various alkylene diphenyl dicarbonate monomers in this study. A typical FTIR spectrum for Bu-1,3-D DPDC is presented in Figure 1(a).

The alkylene diphenyl dicarbonates were also analyzed by NMR to elucidate their chemical structure and support their formation. The $^{1}$H-NMR spectra of the various alkylene diphenyl dicarbonates showed singlet peaks at $\delta = 4.53$, 4.30, and 4.12 ppm due to the protons of the terminal methylene groups (—OOCOCH$_2$—) attached to the carbonate group of the diphenyl dicarbonates of 1,2-ethane diol, Bu-1,4-D, and 2,2-DiMe-Pr-1,3-D, respectively. The $^{1}$H-NMR spectra showed a
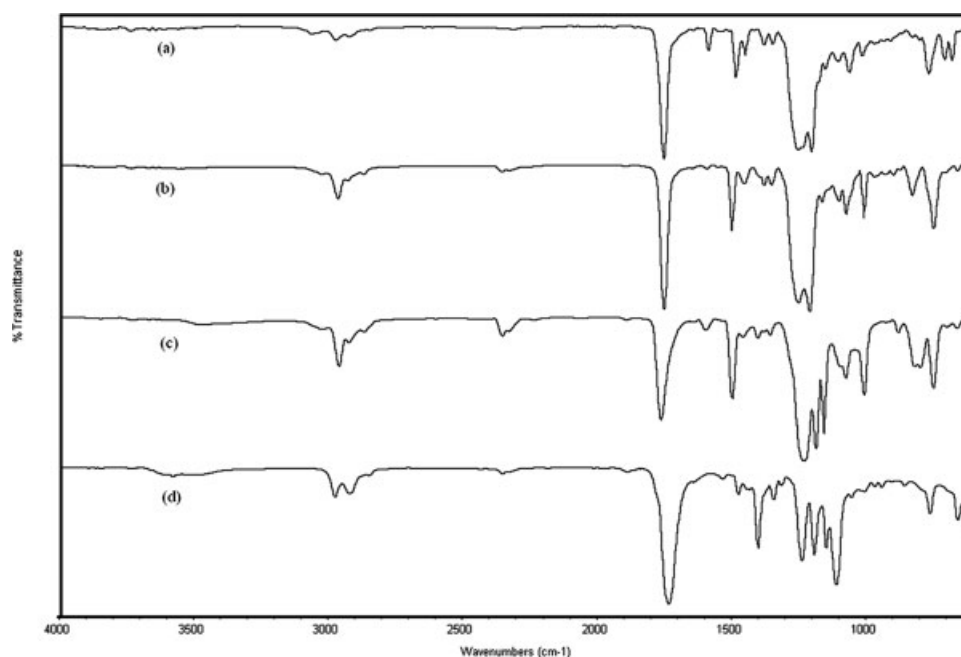
**Figure 1** IR spectra of (a) Bu-1,3-D DPDC, (b) BPA-Bu-1,3-D polycarbonate, (c) the PC homopolymer derived from BPA–Bu-1,3-D polycarbonate, and (d) Bu-1,3-D cyclic carbonate.

doublet peak centered at $\delta = 4.27$ ppm due to the terminal methylene protons of 2-Me-Pr-1,3-D. The ^{1}H-NMR spectra showed triplet peaks at $\delta = 4.40$ ppm due to the protons of the terminal methylene groups attached to the carbonate group for Pr-1,3-D. On the other hand, the ^{1}H-NMR spectra showed multiplet peaks due to the protons of the terminal methylene groups attached to the carbonate group at $\delta = 4.30$ and 4.47 ppm for the dicarbonate of Pr-1,2-D and at $\delta = 4.37$ and 4.44 ppm for the dicarbonate of Bu-1,3-D. The protons of the methylene groups next to the terminal methylene groups ($-OOCOCH_2CH_2-$) in the diphenyl dicarbonates of Pr-1,3-D, 2-Me-Pr-1,3-D, Bu-1,3-D, and Bu-1,4-D showed triplet, multiplet, and singlet peaks, respectively, at $\delta = 1.89–2.39$ ppm. The signals for the aromatic protons of the phenyl rings of the alkylene diphenyl dicarbonates were observed at $\delta = 7.1–7.4$ ppm.

Typical signal positions for the aliphatic and aromatic carbons for all of the prepared DPDC were also obtained with ^{13}C analysis. The downfield shift of the signals of the terminal methylene groups attached to the carbonate groups in both the ^{1}H and ^{13}C spectra were indicative of the formation of carbonate bonds and, thus, suggested the formation of alkylene diphenyl dicarbonate monomers.

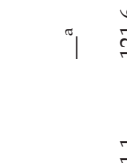In addition to these data, the ^{1}H-NMR and ^{13}C-NMR spectra of the monomers of both of BPA–Pr-1,2-D and BPA–Bu-1,3-D showed two peaks for the methyl groups attached to the carbonate function due to the conformational rotameric structures. The effect was quite evident in the ^{13}C-NMR spectra of

the monomers; each of the aromatic carbons numbered 6–8 (Table II) showed four signals in the form of two close sets of peaks. Each doublet signals (set) had an intensity equal but different from the other set, which could be explained by conformational deference. The difference in position of each set of doublets was due to different chemical environment of the two phenyl rings. For example, carbon number 6 in the Bu-1,3-D DPDC spectrum showed a low equal intensity doublet at 121.024 and 121.147 and another high equal intensity doublet at 121.194 and 121.235. This observation was due to the fact that each conformer showed two different chemical environments. Typical ^{1}H-NMR and ^{13}C-NMR spectra for Bu-1,3-D DPDC are presented in Figure 2. The ^{1}H-NMR and ^{13}C-NMR data for the alkylene diphenyl dicarbonates are presented in Table II.

## Characterization of the polycarbonates

The aromatic–aliphatic polycarbonates were prepared by the interchange reaction of alkylene diphenyl dicarbonates with BPA as the dihydroxyl compound. The reaction proceeded by nucleophilic displacement of the phenoxy group of the alkylene diphenyl dicarbonate with the hydroxyl group of BPA. The polycarbonates were prepared by the melt-phase interchange reaction (step 2 in Scheme 1) of equimolar amounts of alkylene diphenyl dicarbonate with BPA with zinc acetate as the catalyst. Because this reaction was an equilibrium reaction that was conducted at a high temperature and low

**TABLE II**
**¹H-NMR and ¹³C-NMR Data for the Alkylene Diphenyl Dicarbonates**

| Diphenyl dicarbonate | | δ (ppm)[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| (structure 1) | ¹H | 4.53 s, 2H | 4.53 s, 2H | — | — | —[a] | —[a] | —[a] | | | |
| | ¹³C | 65.9 | 65.9 | 153.6 | 151.1 | 121.1 | 129.6 | 126.3 | | | |
| (structure 2) | ¹H | 4.30, 4.47 2m, 2H | 5.19 m, 1H | 1.44 d, 3H | — | — | —[a] | —[a] | —[a] | | |
| | ¹³C | 69.6 | 72.9 | 16.2 | 153.4 | 151.1 | 121 | 129.6 | 126.3 | | |
| (structure 3) | ¹H | 4.40 t, 4H | 2.18 m, 2H | 4.40 t, 4H | — | — | —[a] | —[a] | —[a] | | |
| | ¹³C | 65.0 | 28.0 | 65.0 | 153.7 | 151.1 | 121.1 | 129.6 | 126.2 | | |
| (structure 4) | ¹H | 4.27 d, 4H | 2.39 m, 1H | 4.27 d, 4H | 1.12 d, 3H | — | — | —[a] | —[a] | —[a] | |
| | ¹³C | 69.7 | 32.7 | 69.7 | 13.5 | 153.7 | 151.2 | 121 | 129.6 | 126.2 | |
| (structure 5) | ¹H | 4.12 s, 4H | — | 4.12 s, 4H | 1.09 s, 6H | 1.09 s, 6H | — | — | —[a] | —[a] | —[a] |
| | ¹³C | 73.0 | 35.3 | 73.0 | 21.5 | 21.5 | 153.7 | 151.1 | 121.6 | 129.6 | 126.1 |
| (structure 6) | ¹H | 4.37, 4.44 2m, 2H | 2.11 m, 2H | 5.08 m, 1H | 1.43 d, 3H | — | — | —[a] | —[a] | —[a] | |
| | ¹³C | 64.9 | 34.8 | 73.0 | 20.1 | 153.5 | 151.2 | 121.2 | 129.6 | 126.2 | |
| (structure 7) | ¹H | 4.30 s, 4H | 1.89 s, 4H | 1.89 s, 4H | 4.30 s, 4H | — | — | —[a] | —[a] | —[a] | |
| | ¹³C | 68.1 | 25.2 | 25.2 | 68.1 | 153.8 | 151.1 | 121.1 | 129.6 | 126.1 | |

d = doublet; m = multiplet; p = pentet; s = singlet; t = triplet.
[a] The signals of the aromatic protons appeared in the range of δ = 7.1–7.4.
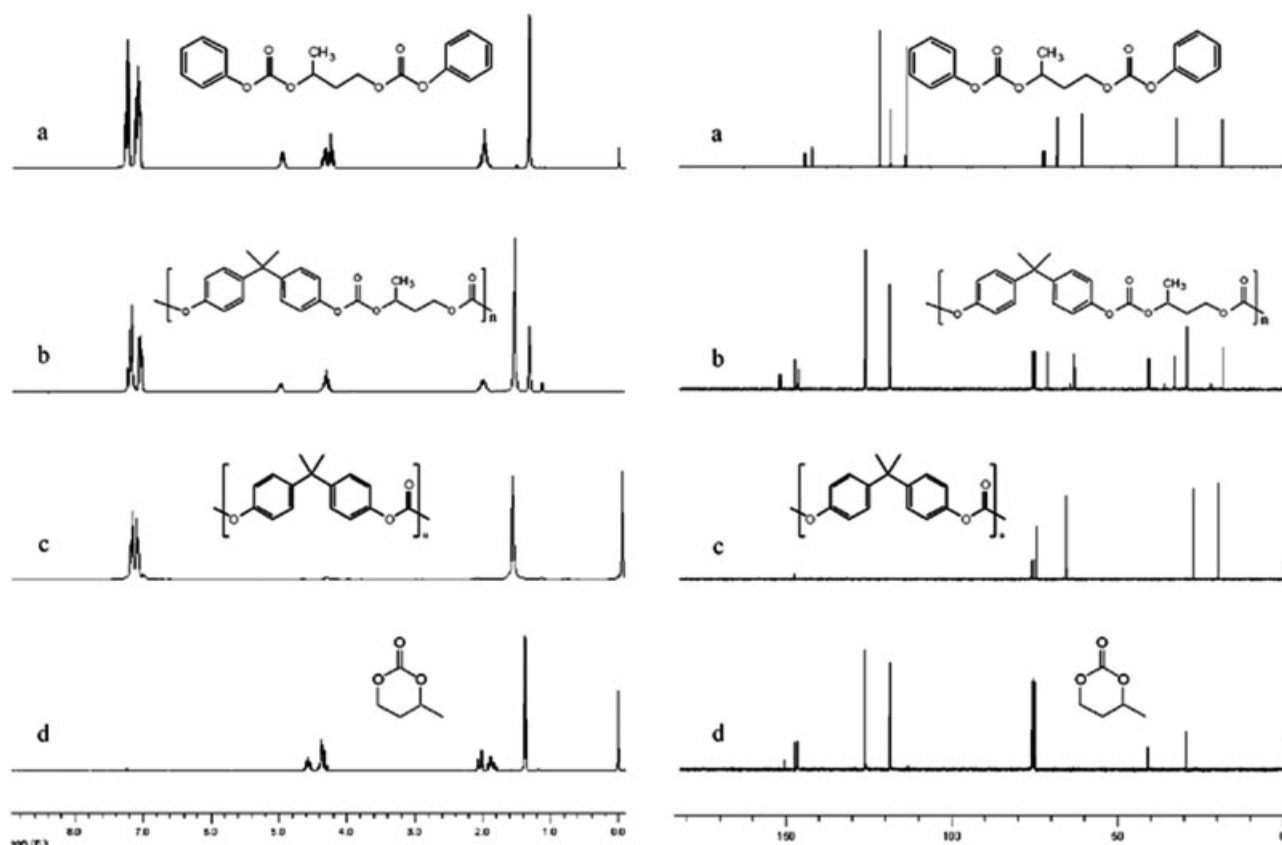
**Figure 2** $^1$H-NMR and $^{13}$C-NMR spectra for (a) (Bu-1,3-D DPDC), (b) BPA–Bu-1,3-D polycarbonate, (c) the PC homopolymer derived from BPA–Bu-1,3-D polycarbonate, and (d) Bu-1,3-D cyclic carbonate.

pressure, the by-produced phenol was completely removed, and the equilibrium reaction was driven toward the formation of the polymer.

Solution viscosity measurements

The intrinsic viscosities of the aromatic–aliphatic polycarbonates were obtained from viscosity measurements of the dilute polymer solutions at four different concentrations in chloroform at 30°C. The polycarbonates had intrinsic viscosities in the range 0.14–0.25 dL/g. Thus, polymers with low to moderate

molecular masses were obtained. Table III summarizes the intrinsic viscosities and the physical properties of the various synthesized polycarbonates.

The results show that the synthesized polycarbonates generally had low intrinsic viscosities. This may have been because of other competing reactions. A possible competing reaction that may have occurred in the reaction mixture in such short alkane chains was the early occurrence of an intrachange reaction that led to the formation and subsequent elimination of the alkylene moieties as cyclic carbonates from the alkylene diphenyl dicarbonate monomers or

**TABLE III**
**Physical Properties of the Polycarbonates as a Function of the Structure of the Dihydroxyl Compound**

| Sample | Polycarbonate | Yield (%)[a] | IR [$v$ (cm$^{-1}$)] | | Intrinsic viscosity (dL/g) |
| | | | C=O | C—O | |
|---|---|---|---|---|---|
| 1 | BPA–EG | 13 | 1762 | 1183, 1257 | 0.14 |
| 2 | BPA–Pr-1,2-D | 34 | 1763 | 1217, 1267 | 0.19 |
| 3 | BPA–Pr-1,3-D | 42 | 1760 | 1214, 1246 | 0.20 |
| 4 | BPA–2-Me-Pr-1,3-D | 41 | 1761 | 1215, 1248 | 0.22 |
| 5 | BPA–2,2-diMe-Pr-1,3-D | 44 | 1761 | 1212, 1264 | 0.23 |
| 6 | BPA–Bu-1,3-D | 49 | 1759 | 1215, 1256 | 0.21 |
| 7 | BPA–Bu-1,4-D | 53 | 1760 | 1215, 1254 | 0.25 |

[a] Based on the amount of the methanol-insoluble polymer.

from the preformed polymer chains. For example, in the case of the reaction of BPA with EG DPDC or with Pr-1,3-D DPDC, the formation and elimination of cyclic ethylene carbonate and cyclic trimethylene carbonate was quite probable under the experimental conditions used for polycarbonate synthesis. This competing reaction would have disturbed the stoichiometric balance of the monomers in the reaction melt and furnished a lower molecular mass polymer. This imbalance can be represented by the possible occurrence of short sequences of repetitive similar monomer units within the polycarbonate chain in addition to the alternating aromatic aliphatic unit sequence of the polymer. Both effects would have resulted in the formation of polycarbonates with lower molecular masses and, thus, lower viscosities.

The structures of the dicarbonate monomers used were specifically selected because they would permit both the reaction with BPA to form the aromatic–aliphatic polycarbonate (according to step 2 in Scheme 1) and cyclization (according to step 3) to form and subsequently eliminate from the reaction mixture cyclic alkylene carbonates.

When one considers that the elimination of cyclic carbonates might occur in step 2 in Scheme 1, the formation of PC in step 3 requires optimum reaction conditions that would provide both a good balance between the polycondensation reaction in step 2 and the elimination of cyclic carbonates in step 3. In this study, we found that when we used heating at 230°C, worked in vacuo, and used titanium tetrabutoxide catalyst, all of the alkylene diphenyl dicarbonates afforded the expected polycarbonates but with widely varying yields and intrinsic viscosities. This highlighted the potential of this reaction for the synthesis of polycarbonates. It seems that these experimental conditions were optimum and, thus, provided a proper procedure that permitted the formation of the desired aromatic–aliphatic polycarbonates.

The yields obtained for the polycarbonate were generally fair (Table III). The yield of BPA–EG polycarbonate was exceptionally low. This result implies that the competing reaction in this case was probably very important. This may be explained when one considers that the distance between the two carbonate functions was short (the carbonate groups were separated by only two methylene units). The oxygen atom of the one carbonate function and the carbonyl carbon of the other carbonate function, for both carbonate groups in the conformation depicted in Figure 3, were practically equal to the actual carbon–carbon single bond length. Therefore, the short distance optimally made the cyclization intrachange reaction more highly promoted than the interchange reaction that led to BPA–EG polycarbonate formation (step 2 in Scheme 1) and thus gave a low yield of BPA–EG polycarbonate. The conformation
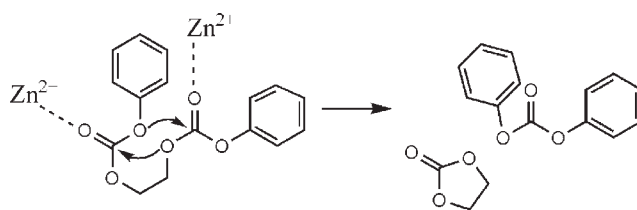


**Figure 3** Mechanism of the intrachange cyclization reaction in EG DPDC or BPA–EG polycarbonate.

required for cyclization could be easily attained by the rotation of only a few carbon–carbon or carbon–oxygen single bonds. Obviously, the required energy was quite available in the high-temperature conditions of the polymerization reaction. Furthermore, the attack by the hydroxyl group of BPA onto the carbonate function of EG DPDC, although more reactive, was less productive than the reaction of the closer atoms involved in the cyclization process because this group was present at a larger distance from the carbonate function. In addition, this side reaction was also promoted because the five-membered ring of the product obtained from the elimination reaction (ethylene carbonate) was a stable molecule. The ease of attainment of the conformation and the distance at which the reacting atoms were posed made the intrachange reaction that led to the cyclization reaction more highly probable than the interchange reaction that led to BPA–EG polycarbonate chain buildup (step 2 in Scheme 1) and, thus, limited polycarbonate formation in step 2 of the scheme.

The higher yield of the polycarbonate in case of Pr-1,2-D compared to that of EG DPDC may have been due to the hindering effect of the methyl group, which might have rendered the cyclization reaction slightly more difficult. The higher yields of the polycarbonates in the Pr-1,3-D cases compared to Pr-1,2-D may have been due to a longer carbon chain between the carbonate functions. This possibly improved the intrachange reaction at the final stage (step 3) and delayed the cyclization reaction in step 2. Again, the higher yield of the polycarbonates in the case of Bu-1,4-D may be attributed to a longer carbon chain distance between the carbonate groups, which increased the intrachange reaction, which led to lower chances for cyclization at the early stage.

## FTIR spectroscopy

The prepared polycarbonates were characterized with FTIR. The FTIR spectra of polycarbonates showed strong absorption bands corresponding to the C=O stretching vibration of the carbonate group from 1759 to 1763 cm$^{-1}$. These frequencies of stretching vibrations are characteristic of aromatic–aliphatic polycarbonates. Strong absorption bands due to the

C—O stretching vibrations were observed in the region from 1212 to 1267 cm$^{-1}$. These IR data, which are typical for the carbonate groups, were in accordance with the data reported in the literature[27,30–37] and, therefore, confirmed the formation of the various polycarbonates. On the other hand, the absorption band due to the hydroxyl groups of the attacking phenol (BPA) was absent in the IR spectra of the final polycarbonates. A typical IR spectrum for BPA–Bu-1,3-D polycarbonate is presented in Figure 1(b), and the results of the FTIR and viscosity analyses are presented in Table III.

## NMR spectroscopy

*$^{1}$H-NMR spectra of the polycarbonates.* The polycarbonates were also analyzed with NMR spectroscopy to elucidate their chemical structure and support their formation. Structurally, the polycarbonates prepared consisted of a BPA unit linked to different alkane chains via a recurring carbonate group. In the $^{1}$H-NMR spectra, the polycarbonates showed a similar pattern of peaks, except for the aliphatic chain. The aromatic protons of the BPA unit were shown as an AB system ranging from 7.0 to 7.3 δ. The methyl protons of the BPA unit were observed as a singlet in the range 1.63–1.68 δ. With regard to the aliphatic chains, the signal for the protons of the terminal methylene groups (—OOCOCH$_2$—) attached to the carbonate function was observed in the range 4.10–4.59 δ for all of the polycarbonates. The protons of the aliphatic methylene groups next to the terminal methylene groups (—OOCOCH$_2$CH$_2$—) in the polycarbonates of BPA with Pr-1,3-D, Bu-1,3-D, and Bu-1,4-D were observed at δ = 1.88–2.17 ppm. The signals of the terminal proton of the CH groups attached to the carbonate function [—OOCOCH(CH$_3$)CH$_2$—] in the polycarbonates of BPA with Pr-1,2-D and Bu-1,3-D were observed at δ = 4.43 and 5.03 ppm, respectively. The signal of the proton of the CH group next to the terminal methylene groups [—OOCOCH$_2$CH(CH$_3$)—] in the BPA–2-Me-Pr-1,3-D polycarbonate was observed at δ = 2.37 ppm. The signals of the protons of the methyl groups attached to the terminal CH group linked to the carbonate function [—OOCOCH(CH$_3$)CH$_2$—] in the polycarbonates of BPA with Pr-1,2-D and Bu-1,3-D were observed at δ = 1,43 and 1.42 ppm, respectively.

The appearance of a singlet peak in the range 1.63–1.68 ppm for the methyl protons of the BPA unit represented experimental evidence for the substitution of the phenyl group of the alkylene diphenyl dicarbonate monomers with the phenyl group of the BPA unit in the formed polycarbonate. These data, deduced from the $^{1}$H-NMR spectra, suggested the formation of the various polycarbonates.

*$^{13}$C-NMR spectra of the polycarbonates.* Apart from the aliphatic moiety, the $^{13}$C-NMR spectra of polycarbonates were similar [Fig. 2(b)]. The position and pattern of the carbon peaks of the BPA unit were observed at about the same positions in all of the polycarbonate spectra. The signal of the aliphatic quaternary carbon atom bearing the methyl groups appeared at about 42.6 ppm, whereas the signal of the methyl carbon atoms invariably appeared at 31 ppm. The signals of all of the other aromatic carbon atoms of 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 were attached, appeared in the range 148.1–148.5 ppm for all of the polycarbonates. The signal of the other quaternary carbon atoms of the aromatic rings next to the oxygen of the carbonate function invariably appeared at 149 ppm. The characteristic signal of the carbonyl carbon of the carbonate function in all of the polycarbonates appeared in the range 153.5–153.9 ppm. The signals of the carbon atoms of the aromatic rings of BPA in the ortho and meta positions to the quaternary carbon atom attached to the carbonate appeared as two singlet peaks at 120.5 and 128 ppm, respectively.

With regard to the aliphatic moiety, the terminal methylene carbon atoms (—OOCOCH$_2$—) attached to the carbonate function showed their signal in the range 64.9–73.0 ppm for all of the polycarbonates. The carbon atoms of the aliphatic methylene groups next to the terminal methylene groups (—OOCOCH$_2$CH$_2$—) in the polycarbonates of BPA with 1,3-propane, 1,3-butane, and 1,4-butane alkane chains were observed at δ = 25.2–34.8 ppm. The signals of the carbon atoms of the terminal CH groups attached to the carbonate function [—OOCOCH(CH$_3$)CH$_2$—] in the polycarbonates of BPA with 1,2-propane and 1,3-butane alkane chains were observed at δ = 72.9 and 73.0 ppm, respectively. The signal of the carbon atom of the CH group next to the terminal methylene groups [—OOCOCH$_2$CH(CH$_3$)—] in the BPA–2-Me-Pr-1,3-D polycarbonate was observed at δ = 32.6 ppm. The signals of the carbon atom of the methyl groups attached to the terminal CH group, which were linked to the carbonate function [—OOCOCH(CH$_3$)—], in the polycarbonates of BPA with 1,2-propane and 1,3-butane chains were observed at δ = 16.2 and 20.1 ppm, respectively.

The signals observed at 42.6 and 31 ppm for the aliphatic quaternary carbon atom bearing the methyl group and the methyl carbon atoms of the BPA unit, respectively, which were absent in the spectra of the monomers, confirmed the attachment of BPA to the carbonate function and, thus, the formation of the various polymers. Furthermore, the $^{13}$C-NMR signals due to the aromatic carbon atoms of BPA

unit were also highly indicative of the formation of the postulated polycarbonates because only two signals were observed. The signals of the carbons of the methyl groups and that of the aliphatic quaternary carbon atom in the ^{13}C-NMR, in particular, confirmed that the phenyl group that was linked to the carbonate group in the monomer was replaced with the BPA unit in the formed polymer. The previous data, deduced from the ^{1}H-NMR and ^{13}C-NMR spectra, proved the formation of the various polycarbonates. The ^{1}H-NMR and ^{13}C-NMR data of aromatic–aliphatic polycarbonates are summarized in Table IV.

## Thermal treatment of the polycarbonates

The thermal treatment of the aromatic–aliphatic polycarbonates (step 3 in Scheme 1) was carried out in vacuo at a temperature of 250°C. It was found that, under these conditions, the catalyzed intrachange reaction could take place and lead to the formation of PC homopolymer and the cyclic aliphatic carbonates, which were subsequently removed from the reaction mixture. The thermal treatment step gave a colorless semisolid effluent condensed in the upper part of the reaction tube and a polymer residue in the bottom. The polymer residue and the effluents were analyzed with FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy.

The interchange reaction (step 2 in Scheme 1) that led to BPA–EG polycarbonate from BPA and EG DPDC gave a low yield, which hindered further thermal treatment. On the other hand, the thermal treatment of BPA–Bu-1,4-D polycarbonate (step 3 in Scheme 1) did not lead to a complete elimination of cyclic tetramethylene carbonate under the experimental conditions used. Peaks due to the aliphatic moieties were still observed in the ^{1}H-NMR spectrum of the BPA–Bu-1,4-D polymer residue after thermal treatment. From the integration of the peaks of the terminal aliphatic methylene protons of tetramethylene unit (—Bu—) and the aromatic ring protons of BPA unit, we calculated that only 51% of the aliphatic moieties were eliminated after 1 h. Therefore, the thermal treatment of both the BPA–EG and BPA–Bu-1,4-D polycarbonates did not constitute a useful nonphosgene route to PC in this study.

The incomplete elimination of the cyclic tetramethylene carbonate upon the thermal treatment of BPA–Bu-1,4-D polycarbonate could be explained by the fact that, for the elimination reaction to take place, the aliphatic chain ends had to meet. In general, the probability of ring formation decreases as the probability of the two terminal functional groups of the aliphatic moieties encountering each other decreases. It seems that these two ends were far enough away to let this meeting occur easily because they were separated from each other by a relatively long alkane chain. The

product obtained was also a less stable, seven-membered ring. Therefore, the elimination reaction (step 3 in Scheme 1) should have been less probable, and thus, elimination occurred only partially.

The situation for the rest of the polycarbonates, in which the BPA unit was linked to the other alkane chains, should have been between the previous two extreme situations. The attainment of the proper conformation for elimination requires rotation about a larger number of carbon–carbon bonds than in BPA–EG polycarbonate but smaller than in BPA–Du-1,4-D polycarbonate. We found experimentally that the structure of the rest of the polycarbonates permitted both the interchange reaction to form the polycarbonate product according to step 2 of Scheme 1 and the complete elimination of the aliphatic moieties according to step 3. This indicated the potential, in the course of this study, for the complete elimination of the alkylene moieties for the polycarbonates involving the other alkane diols and the attainment of the postulated PC homopolymer.

## Analysis of the polymer residue

The IR spectra of polymer residues of the products of the thermal treatment, which were collected from the bottom of the reaction tubes, were consistent with the IR spectra of the PC homopolymer [Fig. 1(c)]. Strong absorption bands of the carbonyl group of the carbonate corresponding to the C=O stretching frequency were observed at about 1770 cm$^{-1}$. The shift in C=O stretching from 1759 to 1770 cm$^{-1}$ confirmed the conversion of the structure of the polymer from an aromatic–aliphatic polycarbonate to an aromatic–aromatic polycarbonate (PC).

The ^{1}H-NMR spectra of the polymers residues were also consistent with the PC homopolymer. They contained only two signals: one at 1.66 δ and another as a doublet of a doublet centered in the range 7.1–7.3 δ, which was attributable to the protons of the methyl groups (6H) and to the protons of the aromatic rings of BPA (8 H), respectively. However, no other signals were observed in the aliphatic region of the spectra for the alkylene chains. The ^{13}C-NMR spectra also did not show any aliphatic signals other than that observed at about 31.0 ppm for the methyl groups of BPA and at about 42.0 ppm for the quaternary aliphatic carbon to which the methyl groups of BPA were attached. On the other hand, the carbonyl carbon peak of the carbonate function shifted slightly in position from about 153 ppm in the aromatic–aliphatic polycarbonate to about 152 ppm in the aromatic PC homopolymer, which was the correct position for the signal of an aromatic–aromatic carbonyl carbon atom.[37] The absence of any absorption signals in the ^{1}H-NMR and ^{13}C-NMR spectra of the residues of thermal treatment for any of the alkane

**TABLE IV**
**¹H-NMR and ¹³C-NMR Data for the Aromatic–Aliphatic Polycarbonates**

| Polycarbonate structure | NMR | δ (ppm) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| (structure 1) | ¹H | 4.59 s, 4H | 4.59 s, 4H | — | — | —a | —a | — | — | 1.68 s, 6H | | | |
| | ¹³C | 66.9 | 66.9 | 153.9 | 149.0 | 121.3 | 128.0 | 148.4 | 42.2 | 31.1 | | | |
| (structure 2) | ¹H | 4.29, 4.44 dd, 2H | 5.17 m, 1H | 1.43 d, 3H | — | — | —a | —a | — | — | 1.65 s, 6H | | |
| | ¹³C | 69.6 | 72.9 | 16.2 | 153.5 | 149.0 | 120.5 | 128.0 | 148.2 | 42.6 | 31.0 | | |
| (structure 3) | ¹H | 4.39 t, 4H | 2.17 m, 2H | 4.39 t, 4H | — | — | —a | —a | — | — | 1.65 s, 6H | | |
| | ¹³C | 65.0 | 28.0 | 65.0 | 153.7 | 149.0 | 120.5 | 128 | 148.2 | 42.6 | 31.0 | | |
| (structure 4) | ¹H | 4.24 d, 4H | 2.37 m, 1H | 4.24 d, 4H | 1.10 d, 3H | — | — | —a | —a | — | — | 1.65 s, 6H | |
| | ¹³C | 69.7 | 32.6 | 69.7 | 13.6 | 153.8 | 149.0 | 120.5 | 127.9 | 148.1 | 42.6 | 31.0 | |
| (structure 5) | ¹H | 4.10 s, 4H | — | 4.10 s, 4H | 1.07 s, 6H | 1.07 s, 6H | — | — | —a | —a | — | — | |
| | ¹³C | 73.0 | 35.3 | 73.0 | 21.5 | 21.5 | 153.8 | 149.1 | 120.5 | 127.9 | 148.1 | 42.6 | |
| (structure 6) | ¹H | 4.36 m, 2H | 2.09 m, 2H | 5.03 m, 1H | 1.42 d, 3H | — | — | —a | —a | — | — | 1.63 s, 6H | |
| | ¹³C | 64.9 | 34.8 | 73.0 | 20.1 | 153.6 | 149.0 | 120.5 | 127.9 | 148.1 | 42.5 | 31.0 | |
| (structure 7) | ¹H | 4.29 s, 4H | 1.88 s, 4H | 1.88 s, 4H | 4.29 s, 4H | — | — | —a | —a | — | — | 1.65 s, 6H | 1.64 s, 6H |
| | ¹³C | 68.1 | 25.2 | 25.2 | 68.1 | 153.8 | 149.0 | 120.5 | 128 | 148.1 | 42.6 | 31.0 | 31.0 |

a The signals of the aromatic protons of the BPA unit appeared in the range of δ = 7.1–7.4.

## TABLE V
## 1H-NMR and 13C-NMR Data for the Cyclic Alkylene Carbonates

| Cyclic alkylene carbonate | | δ (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| (ethylene carbonate)[a] | 1H | 4.47 s, 4H | 4.47 s, 4H | — | | | |
| | 13C | 64.8 | 64.8 | 155.9 | | | |
| (propylene carbonate) | 1H | 3.99, 4.52 t, 1H, t, 1H | 4.82 m, 1H | 1.45 d, 3H | — | | |
| | 13C | 70.8 | 73.7 | 19.5 | 155.2 | | |
| (1,3-propane carbonate) | 1H | 4.43 t, 4H | 2.12 p, 2H | 4.43 t, 4H | — | | |
| | 13C | 68.0 | 21.8 | 68.0 | 148.5 | | |
| (2-methyl-1,3-propane carbonate) | 1H | 4.03, 4.36 d, d, 2H, d, d, 2H | 2.34 m, 2H | 4.03, 4.36 d, d, 2H, d, d, 2H | 1.01 d, 3H | — | |
| | 13C | 73.3 | 26.3 | 73.3 | 12.0 | 148.5 | |
| (2,2-dimethyl-1,3-propane carbonate) | 1H | 4.05 s, 4H | — | 4.05 s, 4H | 1.10 s, 6H | 1.10 s, 6H | — |
| | 13C | 77.5 | 28.5 | 77.5 | 21.2 | 21.2 | 148.2 |
| (1,3-butane carbonate) | 1H | 4.27–4.44 m, 2H | 1.85–2.10 m, 2H | 4.57 m, 1H | 1.37 d, 3H | — | |
| | 13C | 67.1 | 28.6 | 75.9 | 21.1 | 149.1 | |
| (butane-1,4-carbonate)[b] | 1H | 4.18 m, 4H | 1.91 p m, 4H | 1.91 m, 4H | 4.18 m, 4H | — | — |
| | 13C | 70.9 | 27.8 | 27.8 | 70.9 | 155.6 | — |

d = doublet; m = multiplet; p = pentet; s = singlet; t = triplet.
[a] BPA–EG polycarbonate was prepared through the solution polymerization of BPA bis(chloroformate) and EG.
[b] The cyclic carbonate derived from butane-1,4-carbonate was the only solid substance (mp = 74–75°C).

chain signals indicated that complete elimination of these moieties took place and that a PC homopolymer was eventually obtained (Fig. 2).

The complete elimination of the aliphatic moieties and the attainment of the PC homopolymer demonstrated the potential of the method described in Scheme 1 for the preparation of PC from the interchange reactions of the previous alkylene diols diphenyl dicarbonates and BPA. This potential was successfully demonstrated for the diphenyl dicarbonates of 1,2-propane, 1,3-propane, 2-methyl-1,3-propane, 2,2-dimethyl-1,3-propane, and 1,3-butane alkane chains.

### Analysis of the effluents

The analysis of the effluents of the thermal treatment should be important because a more complete view of the whole process would not be realized without the analysis of both the residual part left at the bottom of the reaction tube and the effluent part eliminated from the reaction mixture. Therefore, the effluents of the thermal treatment were characterized with FTIR, 1H-NMR, and 13C-NMR spectroscopy. The analysis of the effluents was in fact quite interesting and informative, as it provided useful information about the evolution of the process. The thermal treatments of the polycarbonates were

initially conducted at 250°C; the residual polymers, which were collected from the bottom of the reaction tube, were, as mentioned previously, the PC homopolymer. The effluents of the thermal treatment process were condensed as colorless semisolid materials at the top of the reaction tube and in the side arm.

Upon optimization of the experimental conditions of the thermal treatment, we carried out the process by heating the polycarbonate samples slowly from 180 to 210°C under a stream of dry nitrogen and maintaining this temperature for 30 min. Heating under these conditions was found to be sufficient for completely removing the effluents. The effluents, which were collected in the upper part of the reaction tube, were separated by dissolution in chloroform and were analyzed with FTIR, $^1$H-NMR, and $^{13}$C-NMR spectroscopy. To test whether the complete elimination of the aliphatic moieties was achieved, the polymer residues were heated under a stream of nitrogen gas and in vacuo up to 250°C. In both cases, negligible amounts of effluent were observed to form.

The cyclic alkylene carbonates were analyzed with FTIR. The FTIR spectra of all semisolid effluents showed strong absorption bands corresponding to the C=O stretching vibration of the carbonate function from 1740 to 1774 cm$^{-1}$ and strong absorption bands due to the C—O stretching vibration in the region from 1214 to 1261 cm$^{-1}$. A typical IR spectrum for the cyclic 1,3-butane carbonate effluent is presented in Figure 1(d). The effluents were also analyzed with $^1$H-NMR and $^{13}$C-NMR spectroscopy; a typical $^1$H-NMR and $^{13}$C-NMR spectra of cyclic 1,3-butane carbonate is presented in Figure 2d. These effluents were identified as the postulated cyclic carbonates of the alkane chains of the various aromatic–aliphatic polycarbonates. The formation of five cyclic carbonates from the five aromatic–aliphatic polycarbonates investigated may introduce a new route for the synthesis of organic cyclic carbonates. The synthesis of these cycles from polycarbonates should be interesting because the reaction mixture involves only one reactant, the polycarbonate. The advantage of this method is that it provides a single pure cyclic aliphatic carbonate from each polycarbonate investigated. This is probably because the polycarbonates containing the alkane moieties and the carbonate function are the only reactants present in the reaction melt, and they can exist, via the possible conformations under the experimental conditions used, in the proper position and dimension for the cyclization reaction. This polymer intrachange reaction may open a new synthetic route, based on polymer thermochemical degradation, to organic cyclic carbonates and possibly to cycles containing other organic functional group types. The peak assignments of the $^1$H-NMR and $^{13}$C-NMR

spectra of the various cyclic carbonates, which were in accordance with the data reported in literature,[38–41] are summarized in Table V.

## CONCLUSIONS

A new, nonphosgene synthetic route for the preparation of a linear PC homopolymer based on the interchange reaction of BPA with alkylene diphenyl dicarbonates was developed. The process consists of three steps: the synthesis of an alkylene diphenyl dicarbonate, the melt polycondensation of the diphenyl dicarbonates with BPA to give an aliphatic–aromatic polycarbonate, and the thermal treatment of the polycarbonate at a high temperature to eliminate the aliphatic moieties and to produce PC. The elimination reaction produced semisolid effluents formed at 180–210°C and composed of cyclic aliphatic carbonates. Heating to 250°C under a dynamic vacuum furnished the pure aromatic PC homopolymer as the residue. The final polymer had a relatively low to moderate viscosity. This polymer intrachange reaction may open a new synthetic route, based on polymer thermochemical degradation, to organic cyclic carbonates and possibly to cycles containing other organic functional group types. With this approach, it was possible to provide a flexible method of the synthesis of PC with diphenyl dicarbonates of alkylene chains composed of two or three methylene groups, from which the PC homopolymer could be prepared. The potential of this method was demonstrated by the successful synthesis of the PC homopolymer from five different aromatic–aliphatic polycarbonates composed of a BPA unit linked to 1,2-propylene, 1,3-propylene, 2-methyl-1,3-propylene, 2,2-dimethyl-1,3-propylene, or 1,3-butylene as the alkane chain units.

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