Chemical conversion of poly(carbonate) to bis(hydroxyethyl) ether of bisphenol A. An approach to the chemical recycling of plastic wastes as monomers

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Abstract

A method for the chemical recycling of poly(carbonate) plastic wastes in the form of a diol monomer, i.e. bis(hydroxyethyl) ether of bisphenol A (BPA), was investigated. Treatment of poly(carbonate) pellets (PC) in ethylene glycol (EG) with a catalytic amount of NaOH (0.1 equiv) produced monohydroxyethyl ether of BPA (MHE-BPA, 42%), bishydroxyethyl ether of BPA (BHE-BPA, 11%) and BPA (42%). When 1.6 mol equiv ethylene carbonate (EC) was added to the same reaction system, BHE-BPA was produced quantitatively. Furthermore, the reaction of BPA with EC was shown to produce both BHE-BPA and MHE-BPA. This result indicates that EC was formed as an intermediate in the base-catalyzed reaction of PC with EG. However, a large proportion of this EC formed from PC was lost by decarboxylation. Therefore, additional EC from an outside source must be supplied for the quantitative preparation of BHE-BPA. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(carbonate); Chemical recycling; Bisphenol-A bis(hydroxyethyl) ether

1. Introduction

The problem of plastic wastes at both the post-manufacturer and post-consumer stages is now an important issue in the global conservation of carbon resources and in the protection of petroleum resources from depletion. In many countries, the major technologies that are used to address this problem are electricity generation, substitute for coke at blast furnaces, and liquefaction to fuel oil. However, these methods do not solve the problem of the depletion of petroleum resources, which are not renewable [1–6]. To address the deplorable worldwide trend of treating plastic wastes as refuse, rather than as recyclable plastic resources, we proposed that plastics be recycled by means of retro-polymerization to monomers and that their reuse as plastics should be the primary solution to this problem, since this would conserve large amounts of manufacturing energy which are inherited in the waste plastics (Fig. 1). Moreover, retro-polymerization is advantageous because it can reproduce virgin

plastics. Based on this concept, we studied the *chemical recycling*[1] of waste plastics consisting of poly(ethylene terephthalate) (PET) [7,8] and bisphenol-A polycarbonate (PC) [9] by conventional methods using simple industrial equipment and low-energy processes.

It should be stressed here that the molecular structure of PC polymer consists of two chemical units on a monomer basis, i.e. bisphenol A (BPA) and carbon monoxide or carbonate, both of which are important industrial chemicals. In this regard, PC can be used as a reagent that is equivalent not only to BPA but also a carbonate derivative or phosgene, as shown in Fig. 2. After reporting the easy retro-polymerization of PC plastic wastes, e.g. compact discs, to a pair of recyclable monomers, i.e. BPA and dimethyl carbonate (DMC) [9], we began to investigate on the reuse of PC as a chemical reagent.[2] In this report, we describe the chemical conversion of PC

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[1] In this report, the term chemical recycling is limited only to methods that can give either virgin plastics or industrial chemicals. The end-use of plastic waste for energy production or as coke-substitutes in blast furnaces is strictly excluded from this definition.

[2] To the best of our knowledge, our concept of using PC plastic wastes as chemical reagents in both laboratory and factory settings, regarding them as a CO synthon or phosgene equivalent, is original.
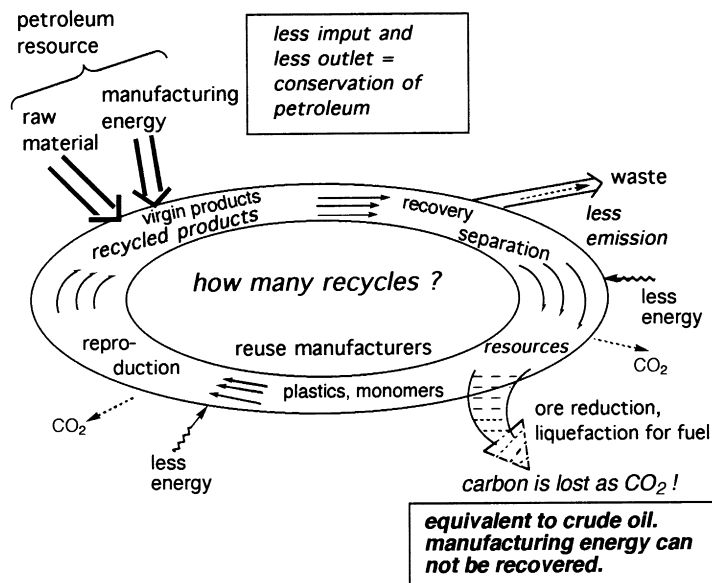
Fig. 1. Conservation of petroleum resources by recycling plastic wastes in the forms of plastics and monomers to save the energies for monomer and plastic production from crude oil.

to bis(hydroxyethyl) ether of BPA (BHE-BPA), which can be used as a diol for polymer production.

2. Results and discussion

On the basis of our previous study in which the easy and quantitative reproduction of the two PC monomers BPA and DMC was achieved by the base-catalyzed methanolysis of PC wastes in a MeOH/toluene mixture [9], we carried out the retro-polymerization of PC in EG in the presence of a catalytic amount of sodium hydroxide (NaOH, 10 mol%). Against our expectation, however, the products obtained were monohydroxyethyl ether of BPA (MHE-BPA, 42%), bishydroxyethyl ether of BPA (BHE-BPA, 11%) and BPA (42%), while EC was not produced (Eq. (1)). Since the independent treatment of BPA with EG under analogous conditions led to the recovery of substrates, it seemed clear to us that the ethylene moiety in the products was derived not directly from EG but rather from a different precursor.
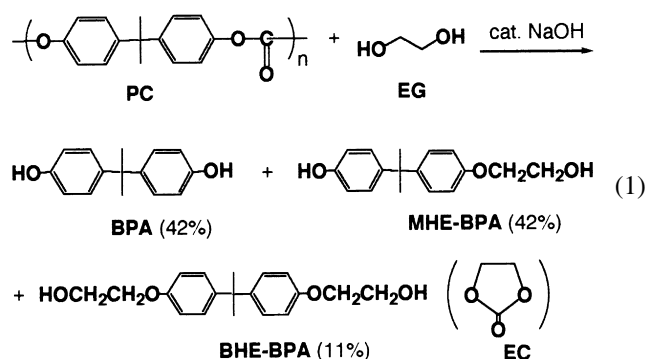
It was reported by Snn and Wang [10,11] and Liaw [12] that BPA reacts with a few cyclic carbonates to give similar hydroxyethyl ethers of BPA. Based on this finding, the most likely mechanism for the production of MHE-BPA and BHE-BPA from PC is that the reaction of PC with EG indeed forms EC, but then EC further reacts with the concurrently formed BPA to give the final products. Indeed, when we examined the reaction of BPA with EC under a variety of conditions to verify not only this mechanism but also to develop a practical approach for the reuse of PC plastic wastes, both MHE-BPA and BHE-BPA were obtained (Table 1, Eq. (2)).

$$ \text{BPA} + \text{EC} \xrightarrow[\text{180°C, EG}]{\text{cat. NaOH}} \text{MHE-BPA} + \text{BHE-BPA} \qquad (2) $$
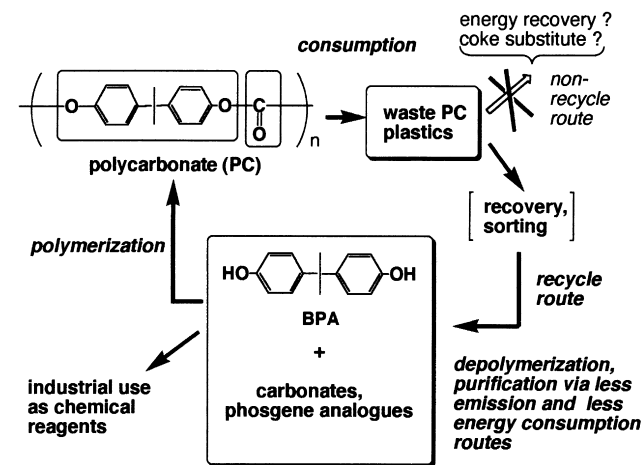

Fig. 2. Recycling of poly(carbonate) plastic wastes in the form of bisphenol A and carbonate derivatives.
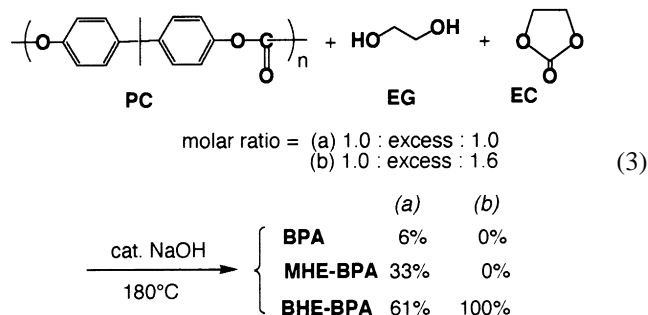
Table 1
Alkali-catalyzed reaction of bisphenol A (BPA) with ethylene carbonate (EC) (reaction scale and conditions: BPA, 6.8 g (30 mmol); EC, 5.3 g (60 mmol); temp, 180°C)

Run	EC (equiv)	Time (min)	Products (yield%)		
			BPA	MHE-BPA	BHE-BPA
1	1	5	37	46	17
2	1	10	34	46	19
3	1	40	29	50	21
4	2	40	3	27	70
5	3	5	0	19	81
6	3	10	0	0	100

Based on this finding, the reaction of PC with a mixture of EG and EC was examined. We expected that if some additional EC was added to the reaction mixture, then BHE-BPA could be produced quantitatively. In this reaction, the amount of extra EC to be added can be less than a stoichiometric amount, i.e. 2 mol EC/1 mol PC.

In the NaOH-catalyzed reaction of PC in EG with 1 mol equiv of EC (Table 2, run 1), MHE-BPA (33%) and BHE-BPA (61%) were obtained together with BPA (6%) (Eq. (2)). This clearly indicates that more than 35% of the hydroxyethyl moiety of MHE-BPA and BHE-BPA was derived from the solvent EG by its reaction with PC, which produced extra EC as an intermediate. The product ratio was not changed by prolonged heating of the product mixture, which therefore, excludes the possibility of a disproportionation reaction among the three products. Increasing the molar ratio of EC to PC from 1.0 to 1.8 (compare runs 2–8), raising the temperature from 150 to 180°C (compare runs 4 with 2 and 3) and prolonging the reaction time (compare run 2 with 3, 5 with 6, and 7 with 8; the rate of dissolution of PC pellets seems to be rate-determining) improved the yield of BHE-BPA to a quantitative level. Thus, the quantitative conversion of PC to BHE-BPA was achieved in EG at 180°C within 20 min by the addition of 1.6 mol equiv of EC, i.e. 60% more than the stoichiometrically required amount. This indicates that a considerable amount of EC is lost by side reactions because, ideally, only

1.0 mol equiv of extra EC is needed. One of the side reactions seemed to be the base-catalyzed decomposition of EC. To examine this possibility, EC was independently treated with a catalytic amount of NaOH (5 mol%) at 180°C for 20 min without solvent. A considerable amount of EC was lost, and this was accompanied by the generation of CO_2. Consequently, the loss of EC can be ascribed primarily to its base-catalyzed decarboxylation under the present conditions regardless of the origin of EC (Table 2).

$$\text{molar ratio} = \begin{array}{l} \text{(a) } 1.0 : \text{excess} : 1.0 \\ \text{(b) } 1.0 : \text{excess} : 1.6 \end{array} \qquad (3)$$

	(a)	(b)
BPA	6%	0%
MHE-BPA	33%	0%
BHE-BPA	61%	100%

cat. NaOH, 180°C

The most plausible reaction mechanism for the formation of BHE-BPA from PC is depicted in Eqs. (4)–(10). EC is formed by the base-catalyzed glycolysis of PC with the conjugate base of EG (slow reaction), although the acid–base equilibrium (Eq. (4)) is shifted more toward EG rather than alkoxide (Sequence A). The resulting EC reacts again with the conjugate base of BPA (1) to form adduct 2 (Eq. (6)), which is accompanied by decarboxylation to form the conjugate base of MHE-BPA (4, Eq. (7)). Aryloxide 4 further reacts with EC in an analogous manner to 1 to form BHE-BPA (Eq. (9), Sequence B). During reaction sequences A and B, a considerable amount of EC is lost by base-catalyzed decarboxylation to produce EG (Eq. (10), Sequence C). If the alkoxide of EG, which is formed in Sequence C, reacts with PC resulting in the formation of MHE-BPA and BHE-BPA, as shown by Sequences A and B, then a simple base-catalyzed treatment of PC with EG will give rise to the quantitative formation of BHE-BPA. However, this was shown not to be the case.

Although the synthon "CO" which is present in the main polymer chain of PC is eventually lost in the final product
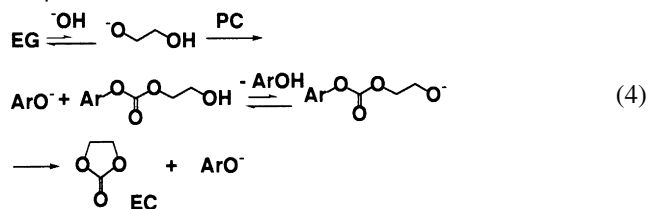
Table 2
Alkali-catalyzed reaction of polycarbonate (PC) with ethylene carbonate (EC) and ethylene glycol (EG) (an excess amount (10 equiv) of EG and a catalytic amount of NaOH (0.1 equiv) were used in every run)

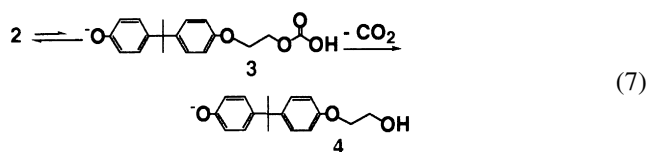| Run	EC (equiv)	Time (min)	Temp (°C)	Products (yield/%)		
				BPA	MHE-BPA	BHE-BPA
1	1.0	45	180	6	33	61
2	1.5	10	180	7	27	67
3	1.5	20	180	0	9	91
4	1.5	960	150	0	3	97
5	1.6	10	180	0.5	4.5	95
6	1.6	20	180	0	0	100
7	1.8	10	180	0	5	95
8	1.8	20	180	0	0	100

BHE-BPA, EC plays an indispensable role in the production of BHE-BPA.
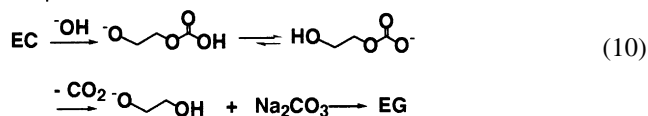
Sequence A

$$EG \xrightarrow{\ ^-OH\ } \ ^-O\diagdown\diagup OH \xrightarrow{\ PC\ }$$

$$ArO^- + Ar\diagup O\diagup O\diagdown\diagup OH \xrightarrow{\ -ArOH\ } Ar\diagup O\diagup O\diagdown\diagup O^- \tag{4}$$

$$\longrightarrow \quad \underset{EC}{\text{(cyclic)}} \quad + \quad ArO^-$$

$ArO^- =$ monophenoxide BPA moiety of PC

Sequence B

$$PC + EG \xrightarrow{\ ^-OH\ } HO\diagdown\!\!\langle\ \rangle\!\!-\!\!\langle\ \rangle\!\!-O^- + EC \tag{5}$$
$$\qquad\qquad\qquad\qquad\qquad 1$$

$$1 + EC \longrightarrow HO-\langle\ \rangle-\langle\ \rangle-O\diagup O\diagdown\diagup O^- \tag{6}$$
$$\qquad\qquad\qquad\qquad\qquad 2$$

$$2 \rightleftharpoons \ ^-O-\langle\ \rangle-\langle\ \rangle-O\diagup O\diagdown\diagup OH \xrightarrow{\ -CO_2\ }$$
$$\qquad\qquad\qquad 3$$
$$\qquad\qquad\qquad \ ^-O-\langle\ \rangle-\langle\ \rangle-O\diagdown\diagup OH \tag{7}$$
$$\qquad\qquad\qquad\qquad 4$$

$$4 \xrightarrow{\ BPA\ } 1 + MHE\text{-}BPA \tag{8}$$

$$4 \xrightarrow{\ EC\ } \longrightarrow BHE\text{-}BPA \tag{9}$$

Sequence C

$$EC \xrightarrow{\ ^-OH\ } \ ^-O\diagdown\diagup O\diagup O\diagdown\diagup OH \rightleftharpoons HO\diagdown\diagup O\diagup O\diagdown\diagup O^- \tag{10}$$

$$\xrightarrow{\ -CO_2\ } \ ^-O\diagdown\diagup OH + Na_2CO_3 \longrightarrow EG$$
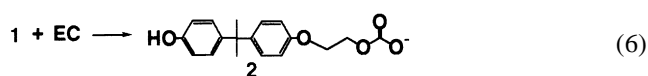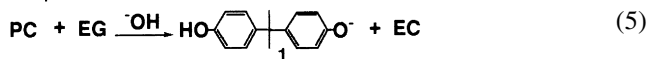
3. Experimental

3.1. Materials and reagents

Pure PC pellets (3 mm length $\times$ 2.5 mm diameter with MW $= 22,000$) were used as model plastics. Commercially available chemical-grade ethylene glycol (EG), ethylene carbonate (EC), bisphenol A (BPA), and NaOH were also used without purification.

3.2. Alkali-catalyzed reaction of PC with EG in the absence of EC

Pellets of NaOH (20 mg, 0.5 mmol) were dissolved in 6.4 g (100 mmol) of EG by heating under a nitrogen atmosphere. To this solution was added 1.27 g of PC pellets (5 mmol/carbonate unit $=$ 10 mmol/ester unit), and the combined mixture was heated at 180°C for 10 min. After cooling, the reaction mixture was poured in MeOH (50 ml) to remove polymeric substances in some runs. The organic residue obtained from the filtrate of MeOH-solution was dissolved again in ether, followed by a flash chromatogra-

phy on a silica gel column (10–40% EtOAc in hexane). Three products, BPA (42%), MHE-BPA (42%) and BHE-BPA (11%), were obtained. For their spectra, see below.

3.3. A general procedure for the alkali-catalyzed reaction of PC with EG in the presence of EC

Pellets of NaOH (20 mg, 0.5 mmol) were dissolved in 6.4 g (100 mmol) of EG. To this solution at ambient temperature were added 1.27 g of PC pellets (5 or 10 mmol on the basis of repeating carbonate or ester units in the polymer chain, respectively) and a specified amount of EC (ranging from 5 to 9 mmol). The combined mixture was heated at a specified temperature (between 150 and 180°C) for 10, 20, 45, or 960 min. After cooling, the reaction mixture was poured into 50 ml MeOH to remove unreacted PC in some runs. In other runs, when unreacted PC was not detected on a tlc plate, this precipitation procedure was omitted. The condensate from MeOH filtrate, or untreated reaction mixture, was subjected to flash chromatography on a silica gel column (10–40% EtOAc in hexane) to yield three products, BPA, MHE-BPA and BHE-BPA, in the yields shown in Table 2. NMR spectral data of the products are as follows.

MHE-BPA. ^{1}H NMR (300 MHz, d_6-DMSO) δ 1.51 (s, 6H), 3.63–3.69 (dt, $J = 5.4$, 5.1 Hz, 2H), 3.90 (t, $J = 5.1$ Hz, 2H), 4.81 (t, $J = 5.4$ Hz, 1H), 6.60–7.70 (m, 8H). ^{13}C NMR (75.6 MHz, d_6-DMSO) δ 31.2, 41.4, 60.0, 69.8, 114.1, 115.0, 127.7, 127.6, 141.2, 143.2, 155.4, 156.7.

BHE-BPA. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.63 (s, 6H), 2.03 (t, $J = 6.3$ Hz, 2H), 3.91–3,96 (dt, $J = 6.3$, 4.5 Hz, 4H), 4.06 (t, $J = 4.5$ Hz, 4H), 6.80–7.15 (m, 8H). ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 31.0, 41.7, 61.4, 69.1, 113.9, 127.7, 143.52, 156.38.

3.4. Alkali-catalyzed reaction of BPA with EC in EG. A general procedure for quantitative product analysis

Pellets of NaOH (120 mg, 3 mmol) and BPA (6.8 g, 30 mmol) were added to EG (18.6 g, 300 mmol) and dissolved by heating the mixture at 180°C under a nitrogen atmosphere. To this solution was added 2 (30 mmol) or 6 ml (90 mmol) of EC. An aliquot (exactly 1.0 ml) of the solution was taken out of the flask periodically by a pipette and, after being weighed, each fraction was filtered through a silica gel column using a mixed solvent (40% EtOAc/hexane) to remove NaOH and EG. After concentrating the filtrate, benzene was added and the mixture was again subjected to azeotropic distillation to remove EtOAc, which disturbs the NMR analysis. The residue was dissolved in a mixed solvent of CDCl$_3$ and d_6-benzene[3] and a weighed amount of *p*-xylene was added as an internal standard for ^{1}H NMR analysis. By comparing the integration of three different

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[3] This mixed solvent was effective for separating the methyl peaks of BPA, MHE-BPA and BHE-BPA.

methyl peaks vs. the internal standard, product yields were determined (see Table 1).

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