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Alkali-catalyzed methanolysis of polycarbonate. A study on recycling of bisphenol A and dimethyl carbonate

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Alkali-catalyzed methanolysis of poly[2,2-bis(4-hydroxyphenyl)propane carbonate] (PC) in a mixed solvent of methanol (MeOH) and toluene or dioxane was studied. Treatment of PC pellets (1.27 g) in 2 ml MeOH with a catalytic amount of NaOH (8.5 mol% per one ester unit of PC) at 60°C for 330 min yielded only 7% bisphenol A (BPA). However, in a mixed solvent of MeOH (1 ml) and toluene (1 ml), the analogous treatment for 70 min completely depolymerized PC to give free bisphenol A (96%) in a solid form and dimethyl carbonate (DMC) (100%) in solution. Characteristics of the catalysis are discussed together with the pseudo-first kinetic feature of the depolymerization. Reaction conditions were investigated for the purpose of recycling PC plastics in the form of bisphenol A and DMC. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polycarbonate; chemical recycling; methanolysis)

INTRODUCTION

For the purpose of recycling of polycarbonate (PC), e.g. poly[2,2-bis(4-hydroxyphenyl)propane carbonate], in the form of an essential monomer bisphenol A (BPA), there have been reported a number of depolymerization methods. Because PC is a polyester in its structure like poly(ethylene terephthalate) (PET), the most common depolymerization methods hitherto reported are the hydrolysis by acids or bases in aqueous media[1–7] and the transesterification to oligomers[8–10]. However, due to the insolubility of PC in water, the aqueous depolymerizations require severe conditions such as long reaction times, high temperatures and pressures. Therefore, instead of using aqueous systems, organic solvent systems such as methylene chloride in combination with ammonia[11], a mixed solvent of phenol and methylene chloride in combination with an alkali catalyst[12,13] have been reported. With organic solvents, however, a tedious product separation process is generally required. We have explored novel avenues, not only to solve such problems but also to enable the chemical recycling of a variety of collected PC plastic wastes which may have different shapes, colors, plastic composites, additive chemicals and metals.

In advance of the present study on PC, we recently reported a highly efficient alkali-decomposition method of PET in nonaqueous ethylene glycol (EG), where disodium terephthalate and EG were reproduced quantitatively under mild treatment conditions[14]. While the use of nonaqueous EG as the solvent is the key to our method, relatively high temperatures 150–180°C are required for this chemical treatment. To lower the temperature, we searched for other simple solvent systems to discover that the combination of nonaqueous ethanol or methanol with dioxane was also effective[15].

We anticipated that this unique method of using nonaqueous alcoholic media for the alkali-depolymerization of PET can be applied to PC. In this paper, we report a highly efficient alkali-catalyzed alcoholysis of PC in nonaqueous alcohols in combination with a hydrocarbon co-solvent, such as toluene, at temperatures lower than 60°C.

EXPERIMENTAL

Materials and reagents

We used pure PC pellets as the model plastics the sizes of which are 3 mm length × 2.5 mm diameter with $Mw = 22\,000$. Commercially available reagent-grade methanol (MeOH), toluene, dioxane, and sodium hydroxide (NaOH) (pellets with $> 96\%$ purity) were used without purification.

General procedure of the alkali-catalyzed depolymerization

Pellets of NaOH (0.01–0.06 g, 0.25–1.5 mmol) were dissolved in MeOH (2 ml), or in a mixed solvent of MeOH (1.0 ml) and toluene or dioxane (0.5–2.0 ml). To this alkali hydroxide solution was added 1.27 g of PC pellets (5 mmol on the basis of repeating monomer unit in the polymer chain) and the PC was decomposed under stirring for a specified period at a specified temperature between 40–60°C. After the depolymerization, the reaction mixture was quenched by pouring it into 40 ml of distilled water, or 5–10 ml of toluene. The quenched solution was allowed to stand at a room temperature for 1 h to crystallize BPA. In

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toluene, in particular, the rate of crystallization was fast separating BPA in flakes, so that product filtration was easy. After drying the crystals, the product yield was determined and the analysis of product purity was performed by FTi.r. and ^{1}H n.m.r. spectroscopy and also X-ray fluorescence analysis.

Quantitative analysis of dimethyl carbonate

For quantitative analysis of dimethyl carbonate (DMC) which is the counterpart product of BPA, an aliquot (50 ml) of the reaction mixture was mixed with 10 ml of *n*-pentane to precipitate both BPA and oligomers of PC if any remained, and 1 ml of the top clear solution was subjected to a gas chromatographic quantitative analysis using standardized DMC solutions for calibration.

RESULTS AND DISCUSSION

Effect of co-solvents on the product formation

First of all, depolymerization of PC in MeOH without co-solvents was investigated. A 1.27-g aliquot of PC pellets was added to 2 ml of MeOH, in which 0.034 g of NaOH (8.5 mol% per one ester bond of PC) was dissolved in advance, and the total mixture was warmed to 60°C with stirring. The weight of pellets decreased for a certain period of the initial reaction stage precipitating a certain amount of white powders of sodium carbonate (Na_2CO_3). However, after this reaction stage, the decrease in the pellet weight slowed down rapidly almost to stop. On the other hand, when the depolymerizations were carried out under the same conditions in the mixed solvents of MeOH (2 ml) and 0.5 ml of toluene or dioxane, the weight of the pellets decreased rapidly to complete dissolution after 240 min. With the increase in the amount of co-solvent, the rate of depolymerization was accelerated to shorten the reaction time. For example, the times required for a complete dissolution of the pellets were shortened from 230 to 70, 40, and 15 min as the amount of toluene increased from 0.5 to 1.0, 1.5, and 2.0 ml, respectively, which was added as a co-solvent to 1 ml of MeOH.

After the reaction was over, the mixture was poured in 40 ml of water to rapidly precipitate white crystalline powders of BPA, which were separated and dried. The yields of BPA thus obtained, are listed in *Table 1*. In MeOH alone, after reaction for 330 min, the yield of BPA was only 7% including even the extracted portion from the acidified solution. In contrast, however, the reactions in mixed solvents of MeOH and toluene or dioxane increased the yield of BPA to 94–96%.*

The infrared spectra (i.r.) of product BPA, obtained after the aqueous precipitation (*vide supra*), showed no characteristic carbonyl absorption of PC whereas the spectra were identical to that of the authentic BPA (*Figure 1*). The analysis of product BPA by X-ray fluorescence spectroscopy did not show the presence of elemental sodium indicating that the product did not contain sodium salts of BPA. Also, its ^{1}H n.m.r spectrum showed two clear-cut singlet and a pair of doublet peaks, which are characteristic of BPA, but none of the other contamination signals.

Instead of pouring in water, when toluene was added to the reaction mixture and cooled, crystalline flakes of BPA were separated nearly quantitatively. However, the BPA flakes may often contain some amount of NaOH and, therefore, they must be washed with water.

Table 1 Yield of BPA obtained from the decomposition of PC in a mixed solvent of methanol and toluene or methanol and dioxane at 60°C[a]

Toluene/MeOH (ml/ml)	Time (min)	Yield of BPA (%)
0.0/2.0	330	7
0.5/2.0	240	95
0.5/1.0	230	94
1.0/1.0	70	96
1.5/1.0	40	96
2.0/1.0	15	96
Dioxane/MeOH		
0.5/2.0	240	96

PC, polycarbonate; DMC, dimethyl carbonate; BPA, bisphenol A; MeOH, methanol

[a] In all experiments, 1.27 g (5 mmol) of polycarbonate and 0.034 g (0.85 mmol) of NaOH were used. To prevent oxidation of BPA, sodium bisulfite ($NaHSO_3$, 0.005 g) was added to the reaction mixture

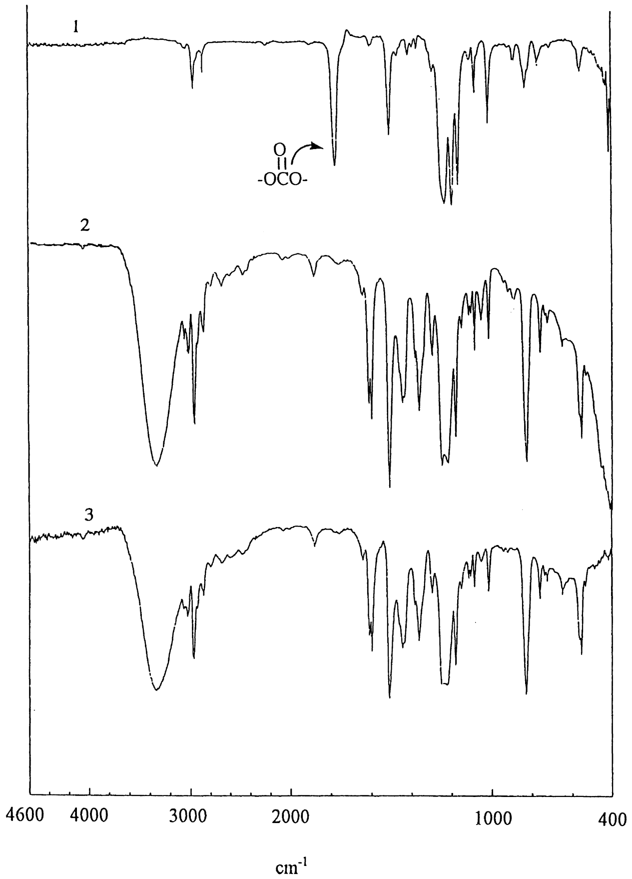

Figure 1 IR spectra of (1) polycarbonate (PC), (2) authentic bisphenol A (BPA), and (3) BPA obtained from the decomposition of PC at 60°C for 70 min in a mixed solvent of methanol and toluene (1 ml each)

Quantitative analysis of dimethyl carbonate (DMC)

Because PC was completely depolymerized to BPA by the use of only 8.5 mol% of NaOH, we presumed that the mechanism governing the present reaction must be alkali-catalyzed methanolysis. In this regard, the formation of another product DMC was analyzed by a gas-chromatographic method.

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* Under alkaline conditions employed for the present procedures, product BPA is apt to color due to its oxidation. To prevent this, addition of sodium bisulfite ($NaHSO_3$, 0.1–0.2 mol% to PC) is effective.

Figure 2 shows the formation of DMC *versus* reaction time in the reaction of PC (1.27 g) with NaOH (0.034 g, 8.5 mol% per one ester bond of PC) in two different types of solvents: (1) in MeOH (2 ml) for 300 min; (2) in a mixed solvent of toluene and MeOH, i.e. 0.5/1.0, 1.0/1.0, 1.5/1.0, and 2.0/1.0 (ml/ml) for the duration of the reaction time, i.e. 230, 70, 40, and 15 min, respectively. To our surprise, it is clearly shown that in the mixed solvents, PC is completely depolymerized to produce DMC quantitatively instead of producing sodium carbonate. DMC thus formed was independently proven to be kinetically stable in the presence of BPA and a catalytic amount of NaOH at 60°C for 120 min in a mixed solvent of toluene and MeOH as described above. Consequently, alkali-catalysis in the present methanolysis was proven unequivocally.

A plausible reason for the rate-acceleration effect of the co-solvents is that they may either dissolve or swell the surface matrices of solid PC to increase the rate of alcoholysis whereas MeOH cannot.†

Reaction mechanism

The mechanism of the present depolymerization is very specific to characterize this methanolysis reaction. With the following four equations (1)–(4), where PC is symbolized with a repeating structure unit –(Ar–OCO$_2$)–, the uniqueness of the mechanism can be described as follows.

First, it was observed that the reaction in pure MeOH produced Na$_2$CO$_3$, which precipitated, whereas it was not the case in the mixed solvent systems. As shown in equation (1), the first cleavage of a carbonate bond by NaOH must produce half salt–half ester **2** of carbonate via the initially formed intermediate monophenoxide **1**. The transformation of **1** to **2** must be controlled by the acidity difference between them, because half acid **1** must have a smaller pK_a value than phenol (pK_a = 10)[16] and carbonic acid (pK_{a1} = 6, pK_{a2} = 10.2)[17]. Then, **2** undergoes additional attack by NaOH to produce an equimolar mixture of half salt **4** of carbonic acid and half salt **5** of BPA via intermediate adduct **3**. The mixture composes an equilibrium with another mixture system of sodium carbonate and BPA (equation (2)) because the pK_a value of **4** is presumed to be smaller than that of **5**. The equilibrium will shift to the right side because Na$_2$CO$_3$ precipitates from the solution and, thus, BPA stays in free phenolic form.

$$\underset{(\mathbf{PC})}{\text{-(Ar-OCO}_2\text{)-}} + \text{NaOH} \longrightarrow \underset{\mathbf{1}}{\text{HOCO}_2\text{-ArONa}} \longrightarrow \underset{\mathbf{2}}{\text{NaOCO}_2\text{-ArOH}} \tag{1}$$

$$\mathbf{2} + \text{NaOH} \longrightarrow \underset{\mathbf{3}}{\text{NaOC(OH)(ONa)O-ArOH}} \longrightarrow$$

$$\underset{\mathbf{4}}{\text{NaO-CO}_2\text{H}} + \underset{\mathbf{5}}{\text{NaO-ArOH}} \rightleftharpoons \text{Na}_2\text{CO}_3\downarrow + \underset{(\mathbf{BPA})}{\text{HOArOH}} \tag{2}$$

Since PC is almost insoluble in methanol, initially formed **2** (equation (1)) will react with NaOH faster than PC does and, therefore, a catalytic amount of NaOH is totally consumed in the form of Na$_2$CO$_3$ to terminate or slow down the depolymerization.

In contrast, in the mixed solvent systems, the surface of the PC pellets is partially dissolved or swollen (more or less elongation of the matrices of solid PC takes place) by toluene or dioxane to increase the relative concentration of the ester functional group for the attack by NaOH, thus consuming most of the alkali in the form of **2**. Because of this alkali consumption or lowering in the alkali concentration, **2** reacts with MeOH to produce half salt of methyl carbonate **7** and BPA via intermediate adduct **6** (equation (3)). Then, carbonate **7** reacts with MeOH to produce DMC together with regenerated NaOH, the latter of which goes back to the catalytic propagation cycle shown in equation (1).

$$\mathbf{2} + \text{MeOH} \longrightarrow \underset{\mathbf{6}}{\text{NaOC(OMe)(OH)O-ArOH}} \longrightarrow \underset{\mathbf{7}}{\text{NaOCO}_2\text{Me}} + \text{BPA} \tag{3}$$

$$\mathbf{7} + \text{MeOH} \longrightarrow \underset{(\mathbf{DMC})}{(\text{MeO})_2\text{CO}} + \text{NaOH} \tag{4}$$

The regenerated NaOH might also attack the accompanying product DMC to shift the equilibrium of equation (4) to the left. In fact, it was separately proven to be the case by the independent treatment of DMC with NaOH in MeOH. However, in the presence of BPA, DMC remained intact despite the presence of NaOH. A more significant observation is that when PC is present in the mixed media, NaOH attacks PC much faster than attacking DMC and, thus, NaOH goes in a catalytic cycle. The reason for this chemoselectivity is that the attack of NaOH to DMC (the inverse of equation (4)) produces MeOH (pK_a = 16) whereas the attack to PC produces a phenolic hydroxyl group (pK_a = *ca.* 10), which is a stronger acid than MeOH. This is the explanation for the unique profile of the present methanolysis reaction.

Amount of MeOH

On a mechanistic basis, more than a stoichiometric amount of MeOH is required for the completion of depolymerization. For example, as shown in *Table 2*, the use of a stoichiometric amount of MeOH (1.0 mol per one ester bond of PC) in combination with co-solvent toluene produced only 80% DMC although the pellets were completely dissolved after the reaction at 60°C for 300 min. Pouring the product mixture into water separated a heavily viscous material. However, using more than a stoichiometric amount of MeOH, DMC was produced in quantitative yields. For example, the use of 1.5 times the stoichiometric amount of MeOH at 60°C for 60 min produced 95% DMC, which reached 100% after 120 min.

However, the use of too much MeOH lowers the yield of BPA because BPA can easily dissolve in MeOH. The data

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† The reaction system is composed of binary liquid–solid phases. Depolymerization takes place rapidly on the solid surface before dissolution of the polymer.

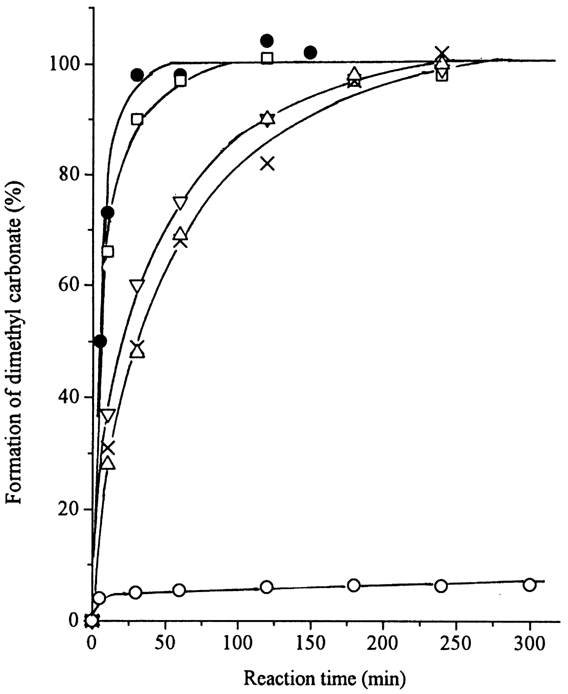

Figure 2 Formation of DMC *versus* reaction time of PC (1.27 g, 5 mmol) with NaOH (0.034 g, 8.5 mol%) at 60°C in various solvent mixtures: in methanol (2 ml) (○), in a mixed solvent of toluene/methanol (0.5 ml/2 ml) (×), (0.5 ml/1 ml) (▽), (1 ml/1 ml) (□), (1.5 ml/1 ml) (●), and dioxane/ methanol (0.5 ml/2 ml) (△)

Table 2 Effect of the molar ratio [methanol/PC] on the yield of DMC and BPA at 60°C[a]

MeOH/PC (mol/mol)[b]	MeOH/toluene (ml/ml)	Products (%)	
		DMC	BPA
1.0	0.4/1.0	80	—
1.5	0.6/1.0	100	96
2.0	0.8/1.0	101	96
2.5	1.0/1.0	100	96
3.8	1.5/1.5	100	94
5.0	2.0/2.0	100	93
6.3	2.5/2.5	100	91

PC, polycarbonate; DMC, dimethyl carbonate; BPA, bisphenol A; MeOH, methanol

[a] In all experiments, 1.27 g (5 mmol) of polycarbonate and 0.034 g (0.85 mmol) of NaOH were used. To prevent oxidation of BPA, sodium hydrogensulfite ($NaHSO_3$, 0.005 g) was added to the reaction mixture. Product yields were determined at the final stage of the decomposition

[b] Moles of MeOH per one ester bond of the PC

shown in *Table 2* indicates that the use of approximately 1.5–2.5 times the stoichiometric amount of MeOH is appropriate.

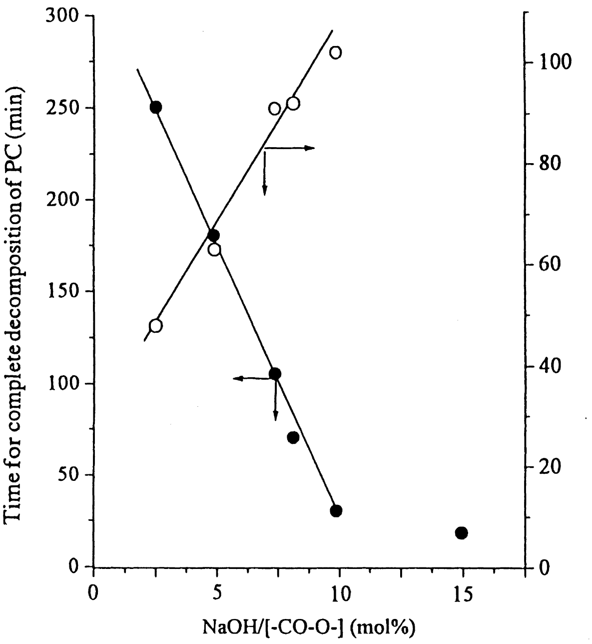

Figure 3 Effect of NaOH concentration on the formation of DMC from PC within 30 min (○) and the time required for complete decomposition of PC at 60°C (●), in a mixed solvent of toluene/methanol (1 ml each)

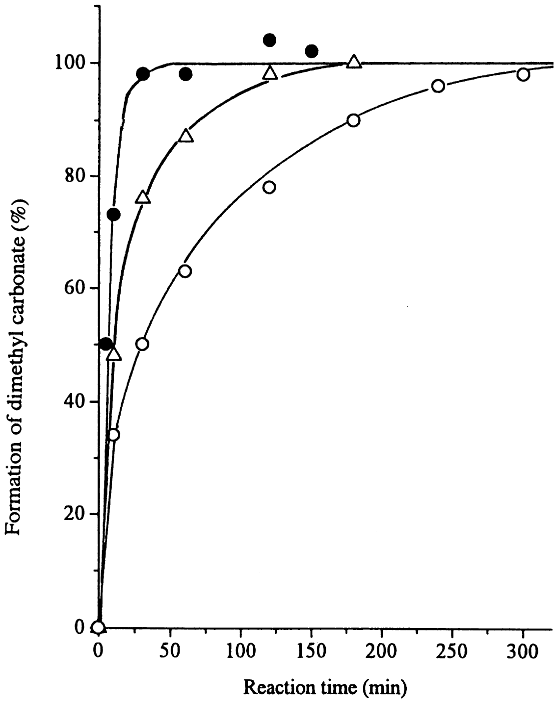

Figure 4 Temperature effect on the formation of DMC *versus* decomposition time of PC (1.27 g) in a mixed solvent of toluene/methanol (1.5 ml/ 1 ml) with NaOH (8.5 mol%) at 40°C (○), 50°C (△) and 60°C (●)

Amount of NaOH

Effects of the amount of catalyst NaOH on both the rate of depolymerization and the yield of DMC were investigated in mixed media of MeOH (1 ml) and toluene (1 ml) at 60°C for 30 min, and results are shown in *Figure 3*. By varying the amount of NaOH (2.5, 5.0, 7.5, 8.5 and 10 mol% per one ester bond of PC) the yield of DMC increased linearly and the time required for complete dissolution of PC pellets decreased linearly to 250, 180, 140, 70, and 30 min, respectively. However, above 10 mol% NaOH, the yield of BPA tended to decrease due to the formation of its sodium salt, which dissolves in water,‡ while the yield of DMC remained unchanged. To summarize, the appropriate amount of NaOH seems to be 5–10 mol%.

Temperature effects

The effect of reaction temperatures (40–60°C) on the rate of depolymerization of PC was investigated by monitoring the yield of DMC in the reaction of PC (1.27 g) with NaOH (0.034 g) in a mixed medium of toluene and MeOH (1.5 ml/ 1.0 ml). Results are shown in *Figure 4*. As the temperature was raised, the rate of depolymerization significantly

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‡ By acidifying the aqueous solution obtained after the separation of BPA, the combined yield of BPA reaches a satisfactory quantitative level.

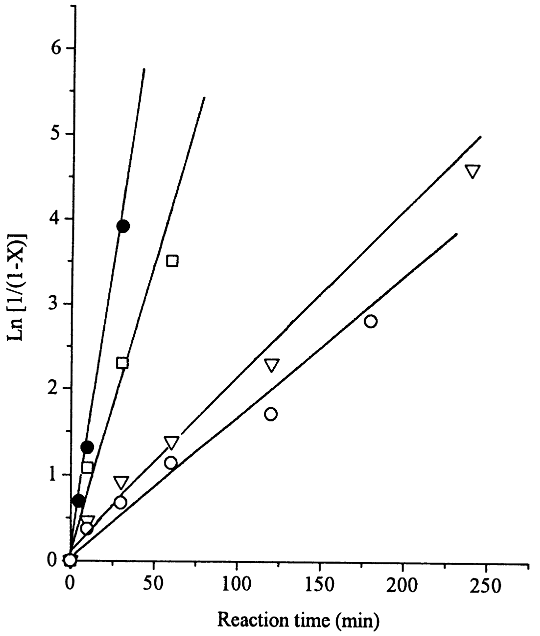

Figure 5 Kinetic expression for the formation of DMC, according to equation (6), at 60°C in a mixed solvent of toluene/methanol: 0.5 ml/2 ml (○), 0.5 ml/1 ml (▽), 1 ml/1 ml (□) and 1.5 ml/1 ml (●)

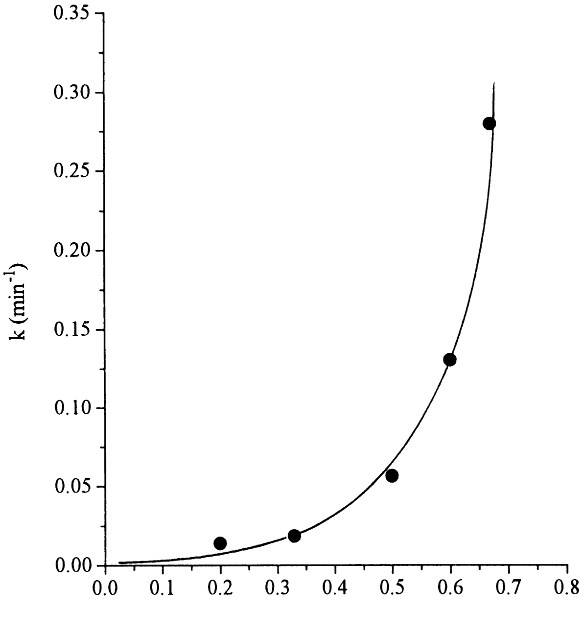

Figure 6 Effect of the mixing ratio of toluene to methanol (vol/vol) on the rate constant of PC decomposition at 60°C with NaOH (8.5 mol%)

increased and the time required for quantitative formation of DMC was 350, 140 and 40 min at 40, 50 and 60°C, respectively. Also the yields of BPA were 96, 95 and 96%, respectively.

Kinetic analysis

The depolymerization of PC proceeds via multi-stage mechanism as shown above with equations (1)–(4). The rate-determining stage seems most likely to be the attack of hydroxide ion on the surface of solid PC. The rates of formation of DMC, shown in *Figure 2*, are controlled under the first-order kinetic equation (5).

$$dX/dt = k(1 - X) \qquad (5)$$

where X is the yield of DMC and k is the pseudo first-order rate constant. Equation (5) is integrated to give equation (6).

$$\mathrm{Ln}[1/(1 - X)] = kt \qquad (6)$$

Kinetic data shown in *Figure 2* are translated into equation (6) and shown in *Figure 5*. In any binary solvent system, a satisfactory linear relation (r = 0.98–0.999) was obtained. Pseudo first-order rate constants, thus obtained, were again plotted against the partial concentration of toluene in the mixed media to give the result shown in *Figure 6*. Here, it is clearly shown that an increase in the toluene fraction within the limit of 50 vol% insignificantly affects the rates, whereas above 50% the increase accelerates the rates significantly. This must be due to the acceleration of dissolution and swelling of the PC pellets by toluene particularly above its 50 vol% fraction in methanol.

The rate constants of the DMC formation at 40, 50 and 60°C, calculated from the data of *Figure 4*, are 0.012, 0.031 and 0.13 min^{-1} (r = 0.992–0.999), respectively, and the energy of activation for this depolymerization is calculated to be 25.6 kcal/mol.

CONCLUSION

The characteristic feature of the present methanolysis is that PC can be depolymerized to its starting monomer components BPA and DMC by the use of a catalytic amount of alkali-metal hydroxide under mild reaction conditions. The monomers can be obtained almost quantitatively in very pure states and they can be recycled as the monomers of PC and epoxy resins. Also, DMC alone is in widespread use as an industrial chemical. Finally, in view of global environmental and resource problems, we would like to conclude that energy-saving and simple chemical recycling technologies for waste plastic materials, such as the present method, will certainly contribute to the worldwide polymer industry.

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