

Depolymerization of polycarbonate by methanol under pressurized microwave irradiation

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Abstract. Depolymerization of polycarbonate (PC) waste by methanolysis without catalyst under pressurized microwave irradiation was proposed in order to get bisphenol A (BPA). The depolymerized products were identified by NMR and FTIR spectroscopy. A maximum BPA yield of 94% was achieved at a reaction temperature and pressure of 190°C and 3 MPa for 3 hours. On the other hand, dimethyl carbonate could not be detected by FTIR analysis. In order to clarify the reaction mechanism, benzyl alcohol was used instead of methanol under the similar condition. Dibenzyl ether was found to be directly produced by the simultaneous reactions of transesterification and decarbonation during the microwave irradiation. The proton ratio of dibenzyl carbonate:dibenzyl ether = 11.2:88.8 was determined from the ¹H-NMR chemical shifts of the reaction mixture. Therefore, dimethyl carbonate in the case of the methanolysis was converted to dimethyl ether, which vaporized at atmospheric pressure after the reaction under pressurized microwave irradiation. The proposed methanolysis method of waste PC can achieved the high efficient recovery of BPA without catalyst use and avoid the need for a further separation process of dimethyl carbonate.

1. Introduction

Polycarbonate (PC) is one of the important engineering plastics having excellent properties of impact resistance, transparency, heat resistance and workability. Commercial PCs have been produced mainly through a polycondensation of 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A, BPA) with carbonyl chloride, dimethyl carbonate (DMC) or diphenyl carbonate. A major application of PC is the data storage products such as CD, DVD and Blue-ray Disc. Extended production of PC results in huge amount of PC waste, which should be recycled for the fossil fuel resources conservation and carbon dioxide emission control. However, the main treatments of PC waste are the landfill and the incineration disposal. Chemical depolymerization methods of waste PC to recover starting materials, such as BPA and carbonate, have attracted attention over the years. Alkali-catalyzed methanolysis of PC in a mixed solvent of methanol and toluene was performed and gave free BPA (96 %) in a solid form and DMC (100 %) in solution [1]. Chemical recycling of PC by the thermal decomposition with steam at 500°C was investigated. The addition of Ca(OH)₂ catalyst in the chemical recycling of PC with steam at 500°C



led to the phenol yield of 70 mol% [2]. The solubility of PC was improved by using ionic liquid for the methanolysis depolymerization of PC [3]. To maintain the yield of product is the main advantage in this recycle use of ionic liquid. In the method for the depolymerization of PC in supercritical ethanol, PC was completely degraded into diethyl carbonate and BPA [4]. The microwave irradiation for the depolymerization of PC could accelerated the reaction rate [5, 6]. In our previous research, efficient recycling processes were achieved by using pressurized microwave irradiation for the hydrolytic depolymerization of poly(ethylene terephthalate) [7] and the alcoholysis of polyester resin in glass fiber reinforced plastics [8] due to the enhancement of compatibility between waste plastic and solvent in addition to the rapid heating.

In this study, non-catalyzed depolymerization of PC in methanol was carried out under the condition of pressurized microwave irradiation at 190°C and 3.0 MPa. In order to clarify the reaction mechanism, depolymerization of PC in benzyl alcohol was examined under the similar condition to the methanolysis. The formation of the ether compounds by decarbonation reaction of the carbonate products was investigated.

2. Experiments

2.1 Materials and Reagents

Pure PC pellets (L-1225LM, diameter = *ca.* 3 mm, thickness = *ca.* 3 mm) were supplied from the Teijin Chemical Ltd., Japan. Commercially available analytical reagent grade methanol (MeOH), benzyl alcohol (BnOH), 2,2-bis(-hydroxyphenyl) propane (BPA), dibenzyl carbonate (DBnC) and dibenzyl ether (DBnE) were used without further purification. MeOH and BnOH were used as solvents, and BPA, DBnC, and DBnE were used as standard reagents.

2.2 Depolymerization of PC with methanol and water

The pellets of PC (0.257 g, 1.01 mmol) was added to MeOH (4.02 g, 1.25 mmol) for methanolysis or to water (5.22 g, 290 mmol) for hydrolysis in a 10 mL sealed tube equipped with a stir bar. Microwave was irradiated to the tube attached in the microwave apparatus (Initiator+8 with single mode microwave irradiation, Biotage AB). Microwave irradiation (2.45 GHz, 300 W) was applied for 3 h at the reaction temperature of 190°C, and reaction pressure of 3.0 MPa. After the microwave irradiation, the reaction mixture was transferred from reaction tube to Kugelrohr flask by using MeOH (30 mL). MeOH was distilled from the solution by using Kugelrohr apparatus (Sigma-Aldrich Chemie GmbH). MeOH containing low boiling components was trapped the tube in chilled bath (40°C, 110 Pa). BPA as a white solid product was remained in Kugelrohr flask. The BPA yield was calculated as the actually produced amount of BPA and the maximum amount of BPA obtained theoretically as the following.

$$BPA \text{ yield (\%)} = \frac{\text{produced amount of BPA}}{\text{maximum amount of BPA}} \times 100 \quad (1)$$

2.3 Depolymerization of PC with benzyl alcohol

The pellets of PC (0.256 g, 1.01 mmol) and BnOH (4.01 g, 125 mmol), were added in a 10 mL sealed tube equipped with a stir bar. The subsequent reaction procedures were almost similar to the methanolysis described in experimental section 2.2. The reaction temperature and pressure were changed to 250°C and 0.3 MPa, respectively. The unreacted BnOH and the solvent mixture of DBnC and DBnE containing trace BnOH were distilled from the reaction solution by Kugelrohr distillation apparatus at 80°C / 140 Pa and at 130°C / 120 Pa, respectively. Trace BnOH was completely recovered from the distilled solvent mixture by column chromatography (silica-gel: Wakosil C-200, eluent (50 mL); chloroform to hexane weight ratio of 3:1) Finally the eluent was evaporated under reduced pressure to obtain the mixture of DBnC and DBnE.

2.4 Products characterization

The chemical structure of BPA, DBnC, and DBnE were confirmed with FTIR spectrometer (Spectrum 100, PerkinElmer Inc.), FT-NMR spectroscopy (JNM-EX270, JEOL Ltd.). The proton ratio of DBnC:DBnE was determined from the chemical shifts of methylene moiety of benzyl group in ^1H -NMR spectra.

3. Results and discussion

3.1 Depolymerization of PC with H_2O and MeOH

As indicated in Entry 1 of table 1, hydrolysis of PC at the microwave irradiation condition of 190 °C at 3.0 MPa achieved at the maximum output of the microwave apparatus for 3 hours gave little BPA (BPA yield = 6 %) and left the unreacted PC due to the low affinity of PC to water. Hydrolysis of PC under microwave irradiation required acid or basic catalyst [5, 6]. Meanwhile, methanolysis of PC under the same reaction condition readily progressed to give BPA in a higher yield (94 %) as indicated in Entry 4. As shown in figure 1, the BPA yield became the maximum value at the reaction time of 3 hours and then gradually decreased due to the decomposition of BPA. On the other hand, DMC produced from methanolysis could not be detected by IR analysis of the reaction mixture. Methyl group on DMC can barely be detected by the NMR analysis. DMC and the related compounds might disappear unexpectedly from the reaction mixture during the depolymerization process.

Table 1. Depolymerization of polycarbonate under pressurized microwave irradiation^a

| Entry | PC /mmol | R-OH /mmol | Time /hour | Yield of BPA /% |
|-------|-------------|--------------------------|---------------|--------------------|
| 1 | 1.06 | H_2O 290 | 3.0 | 6 |
| 2 | 1.06 | MeOH 127 | 12.0 | 90 |
| 3 | 1.06 | MeOH 127 | 6.0 | 92 |
| 4 | 1.01 | MeOH 127 | 3.0 | 94 |
| 5 | 1.01 | MeOH 127 | 1.0 | 20 |

^aThe reaction temperature and pressure were fixed at 190°C and 3.0 MPa, respectively.

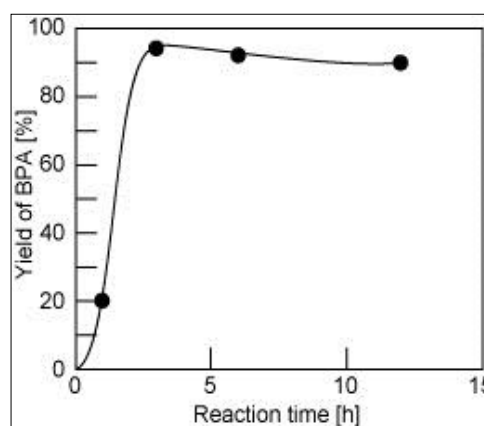


Figure 1. Yield of BPA

3.2 Depolymerization of PC with BnOH

In order to understand the disappearance of DMC from the reaction mixture, the alcoholysis of PC with benzyl alcohol (BnOH) was investigated. After the reaction at 250°C and at 0.3 MPa for 3 hours, BPA yield was as high as 100 %. The evaporation of the eluent in column chromatography operation gave the clear, colorless oil residue (0.254 g) which might be the carbonate compound with high boiling point. Figure 2 shows the ^{13}C -NMR spectra of the oily residue, dibenzyl carbonate (DBnC) and dibenzyl ether (DBnE). The chemical shifts of CH_2 of benzyl group ($A = 69.88$ ppm), quaternary carbon of phenyl group ($B = 135.31$ ppm), and carbonyl carbon of carbonate ($C = 155.23$ ppm) were observed in the standard samples of DBnC in Figure 2(b). The chemical shifts of CH_2 of benzyl group ($A = 72.12$ ppm) and quaternary carbon of phenyl group ($E = 138.29$ ppm) were observed in the standard samples of DBnE in Figure 2(c). The ^{13}C -NMR chemical shifts of the oily residue (Figure 2(a)) was compared with chemical shifts of figure 2 (b) and (c). Consequently, the oily residue was found to be composed of DBnC and DBnE. As a result of ^1H -NMR analysis of benzyl alcohol solution recovered from the reaction mixture of Entry 3, the proton ratio of DBnC:DBnE = 11.2:88.8 was determined from the chemical shifts of methylene moiety of benzyl group.

The main reaction products of alkali-catalyzed methanolysis were reported to be BPA and DMC [1]. However, BPA and dimethyl ether might be produced predominantly in the non-catalytic methanolysis under pressurized microwave irradiation as shown in figure 3. Therefore, dimethyl ether with the boiling point of -24°C can easily escape at the depressure procedure of the microwave apparatus.

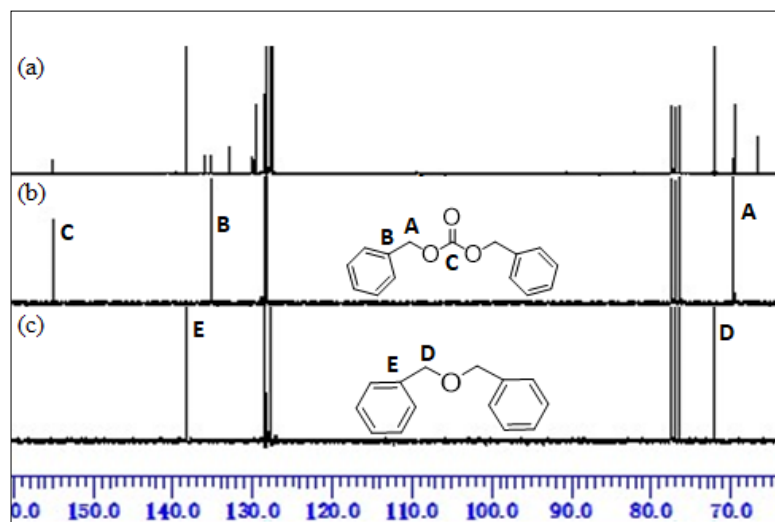


Figure 2. ^{13}C -NMR spectra of (a) the mixture removed BnOH by Silicagel column chromatography with $\text{CHCl}_3\text{-C}_6\text{H}_6$ eluent in Entry 4, (b) the standard sample of DBnC, and (c) the standard sample of DBnE.

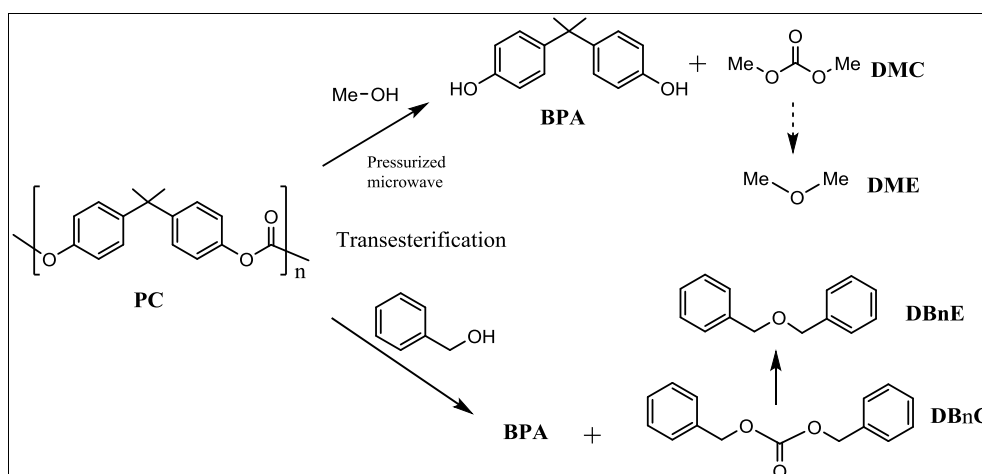


Figure 3. Depolymerization of polycarbonate by methanol and benzyl alcohol under pressurized microwave irradiation

Figure 4 shows the postulated production mechanism of dialkyl ether in the non-catalyzed decomposition of PC under pressureized microwave irradiation. The pathway A indicates the step-wise production of dialkyl ether by way of decarbonation of dialkyl carbonate. The pathway B indicates the simultaneous reaction of transesterification. To determine the production pathway of DBnE, the decomposition of PC with MeOH in the presence of DBnC was examined. The decarbonation of DBnC could not proceed during the methanolysis. This result strongly supports the formation of DBnE by the simultaneous reaction pathway B.

The proposed methanolysis method of waste PC under pressurized microwave irradiation can achieved the high efficient recovery of BPA without catalyst use and avoid the need for a further separation process of dimethyl carbonate.

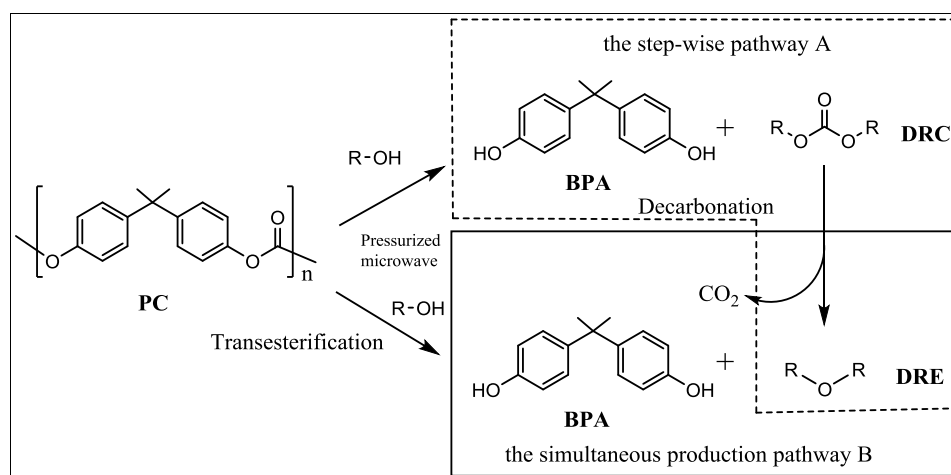


Figure 4. Postulated production mechanism of dialkyl ether in the non-catalyzed decomposition of PC under pressurized microwave

4. Conclusion

Chemical recycling of polycarbonate waste by non-catalyzed methanolysis under pressurized microwave irradiation was studied in this paper. The maximum yield of BPA of 94% was achieved at reaction temperature and pressure of 190°C and 3.0 MPa for 3 hours. On the other hand, trace amount of dimethyl carbonate was detected by NMR. From the result of depolymerization of PC with BnOH to confirm the reaction pathway to DBnE, BPA and DBnE were found to be directly formed by way of the transesterification. Less reactivity for the decarbonation of DBnC during the methanolysis strongly suggests the direct formation of DBnE in the transesterification of PC with alcohol. The depolymerization process can be considered as a high efficiency, convenient process from the viewpoint of non-catalyst use and the easy separation of BPA from dimethyl ether.

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