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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Monomer recovery of waste plastics by liquid phase decomposition and polymer synthesis

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Abstract Polycarbonate was decomposed into phenol, bisphenol A and *p*-isopropenylphenol by the reaction at 130–300 °C in water. The decomposition reaction was accelerated by the addition of Na_2CO_3, and the yield of identified products reached 68% in the reaction at 250 °C for 1 h. By using the decomposed products, the prepolymer of phenol resin was synthesized.

Introduction

The chemical recycling of waste plastics has been gaining greater attention in recent years as a means of obtaining valuable products from wastes [1]. Thermal cracking of thermoplastic resin is a well-known technique and fluidized-bed pyrolysis technology has been under development [2, 3]. It is well known that water under supercritical conditions is much less polar and can homogenize substantial amounts of non-polar organic compounds [4, 5]. Furthermore, it is pointed out that the supercritical water is emerging as a medium, which could provide the optimum conditions for a variety of chemical reactions [6], among them the destruction of hazardous waste [7]. We have already confirmed that waste plastics such as phenol resin decompose into their monomeric compounds in sub and supercritical water [8, 9]. In this study, the decomposition reactions of polycarbonate in high temperature water were carried out and have studied the mechanism for decomposition of polycarbonate. To reduce recycling cost, decomposition reaction under mild conditions than ever was attempted, and the prepolymer of phenol resin was synthesized by using the decomposed products to make clear the effectiveness of decomposition products as chemical raw materials.

Experimental procedure

Polycarbonate was reacted after pulverizing. A 10 mL tubular bomb reactor was used as the reactor in which the reaction temperature was attained within 2 min [10]. The typical reaction was carried out for 0.1 g of polycarbonate in 3 mL water. After the reaction, products were extracted by ether and measured by GC/MS and GC. In the thermal analysis the temperature increasing rate was 10 °C/min.

Results and discussions

Thermal stability of polycarbonate resin

Figure 1 shows the weight loss curve of polycarbonate resin under an inert atmosphere. Polycarbonate resin was stable thermally below 400 °C and weight loss started from around 450 °C indicating high thermal stability of polycarbonate in dry conditions. The final weight loss reached 72.8% at 600 °C.

The decomposition reaction of polycarbonate in high temperature water

In order to clarify the reactivity of polycarbonate resin, reactions of polycarbonate were carried out at 300 °C for

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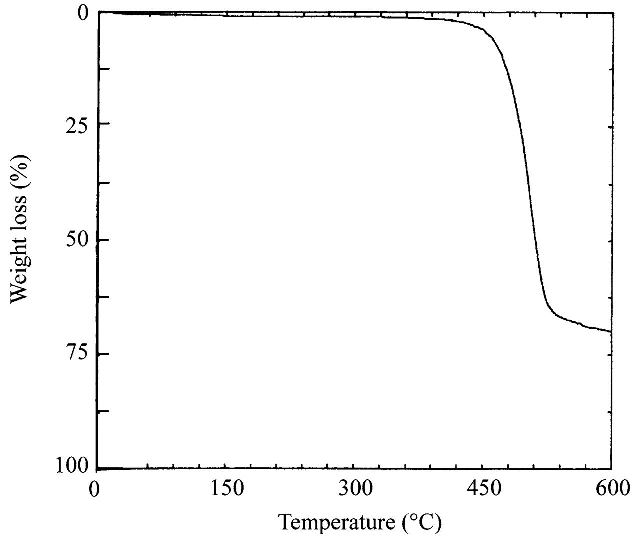


Fig. 1 Weight loss curve of polycarbonate resin

10 h without solvent, or in solvents such as water, toluene and benzene. No reaction occurred where polycarbonate resin alone was heated at 300 °C for 10 h. Though the reaction temperature is over the melting point (240 °C) of the polycarbonate resin, the decomposition reaction was observed in the reaction with water at 300 °C. The resin was decomposed into monomers such as phenol, *p*-isopropenylphenol and bisphenol A. Its total yield reached near 50 wt% at 300 °C for 10 h. On the other hand, the decomposition reaction was not confirmed in the reaction in toluene and benzene. It was suggested that water is excellent solvent and reactant for hydrolysis in the decomposition reaction of polycarbonate resin.

Effect of additives on the decomposition reaction

In order to accelerate decomposition of polycarbonate resin at low reaction temperature, the reaction was carried out in the presence of additives at 250 °C. Table 1 shows the results of reactions with additives. Various acids, basic compounds and salts were used as additives. As shown in Table 1, acidic additives had no effect, but alkaline additives had a large positive effect on the decomposition reaction. In the addition of Na_2CO_3, the whole yield reached over 60 wt% and phenol was as much as 47.5 wt%. In the addition of NH_4OH and $CO(NH_2)_2$, the yield of bisphenol A was larger than that of phenol. Without additives the decomposition reaction scarcely occurred at 250 °C for 1 h even in water. The addition of a small amount of alkaline compound accelerated the decomposition reaction of polycarbonate resin even at low temperature such as 250 °C.

Decomposition reaction under mild conditions in Na_2CO_3 aqueous solution

As shown in Table 1, Na_2CO_3 was effective to increase the yields of monomeric compounds. Figure 2 shows the yield of identified products in the reaction of polycarbonate with Na_2CO_3 aqueous solution of various concentrations at 250 °C for 1 h. It was confirmed that decomposition reaction of polycarbonate was accelerated by an increase of concentration of Na_2CO_3. In the case of 100 mM Na_2CO_3 aqueous solution, the yield of phenol reached 65.0 wt%. However, the high concentration of Na_2CO_3 more than 300 mM was not effective to increase the yield.

Decomposition reaction under mild conditions than ever was carried out in Na_2CO_3 aqueous solution. Figure 3 shows the yield of identified products in the reaction of polycarbonate with Na_2CO_3 aqueous solution at lower temperature than 250 °C for 0.5 and 1 h. In the reaction at low temperature, yield of bisphenol A and *p*-isopropenylphenol, *p*-*tert*-butylphenol increased while the yield of phenol decreased. These results suggested that the secondary decomposition of bisphenol A and *p*-isopropenylphenol had occurred. The residue of un-reacted polycarbonate remained at 190 °C for 0.5 h although completely decomposed at 190 °C for 1.0 h indicating secondary decomposition reaction of bisphenol A.

Figure 4 shows the reaction of polycarbonate at lower temperature than 170 °C. The un-reacted polycarbonate has remained though the reaction time was extended to 3 h at 170 °C in 100 mM Na_2CO_3 aqueous solution. Therefore, the concentration of Na_2CO_3 aqueous solution was increased. In the case of 500 mM Na_2CO_3 aqueous solution, polycarbonate completely decomposed even in the reaction at 150 and 170 °C. The residue of un-reacted polycarbonate remained at 130 °C in 500 mM, which completely decomposed in 1,000 mM. The polycarbonate could be decomposed at considerably low temperature by raising the concentration of Na_2CO_3 aqueous solution.

Consideration of the mechanism in the decomposition reaction of polycarbonate

Because the possibility of the secondary decomposition of bisphenol A and *p*-isopropenylphenol was suggested, these compounds were reacted in the Na_2CO_3 aqueous solution at 170–250 °C to obtain information on the decomposition reaction mechanism of polycarbonate. Figure 5 shows the reaction products of bisphenol A in 100 mM Na_2CO_3 aqueous solution for 1 h. In the case of the reaction at lower than 250 °C, production of phenol and *p*-isopropenylphenol was confirmed while only the phenol was recovered in the reaction at 250 °C and the yield reached

Table 1 The decomposition reaction of polycarbonate with additive at 250 °C for 1 h

Additive	Weight ratio (wt%)	Yield of product (wt%)		
		Phenol	*p*-isopropenylphenol	Bisphenol A
–	–	0.0	0.0	0.0
HCl	4.0	0.0	0.0	0.0
H_2SO_4	4.0	0.0	0.0	0.0
HNO_3	4.0	0.0	0.0	0.0
CH_3COOH	4.0	0.0	0.0	0.0
Na_2CO_3	4.0	47.5	8.0	5.1
NH_4OH	4.0	8.7	2.3	37.9
$CO(NH_2)_2$	4.0	0.0	1.6	39.8
CH_3CH_2OH	4.0	0.0	0.0	0.0
$CaCO_3$	4.0	0.0	0.0	0.0
NaCl	4.0	0.0	0.0	0.0

Weight ratio (wt%): weight of additive/weight of polycarbonate

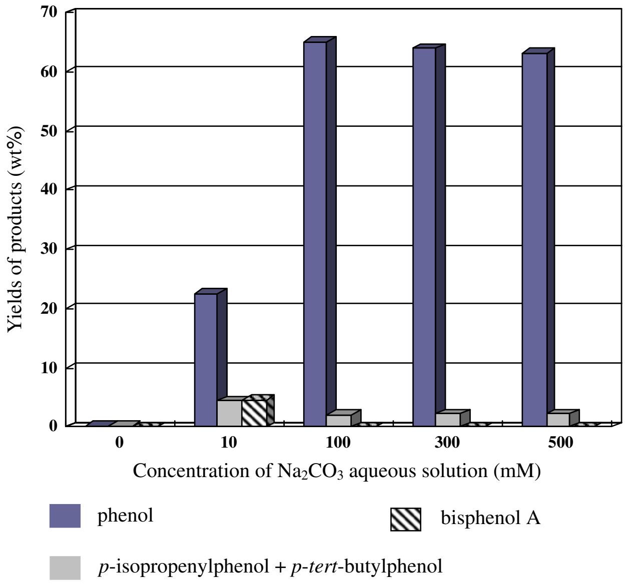


Fig. 2 Decomposition reaction of polycarbonate in 0–500 mM Na_2CO_3 aqueous solution at 250 °C for 1 h

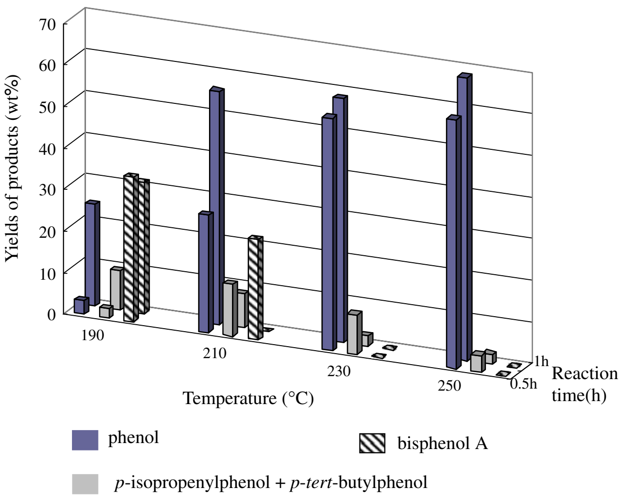


Fig. 3 Decomposition reaction in 100 mM Na_2CO_3 aqueous solution at 190–250 °C for 0.5–1 h

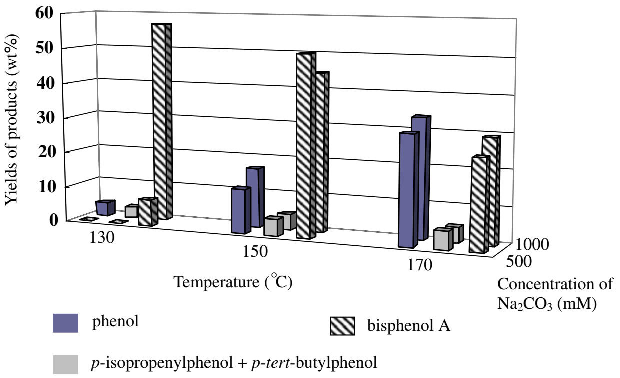


Fig. 4 Decomposition reaction of polycarbonate in 500 (pH 11.3)–1,000 mM (pH 11.5) Na_2CO_3 aqueous solution at 130–170 °C for 3 h

98%. This suggested that *p*-isopropenylphenol decomposed to phenol. In the reactions of *p-tert*-butylphenol and phenol in 100 mM Na_2CO_3 aqueous solution at 250 °C for 1 h, recovery reached 88.9% and 87.0%, respectively, suggesting that these products are thermally stable at 250 °C. *p-tert*-Butylphenol was contained in the polycarbonate resin as a molecular weight adjustment regulator in the course of polycarbonate preparation. The presence of *p-tert*-butylphenol in the products suggested that it was melted in the decomposition reaction of polycarbonate. As shown in Scheme 1, the mechanism for the decomposition reaction of polycarbonate is considered that bisphenol A is produced in the first step of the decomposition of polycarbonate, and *p*-isopropenylphenol and phenol are produced in the next step by the reaction of bisphenol A, and then phenol is produced by the decomposition of various intermediate products.

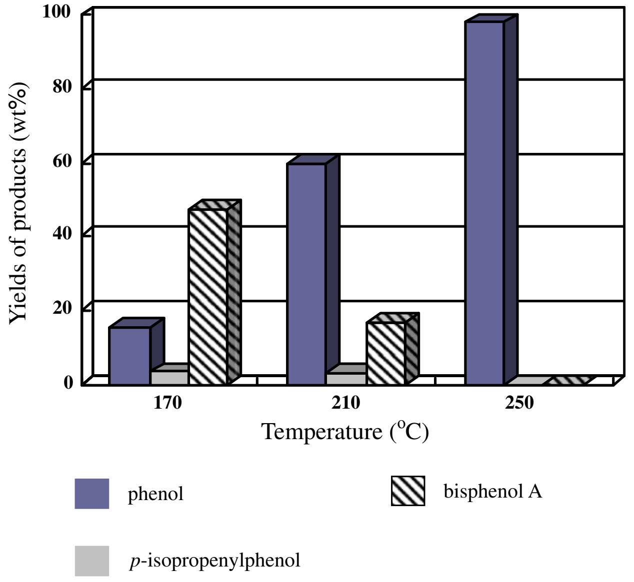
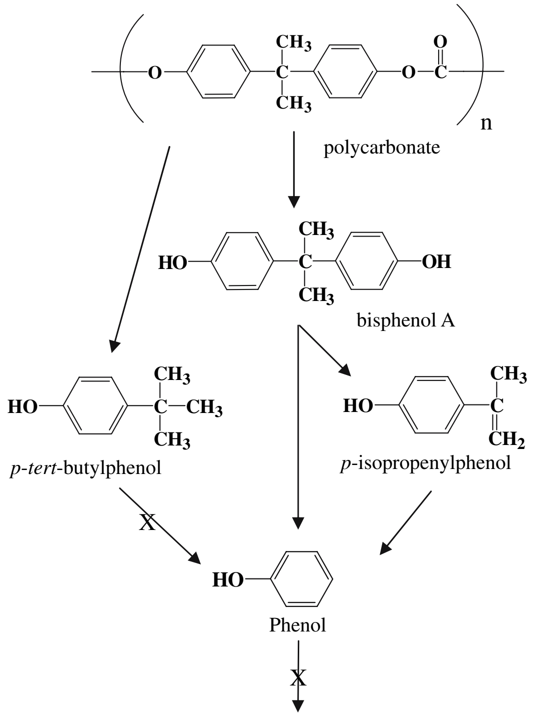


Fig. 5 Decomposition reaction of bisphenol A in 100 mM Na_2CO_3 aqueous solution at 170–250 °C for 1 h



Scheme 1 Decomposition reaction of polycarbonate

Synthesis of phenol resin by using decomposition products of polycarbonate

The prepolymer of phenol resin was prepared by the conventional preparation method from the decomposition products. Two kinds of the prepolymer of phenol resin were prepared by using the pure phenol and decomposition products of polycarbonate. The decomposition products were obtained by decomposing polycarbonate at 250 °C in 100 mM Na_2CO_3 aqueous solution. Formaldehyde and the hydrochloric acid are added to the phenol or decomposition products, and then were heated at 85 °C with stirring for 2 h. The obtained products were cooled, and were heated at 175 °C to remove un-reactive materials. Thus, the molecular weights of solid products were determined by GPC analysis.

Figure 6 shows the molecular weigh distribution measured by GPC analysis. The prepolymer yield prepared by using pure phenol was 71.0% (a) while the yield using decomposition products was 51.2% (b). The molecular weight of products prepared by using decomposition products was almost equal to the molecular weight of the prepolymer synthesized from the pure phenol, suggesting that the prepolymer of phenol resin can be synthesized by using decomposition products.

Conclusions

We have confirmed that the decomposition reaction of polycarbonate occurred even at 130 °C. In the reaction at 300 °C for 10 h in water alone, phenol yield reached more than 40% although no production of phenol was observed

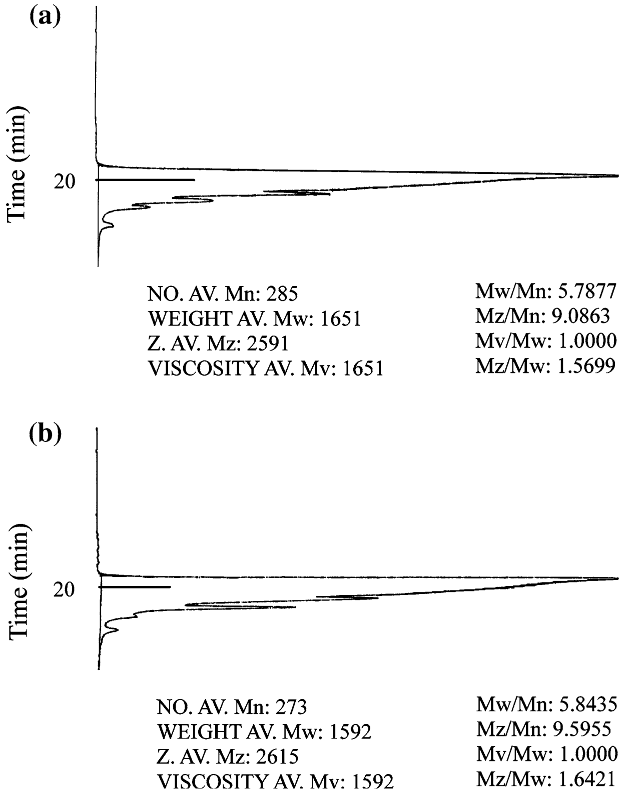


Fig. 6 GPC chart of prepolymer of phenol resin synthesized with pure phenol (**a**) and decomposition products (**b**)

in the neat reaction of polycarbonate without water. Water is not expensive and non-toxic solvent. Our results indicate that high temperature water is also a superior medium for the decomposition reaction of polymeric compounds.

References

1. Müller-Hagedorn M, Bockhorn H (2005) Feedstock recycling of plastics. Universitäts Verlag, Karlsruhe
2. Mertincat J, Kirsten A, Predel M, Kaminsky W (1999) J Anal Appl Pyrol 49:87
3. Scheirs J, Kaminsky W (2006) Feedstock recycling and pyrolysis of waste plastics. Wiley, Chichester
4. Shaw RW, Bill TB, Clifford AA, Eckert CA, Frank EU (1991) Chem Eng News 12:26
5. Kiran E, Sengers J (1994) Supercritical fluids, NATO ASI Ser E, vol 273. Kluwer Academic Publishers
6. Abraham MA, Sunai AK (1994) Supercritical fluids, vol 273. ACS Symposium Ser., Kluwer Academic Publishers
7. Savage PE, Gopalan S, Mizan TI, Martino CJ, Brock EE (1995) Am Inst Chem Eng J 41:1723
8. Suzuki Y, Tagaya H, Asou T, Kadokawa J, Chiba K (1999) Ind Eng Chem Res 38:1391
9. Tagaya H, Kato K, Kadokawa J, Chiba K (1999) Polym Degrad Stab 64:289
10. Townsend SH, Abraham MA, Huppert GL, Klein MT, Paspek SC (1988) Ind Eng Chem Res 27:143