

## The Reaction of Model Compounds of Plastics in Sub- and Supercritical D<sub>2</sub>O

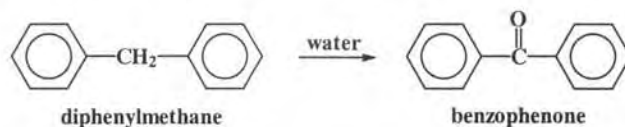
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Model compounds of waste plastics including thermoplastic and thermosetting resins were reacted in sub- and supercritical D<sub>2</sub>O to make clear the role of water on the decomposition reaction of polymers in sub- and supercritical water. Chemical participation of water on the bond cleavage reaction and hydrogenation reaction were confirmed by the analyses of the reaction products.

### Introduction

During a past decade, a number of oxidative destruction of hazardous waste in supercritical water have been investigating. In the reactions, oxidizing agents like air, oxygen, or hydrogen peroxide can initiate and promote the oxidation reactions [1-3]. Water is an attractive solvent because of their excellent physical properties, nontoxicity and low cost. We have already reported that not only thermoplastic resins, but also thermosetting resins were decomposed into their monomers in sub- and supercritical water [4-7]. Interestingly, the reactions were performed even under argon atmosphere, and cleavage of methylene bond connecting aromatic units in phenol resin was also confirmed. In the reaction of diphenylmethane in supercritical water, the production of benzophenone was confirmed indicating the presence of oxygen source as shown below. Also in the reaction of diphenylmethane in supercritical H<sub>2</sub><sup>18</sup>O, the production of benzophenone containing <sup>18</sup>O was confirmed [8]. It indicated the presence of chemical participation of water on the decomposition reaction of polymers in supercritical water.

In this study, to make clear the role of water on the bond cleavage reaction of plastics under argon atmosphere, model compounds of plastics were reacted in D<sub>2</sub>O.



### Experimental

Model compound of plastics and H<sub>2</sub>O or D<sub>2</sub>O were introduced into the 10 ml tubing bomb reactor. Typically, 0.1g of model compounds were reacted in 1ml water. The

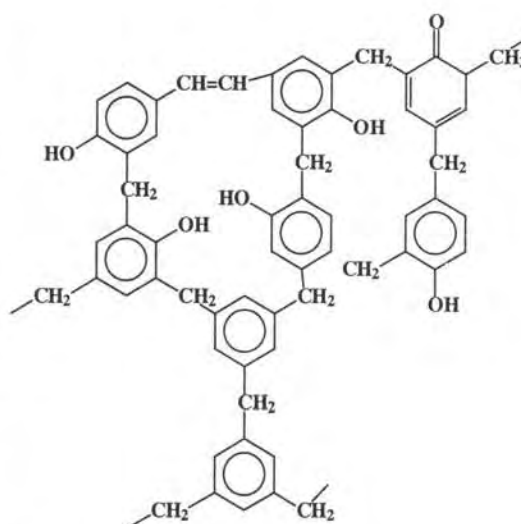
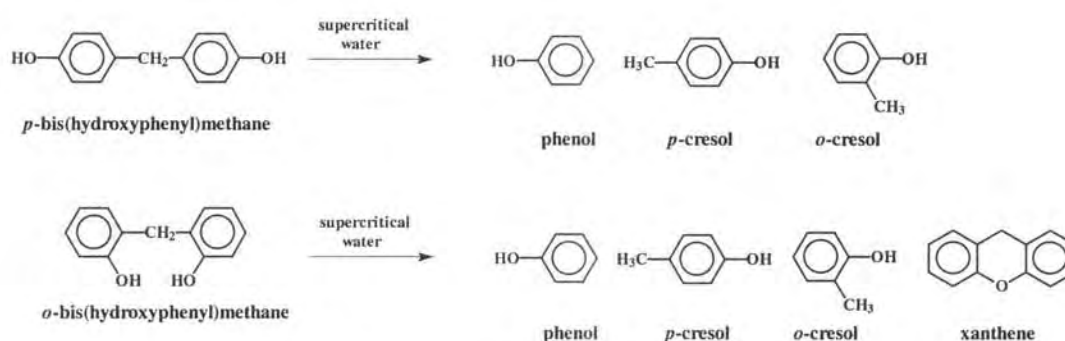


Figure 1 Representative structure of molding materials of phenol resin in which methylene bonds connect aromatic units.

reactions were carried out after flushing the reactor with argon gas. The reaction temperature was attained within 2min by putting the reactor into sand bath. Reaction products were analyzed by GC, GC/MS, HPLC and  $^1\text{H-NMR}$ .

## Results and Discussions

Cleavage reactions of methylene bonds in supercritical water were confirmed in the reactions of model compounds such as bis(hydroxyphenyl)methanes of phenol resin. Phenol, *o*-cresol and *p*-cresol were main monomeric products obtained by the reactions in supercritical water. Production of xanthene was also confirmed in the reaction of *o*-bis(hydroxyphenyl)methane. In the decomposition reaction of prepolymers of phenol resin, yields of identified products reached more than 90% indicating the presence of hydrogen donor compounds [6].



Reaction of bis(hydroxyphenyl)methanes in  $\text{D}_2\text{O}$  In the reaction of two bis(hydroxyphenyl)methanes in  $\text{D}_2\text{O}$ , products containing deuterium were obtained. In the case of phenol, molecular mass number increased from 94 to 97 by replacement  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$ . It indicated the presence of H-D exchange reactions between  $\text{D}_2\text{O}$  with hydrogen on benzene ring. To obtain information on H-D exchange reaction, phenol was treated in  $\text{D}_2\text{O}$  at 430

$^\circ\text{C}$ . It was confirmed that by the  $\text{D}_2\text{O}$  treatment, molecular mass number of phenol increased from 94 to 97. We also confirmed that molecular mass number change was not observed in the thermal treatment of cyclohexanol and naphthalene in  $\text{D}_2\text{O}$  as shown in Figure 2. It suggests that hydroxyl groups on aromatic ring play the important role on H-D exchange reactions.

Also 1-naphthol and three kinds of dihydroxynaphthalene were treated in supercritical  $\text{D}_2\text{O}$  at 430 $^\circ\text{C}$  for 1h. Mass number changes were +2 and +4 as shown in Figure 2. In  $^1\text{H-NMR}$  spectrum of phenol, peaks of a part of aromatic hydrogen disappeared by the thermal treatment in  $\text{D}_2\text{O}$  indicating occurrence of H-D exchange reaction. To confirm the position of H-D exchange reaction, 4-phenylphenol was treated in  $\text{D}_2\text{O}$  at 430 $^\circ\text{C}$ . By the thermal treatment of 4-phenylphenol, molecular mass

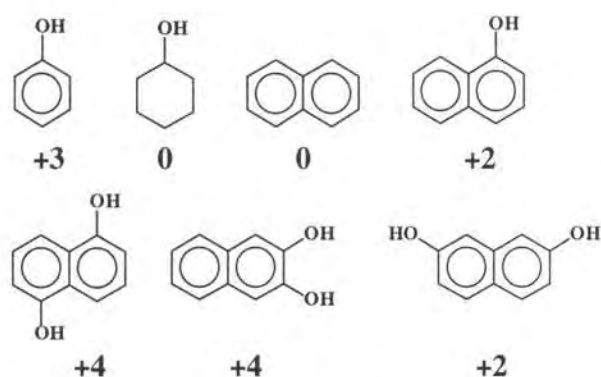


Figure 2 Thermal treatment in  $\text{D}_2\text{O}$ . The numbers indicated below the compounds are changes of molecular mass number.

number increased from 170 to 172. These results and  $^1\text{H-NMR}$  spectrum of 4-phenylphenol suggested that hydrogens at the ortho position to hydroxyl groups were exchanged as shown in Figure 3.

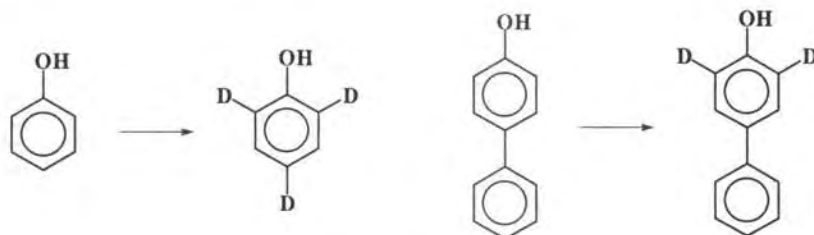


Figure 3 H-D exchange reaction of phenol and 4-phenylphenol in  $\text{D}_2\text{O}$  at  $430^\circ\text{C}$ .

Reaction of benzylalcohol in  $\text{D}_2\text{O}$  Three benzyl compounds were reacted in  $\text{D}_2\text{O}$  to obtain information on the role of water. Toluene was obtained by the reaction of benzylbromide, benzylchloride and benzylalcohol in supercritical water at  $430^\circ\text{C}$  as shown in Figure 4.

The production of toluene suggested the possibility of hydrido ion attack to benzyl cation.

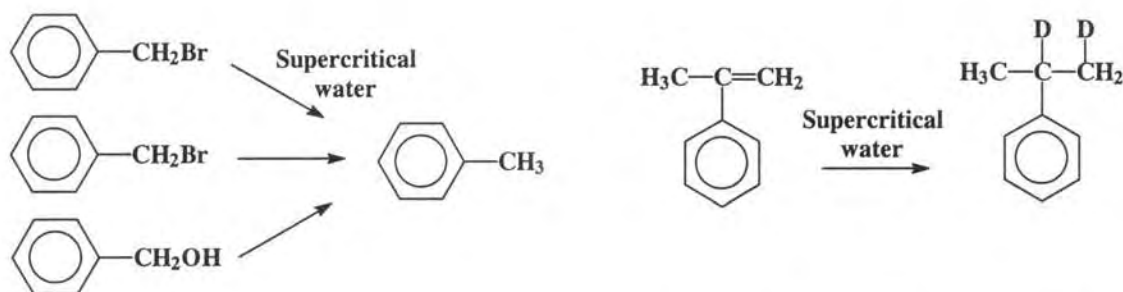


Figure 4 Thermal treatment of benzyl compounds in  $\text{D}_2\text{O}$  at  $430^\circ\text{C}$ .

Figure 5 Thermal treatment of  $\alpha$ -methylstyrene in  $\text{D}_2\text{O}$  at  $430^\circ\text{C}$ .

Reaction of  $\alpha$ -methylstyrene in  $\text{D}_2\text{O}$   
By the reaction of  $\alpha$ -methylstyrene in  $\text{D}_2\text{O}$ , the production of cumene was confirmed. Molecular weights of cumene obtained by the reaction in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  were 120 and 122, respectively, as shown in Figure 6. It indicated the occurrence of hydrogen supply reaction from water to  $\alpha$ -methylstyrene in the reaction of supercritical conditions. Direct hydrogen addition was difficult to consider. As shown in Figure 4, benzylalcohol was hydrogenated to toluene. In the production of cumene,

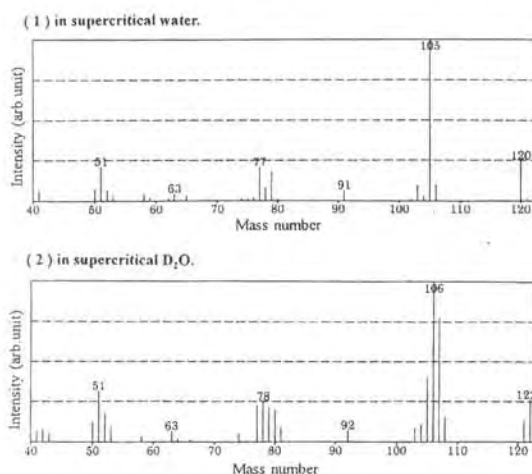


Figure 6 GC/MS spectra of cumene obtained by the reaction of  $\alpha$ -methylstyrene in  $\text{D}_2\text{O}$  at  $430^\circ\text{C}$ .

intermediate compound having hydroxyl groups might be produced.

### Conclusions

Chemical participation of water in the reactions in supercritical conditions was confirmed by using D<sub>2</sub>O instead of H<sub>2</sub>O. Recently, organic chemical reactions in supercritical water are attracting increased attention [9]. We believe supercritical water has a potential as an excellent medium for chemical recycling of plastics.

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