Relative Reactivity of Phenols and Formation of Phenolic Co-condensed Resins

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ABSTRACT: Relative reactivities of various phenols (*i.e.*, *m*-cresol (*m*-CR), *p*-cresol (*p*-CR), phenol (Ph), *p*-*t*-butylphenol (*p*-BP), and *p*-ethylphenol (*p*-EP)) were determined when the reactivity of *m*-CR was taken as unity. Co-condensation for *m*-CR/*p*-BP/formaldehyde and *m*-CR/*p*-EP/formaldehyde systems was done and the reactivity of the phenols and molecular structure were examined. The reactivity ratios of *p*-BP and *p*-EP to *m*-CR in the co-condensation were higher than in the condensation. The composition of *m*-CR/*p*-BP co-condensed resins was strongly affected by feed composition, molecular weight of co-condensed resin, and degree of reaction when the resin was formed. These features were due to differences in reactivity between *m*-CR and *p*-BP.

KEY WORDS Co-condensation / *m*-Cresol / *p*-*t*-Butylphenol / *p*-Ethylphenol / Relative Reactivity / Composition of Co-condensed Resin /

Phenolic resins have superior characteristics such as heat resistance, dimensional stability, and electric insulation, which are very important industrially. However, they have also serious defects like brittleness, which has limited their applicable field. To improve this property, some modifications are needed. Co-condensation of various phenols is useful to give high-performance properties to phenolic resins as engineering material.

In view of the importance of the co-condensation of phenols in the manufacture of phenolic resins, surprisingly few papers have been reported concerning the formation mechanism of phenolic co-condensed resin kinetically and statistically, and molecular structures of co-condensed resins. Since the formation reaction is very complex because the reaction consists of addition and condensation, the reactivities of phenolic monomers are different, and gelation easily occurs, it takes much time to analyze them. To elucidate the complex reaction mechanism of phenolic resins, we proposed a Monte Carlo (MC) computer simulation technique.¹⁻⁷ In the previous paper,⁷ the co-condensation mechanism of phenol and *p*-*t*-butylphenol with formaldehyde was analyzed by simulation, and the reactivity ratio of phenol to *p*-*t*-butylphenol was determined and the effect on the molecular structure of co-condensed resins was discussed. However, further information about the relationship between the reactivity of phenols and molecular structure is needed to make the co-condensation mechanism of phenols clearer.

In this paper, the co-condensation mechanism of the two kinds of phenols, whose reactivities are much different each other, is analyzed. The co-condensation of *m*-cresol/*p*-*t*-butylphenol/formaldehyde and *m*-cresol/*p*-ethylphenol/formaldehyde systems was done and the reactivity of the phenols and molecular structures are examined. In particular, the composition of *m*-cresol/*p*-*t*-butylphenol co-condensed resins is determined as functions of feed composition, molecular weight of co-condensed resin and degree of reaction when the resin was formed. The reaction mechanism of the co-condensation is discussed using model compounds.

EXPERIMENTAL

Materials

Commercially available *m*-cresol (*m*-CR), *p*-cresol (*p*-CR), phenol (Ph) were distilled before use. *p*-*t*-Butylphenol (*p*-BP) and *p*-ethylphenol (*p*-EP) were used without further purification. Commercially available 37% formalin and conc. HCl were used without further purification. Acetone was distilled and used for fractionation of co-condensed resins. Hexane was used after drying over molecular sieves (4A) for 2 days. Tetrahydrofuran (THF) was distilled and used for gel permeation chromatography (GPC) measurement.

Condensation of Each Phenol. 0.1 mol of phenols (*m*-CR, *p*-CR, Ph, *p*-BP, and *p*-EP), 10.8 g of 37% formalin (as 0.1 mol of formaldehyde), and 0.16 mL of conc. HCl (2 mmol) as catalyst were charged into a 100 mL three-necked flask equipped with a reflux condenser and stirrer. The mixture was heated at 75°C for 2 h.

Co-condensation of Phenols. *m*-CR/*p*-BP and *m*-CR/*p*-EP co-condensed resins were prepared as follows. *m*-CR/*p*-BP or *m*-CR/*p*-EP, 37% formalin, and conc. HCl as catalyst were charged into a 100 mL three-necked flask equipped with a reflux condenser and stirrer. The mixture was heated at 75°C. Reaction conditions for the preparation of samples are summarized in Tables I and II.

Preparation of Model Compounds. The synthetic pathways are shown in Scheme 1. The procedure is described below.

Preparation of 2,6-Bis[3-(2-hydroxy-5-*t*-butylbenzyl)-2-hydroxy-5-*t*-butylbenzyl]-4-*t*-butylphenol (5BP). 5BP was prepared according to the literature.⁸

Preparation of 2,6-Bis[3-(2-hydroxy-4-methylbenzyl)-2-hydroxy-5-*t*-butylbenzyl]-4-*t*-butylphenol (5mT). 2,6-Bis(2-hydroxy-5-*t*-butylbenzyl)-4-*t*-butylphenol (3BP) was prepared according to the literature.⁸ 47.4 g of 3BP (0.1 mol) was dissolved in a mixture of 100 mL of 10 *N* NaOH aqueous solution and 100 mL of ethanol. Four 108 g portions of 37% formalin (as total 4.0 mol of

Table I. Reaction conditions and degree of reaction (*p*) for *m*-CR/*p*-BP co-condensation

Sample code	Molar ratio in feed				Temp	Time	<i>p</i>
	<i>m</i> -CR	<i>p</i> -BP	HCHO	HCl	°C	min	
A	1	4	5	0.10	75	420	0.74
B	1	4	5	0.10	75	30	0.37
C	1	2	3	0.06	75	210	0.65
D	1	2	3	0.06	75	65	0.60
E	1	2	3	0.06	75	16	0.45
F	2	3	5	0.10	75	120	0.69
G	2	3	5	0.10	75	15	0.45
H	1	1	2	0.04	75	120	0.73
I	3	2	5	0.10	75	120	0.73

Table II. Reaction conditions and degree of reaction (*p*) for *m*-CR/*p*-EP co-condensation

Sample code	Molar ratio in feed				Temp	Time	<i>p</i>
	<i>m</i> -CR	<i>p</i> -BP	HCHO	HCl	°C	min	
J	2	3	5	0.10	75	180	0.79
K	1	1	2	0.04	75	120	0.75
L	3	2	5	0.10	75	90	0.80

Scheme 1. Synthetic pathway of 5BP and 5mT.

formaldehyde) were added dropwise at 24 h intervals and the mixture was stirred at room temperature for additional 72 h. After neutralized with 2 *N* HCl aqueous solution, dimethylol of 3BP (3BPM) was precipitated and filtrated. To remove formaldehyde, the precipitate was washed with water and dried. 16 g of 3BPM (0.03 mol), 13 g of *m*-CR (0.12 mol), and 1.6 mL of conc. HCl (0.02 mol) were dissolved in 200 mL of ethanol and the mixture was refluxed for 3 h. The solvent was removed under vacuum and the residue was washed with 0.025 *N* NaOH aqueous solution to remove unreacted *m*-CR. The product was recrystallized from acetone–hexane=(1:1, v/v). The structure was confirmed by ¹H NMR and GPC.

Model Co-condensation. 5BP or 5mT (2.5 mmol) and 3.0 g of *p*-BP (20 mmol) were charged into a 100 mL three-necked flask equipped with a reflux condenser and stirrer and melted at 90°C. After cooling to room temperature 2.7 g of 37% formalin (as 25 mmol of formaldehyde) and 2.5 mL of 1 *N* HCl aqueous solution were added and stirred at 90°C for 90 min.

Fractionation of Co-condensed Resin. *m*-CR/*p*-BP and *m*-CR/*p*-EP co-condensed resins were fractionated by successive solution fractionation method with acetone as solvent and hexane as nonsolvent or silica gel chro-

matography using acetone–hexane=(1:1, v/v) as an eluent. The fractions were used to determine the compositions and molecular structures of co-condensed resins.

Measurements

GPC measurement was carried out by a JASCO HPLC 880-PU equipped with three polystyrene gel packed column sets (Tosoh TSKgel G3000H8+G2000H8+G2000H8, Tosoh TSKgel G1000H_{HR} × 2, and Tosoh TSKgel GMH_{HR} × 2) and Tosoh UV-8011 (wave length 270 nm) as a detector. THF was used as the mobile phase. The flow rate was 1.0 mL min⁻¹ for TSKgel G1000H_{HR} × 2 and TSKgel GMH_{HR} × 2 columns, and 1.5 mL min⁻¹ for TSKgel G3000H8+G2000H8+G2000H8 columns. Concentration of the sample in THF was 0.5 wt%. The molecular weight of each fraction was determined by GPC using polystyrene standards. The amount of unreacted monomers was determined by GPC and the degree of reaction of resin was calculated from the ratio of peak area of monomer to that of the others. ¹H NMR spectra were obtained with a JEOL JNM-FX100 spectrometer (100 MHz). Deuteriochloroform and penta-deuteropyridine were used as solvents and tetra-

methylsilane (TMS) was used as reference.

RESULTS AND DISCUSSION

Relative Reactivity of Phenols

The reactivities of various phenols (*i.e.*, *m*-CR, *p*-CR, Ph, *p*-BP, and *p*-EP) were determined from the rate of disappearance of them to form resins. The time dependence of the amounts of unreacted phenols in the condensation with formaldehyde at 75°C by using HCl catalyst is shown in Figure 1. The initial slope indicated by each solid line in the figure represents the rate of disappearance of phenols, since the reaction rate followed a first order rate law with respect to the concentrations of phenols under acidic conditions.⁹ The reactivity of various phenols is listed in Table III, when the reactivity of *m*-CR is taken as unity. The reactivity of *m*-CR was highest and that of *p*-BP, lowest. The ratio of the reactivity of *p*-BP to *m*-CR is 0.03, and that of *p*-EP to *m*-CR is 0.09. Co-condensation in this study was done by using *m*-CR/*p*-BP and *m*-CR/*p*-EP systems, whose reactivities much differ. The typical time dependence of the amounts of unreacted monomers in the co-condensation for *m*-CR/*p*-BP/formaldehyde and *m*-CR/*p*-EP/formaldehyde systems at 75°C by using HCl catalyst is shown in Figures 2 (a) and 2 (b). The ratio of reac-

tivity of *p*-BP and *p*-EP to *m*-CR in the co-condensation was calculated from the slope of each solid line in the figures. The values at various molar ratios of monomers in feed are listed in Table IV. The ratios of reactivity of *p*-BP and *p*-EP to *m*-CR in the co-condensation were constant regardless of variation of molar ratios of monomers in feed and relative reactivities of *p*-BP to *m*-CR and *p*-EP to *m*-CR were higher than in the condensation as listed in Table III. This seems to be due to 1) decrease of reactivity of *m*-CR and 2) increase of reactivity of *p*-BP or *p*-EP in the co-condensation. The change of the reactivity ratios is discussed in Model Co-condensation.

Table III. Relative reactivities of various phenols in condensation

Compound	Relative reactivity ^a
<i>m</i> -Cresol	1.00
<i>p</i> -Cresol	0.18
Phenol	0.59
<i>p</i> - <i>t</i> -Butylphenol	0.03
<i>p</i> -Ethylphenol	0.09

^a *m*-Cresol taken as unity.

Table IV. Relative reactivities of phenols in co-condensation under various molar ratio of monomers in feed

Molar ratio in feed	Relative reactivity ^a		
	<i>m</i> -CR	<i>p</i> -BP	<i>p</i> -EP
<i>m</i> -CR/ <i>p</i> -BP			
2/3	1.00	0.09	
1/1	1.00	0.08	
3/2	1.00	0.06	
<i>m</i> -CR/ <i>p</i> -EP			
2/3	1.00		0.14
1/1	1.00		0.16
3/2	1.00		0.14

^a *m*-Cresol taken as unity.

Figure 1. Comparison of reactivities of phenols in condensation with formaldehyde at 75°C.

Figure 2. Comparison of reactivities of *m*-CR and *p*-BP (a) and *m*-CR and *p*-EP (b) in the co-condensation with formaldehyde at 75°C. (Molar ratios of *m*-CR/*p*-BP and *m*-CR/*p*-EP are 2/3, respectively.)

Figure 3. ^1H NMR spectrum of $m\text{-CR}/p\text{-BP}$ co-condensed resin obtained from the molar ratio of $m\text{-CR}/p\text{-BP}=2/3$ in the feed in pentadeuteropyridine. Peaks corresponding to solvent are marked with $\circ$.

Figure 4. Plots of composition of $m\text{-CR}/p\text{-BP}$ co-condensed resin obtained from various molar ratios of $m\text{-CR}$ to $p\text{-BP}$ in the feed against molecular weight. (Degree of reaction = 0.7–0.8).

Composition of Co-condensed Resins

The compositions of fractionated co-condensed resins for $m\text{-CR}/p\text{-BP}$ system were determined with ^1H NMR in pentadeuteropyridine. The typical spectrum of $m\text{-CR}/p\text{-BP}$ co-condensed resin obtained from the molar ratio of $m\text{-CR}/p\text{-BP}=2/3$ in feed is shown in Figure 3. From the ratio of peak areas of methyl protons of t -butyl group of $p\text{-BP}$ units at 1.1–1.3 ppm and methyl protons of $m\text{-CR}$ units at 2.1–2.4 ppm, composition could be calculated. The results were obtained as functions of compositions of monomers in feed, molecular weight of the co-condensed resin, and degree of reaction p when the resin was formed. Figure 4 shows the content of $m\text{-CR}$ in co-condensed resins formed at $p=0.7$ –0.8 as a function of the molecular weight at various molar ratios of $m\text{-CR}$ and $p\text{-BP}$ in feed. The compositions of copolymers depend on the composition of monomers in feed for radical and ionic copolymerizations. The content of $m\text{-CR}$ in co-condensed resin is much higher than that in feed, according to the higher reactivity of $m\text{-CR}$ than that of $p\text{-BP}$. The content of $m\text{-CR}$ becomes higher as the molecular weight increases. The compositions of co-condensed resins were strongly affected by the composition of monomers in feed as well as molecular weight. The same was found in $m\text{-CR}/p\text{-EP}$ co-condensation system.

Figure 5 shows the content of $m\text{-CR}$ in co-condensed resins as functions of molecular weight and degree of

Figure 5. Plots of composition of $m\text{-CR}/p\text{-BP}$ co-condensed resin obtained from the molar ratios of $m\text{-CR}$ to $p\text{-BP}$ 1/2 and 2/3 in the feed against molecular weight.

Figure 6. Plots of composition of $m\text{-CR}/p\text{-BP}$ co-condensed resin against the feed composition.

reaction when the resin was formed. The content of $m\text{-CR}$ is higher as the degree of reaction is lower. This means that $m\text{-CR}$ is preferentially consumed to form the co-condensed resins with higher content of $m\text{-CR}$ units in the initial stage of the co-condensation. Figure 6 shows the effects of monomer composition in the feed on the composition of co-condensed resins as functions of molecular weight and degree of reaction of the co-condensed resins. As shown in Figure 6, the composition of co-condensed resins for $m\text{-CR}/p\text{-BP}$ system is strongly affected by the monomer composition in the feed, molecular weight, and degree of reaction. The effect of the degree of reaction may be the same as that of the monomer composition in the feed, because the monomer composition changes continuously and widely from the beginning to end of co-condensation. These features arise from differences in reactivity between $m\text{-CR}$ and $p\text{-BP}$.

Model Co-condensation

According to GPC chromatograms of co-condensed resins for $m\text{-CR}/p\text{-BP}$ system, it became obvious that higher molecular weight components did not form at larger molar ratio of $p\text{-BP}$ to $m\text{-CR}$ in feed. It is consider-

Figure 7. GPC chromatograms of 5BP/*p*-BP (a) and 5mT/*p*-BP (b) co-condensed resins.

Figure 8. Time dependences of weight percentage of oligomers obtained from 5BP/*p*-BP (a) and 5mT/*p*-BP (b) systems.

ed that the high content of *p*-BP in the co-condensed resin must make the reactivity of the resin lower, leading to less molecular weight. To confirm this, model co-condensation was done using 5-membered linear oligomer of *p*-BP (5BP) and oligomer obtained by end-capping 3-membered oligomer of *p*-BP by *m*-CR (5mT). The synthetic pathway and molecular structure of 5BP and 5mT are shown in Scheme 1. The reactive sites of 5BP are in *p*-BP units at both ends and those of 5mT are in *m*-CR units. GPC chromatograms of the co-condensed resins obtained from 5BP/*p*-BP/formaldehyde and 5mT/*p*-BP/formaldehyde systems are shown in Figures 7 (a) and 7 (b). In the figures the elution volume (E.V. in mL) and degree of polymerization of *p*-BP (*N*-mer) are used as scale. In the GPC chromatograms for 5BP/*p*-BP system, the peak of 5BP did not vary, but the peaks of 2–4 membered oligomers of *p*-BP appeared and the peak areas were increasing with time (Figure 7 (a)). In GPC chromatograms for 5mT/*p*-BP system, the peak area of 5mT decreased and a new peak appeared

in the higher molecular weight region than 5mT with time (Figure 7 (b)). The time dependences of weight percentages of oligomers obtained from 5BP/*p*-BP and 5mT/*p*-BP systems are shown in Figures 8 (a) and 8 (b). Obviously, *p*-BP was consumed to form 2–4 membered oligomers of *p*-BP, not to react with 5BP, in the 5BP/*p*-BP system (Figure 8 (a)), whereas *p*-BP was consumed to react with 5mT and/or the condensation between 5mT occurred to form higher molecular weight oligomers in the 5mT/*p*-BP system (Figure 8 (b)). From these results, it is obvious that the reactivity of 5BP is lower than that of 5mT. The lower reactivity of the co-condensed resin with higher content of *p*-BP can be attributed to the lower reactivity of reactive sites in *p*-BP unit than in *m*-CR unit, and fewer reactive sites in the co-condensed resin with high content of *p*-BP than in the resin with high content of *m*-CR.

The fact that *p*-BP reacted with *m*-CR units in 5mT, but not with *p*-BP units in 5BP, means that the reactivity of *p*-BP in 5mT/*p*-BP system is higher than that in

5BP/*p*-BP system. The reactivity of monomer in co-condensation may be dependent on the reactivity of the object to react. Therefore, the reason for the increase of relative reactivity of *p*-BP in *m*-CR/*p*-BP co-condensation is the reaction of *p*-BP with higher reactive *m*-CR and *m*-CR units in the co-condensed resin. The decrease of relative reactivity of *m*-CR in the co-condensation is due to the reaction of *m*-CR with lower reactive *p*-BP and *p*-BP units.

To summarize, the reactivity of various phenols was determined in condensation and the *m*-CR/*p*-BP and *m*-CR/*p*-EP co-condensation systems. In co-condensation the ratios of reactivity of *p*-BP and *p*-EP to that of *m*-CR were found to be higher than in the condensation. The composition of *m*-CR/*p*-BP co-condensed resins was strongly affected by monomer composition in the feed, molecular weight, and degree of reaction when the resin was formed. More detailed discussion for the mechanism of co-condensation for *m*-CR/*p*-BP system will be made

by computer simulation.

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