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Green Polymerization of Phenol in Ionic Liquids

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ABSTRACT: Polymerization of phenol with paraformaldehyde and catalytic sulfuric acid was carried out in room temperature ionic liquids based on imidazolium salts. The properties of ionic liquids were systematically varied by employing six different anions such as chloride, bromide, iodide, tetrafluoroborate, trifluoromethanesulfonate and hexafluorophosphate. In case of hydrophilic ionic liquids having chloride or bromide anion, phenol polymers with low molecular weight and narrow polydispersity were obtained. In contrast, using hydrophobic ionic liquids such as tetrafluoroborate and trifluoromethanesulfonate anions, high molecular weight phenol polymers were prepared. It is because interaction of the hydrophilic ionic liquids with phenol is stronger than that of the hydrophobic ionic liquids. The interaction between phenol and ionic liquids was investigated by ^{1}H NMR measurements. Moreover, by using Brønsted acid ionic liquid carrying sulfuric acid moiety as a solvent, catalytic acid-free green polymerization of phenol with paraformaldehyde was accomplished. The ionic liquid was efficiently recovered and reused in new polymerization process of phenol.

Introduction

With the increase in environmental awareness, it is a matter of great concern for scientists to develop more efficient and clean "green" reaction systems. To avoid use of volatile organic solvents, one of the most useful methodologies is using room temperature ionic liquids for reaction media. In recent years, ionic liquids have been extensively employed as replacement of common organic solvents for green synthesis in various chemical reactions.[1−5] Advantages using ionic liquids as solvent are nonvolatile, noncorrosive, excellent solubility for both organic and inorganic compounds, and high thermal stability. Moreover, because polarity of ionic liquids depends on the kinds of counterions,[6,7] by selecting appropriate counterions, desirable reaction conditions can be controlled.

Because of these superior advantages using ionic liquids, use of ionic liquids as solvent for polymerization reactions has been also reported. Free radical,[8−13] atom transfer radical polymerization,[14−17] cationic,[18−20] cationic ring-opening,[21] and metathesis[22] polymerizations have been performed. However, there is only one example of polycondensation in ionic liquids. Polycondensation synthesis of polyamide in ionic liquids was reported by Vygodskii and co-workers.[26−28] In this study, we describe synthesis of phenol polymers in ionic liquids by polycondensation of phenol with paraformaldehyde (Figure 1). Phenol polymers, which are typically synthesized by polymerization of phenol or phenol derivatives such as *o*-cresol, *p*-cresol, and *p-tert*-butylphenol with aldehydes, exhibit excellent thermal stability, mechanical, and electrical insulating properties.[23−25] However, for the synthesis of phenol polymers, volatile organic common solvents and strong acids have been generally used, and new reaction media for synthesis of phenol polymers have been desired. Therefore, in this study, polymerization of phenol in various ionic liquids was carried out. Polymerization of phenol proceeded in ionic liquids, and interestingly, molecular weight of phenol polymers was dependent on polarity of ionic liquids. In hydrophilic ionic liquids having chloride or bromide anion, oligomer and low molecular weights phenol polymer were obtained. In contrast, phenol polymers prepared in hydrophobic ionic liquids having tetrafluoroborate or trifluoromethanesulfonate anion exhibited high molecular weight (Figure 1a). We reveal relationships between the kinds of ionic liquids and molecular weights of phenol polymers obtained. Moreover, by using Brønsted acid ionic liquid having sulfuric acid as a solvent, high molecular weight phenol polymers were successfully prepared without catalytic sulfuric acid (Figure 1b). Brønsted acid ionic liquid acted as both solvent and catalyst for the polymerization of phenol. The ionic liquids used for the polymerization were recyclable due to nonvolatile and noncorrosive ionic liquids. Synthesis of resins in ionic liquids is little known, very simple, and thus will be industrially applicable.

Experimental Section

Materials. All solvents and reagents were used as supplied except the following. 1-Bromohexane and 1-chlorohexane were dried and distilled under reduced pressure and stored under a nitrogen atmosphere. 1-Methylimidazole was dried and distilled over sodium and stored under a nitrogen atmosphere.

Measurements. The ^{1}H NMR spectra were recorded at 270 MHz, and ^{13}C NMR spectra were recorded at 67.5 MHz with a JEOL-JNM EX270 spectrometer. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on Shodex GPC LF804 by using THF as an eluent at 25 °C at the flow rate of 1 mL min^{-1} after calibration with the standard polystyrene samples.

Synthesis of Ionic Liquids. 1-Hexyl-3-methylimidazolium chloride ([C$_6$mim][Cl$^-$]), 1-hexyl-3-methylimidazolium bromide ([C$_6$mim][Br$^-$]), 1-hexyl-2-methyl-3-methylimidazolium bromide ([C$_6$mmim][Br$^-$]), 1-hexyl-3-methylimidazolium trifluoromethanesulfonate (([C$_6$mim][CF$_3$SO$_3$$^-$]), 1-hexyl-3-methylimidazolium tet-

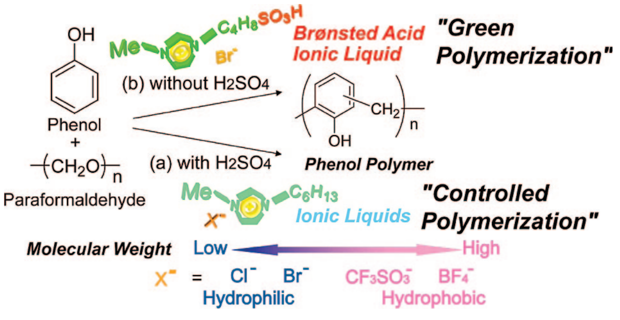

Figure 1. Polymerization of phenol in (a) hydrophilic, hydrophobic, and (b) Brønsted acid ionic liquids.

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Scheme 1. Ionic Liquids for Polymerization of Phenol

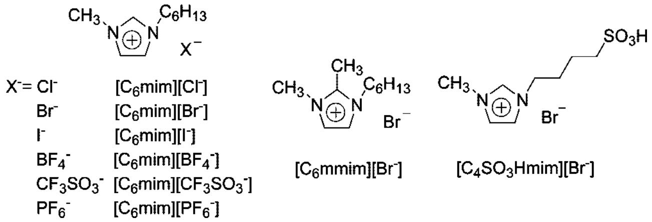

Table 1. Effect of Time and Temperature on the Polymerization of Phenol in [C_6mim][Br^-][a]

run	temp (°C)	time (h)	M_w	M_w/M_n
1	80	3	2400	1.7
2	100	3	3400	1.9
3	130	3	2900	2.0
4	100	1	3100	2.2
5	100	5	6100	2.8

[a] Phenol (5 mmol), paraformaldehyde (5 mmol), H_2SO_4 (0.2 mL), and [C_6mim][Br^-] (3.75 mL) were used for polymerization.

rafluoroborate ([C_6mim][BF_4^-]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6mim][PF_6^-]), and Brønsted acid ionic liquid ([C_4SO_3Hmim][Br^-]) were prepared according to previous papers.[5,29]

Synthesis of Phenol Polymer in Ionic Liquids with Catalytic Sulfuric Acid. A typical polymerization procedure is as follows. To ionic liquid (3.75 mL), phenol (0.47 g, 5.00 mmol) and paraformaldehyde (0.16 g, 5.00 mmol) were added at room temperature. Then, catalytic sulfuric acid (0.2 mL) was slowly added to the solution at 0 °C. The mixture was stirred and then heated for certain time. The resulting solution was poured into water. The solid was collected by filtration and then dissolved in DMF. The solution was poured into aqueous solution. The reprecipitation cycle was repeated three times to remove remaining ionic liquid completely.

Synthesis of Phenol Polymer in Brønsted Acid Ionic Liquid without Catalytic Sulfuric Acid. To [C_4SO_3Hmim][Br^-] (2.5 g), phenol (0.47 g, 5.00 mmol) and paraformaldehyde (0.16 g, 5.00 mmol) were added at room temperature. The resulting mixture was stirred and then heated at 100 °C for 3 h. The solution was poured into water. The solid was collected by filtration and then dissolved in DMF. The solution was poured into aqueous solution. The reprecipitation process was repeated three times to remove [C_4SO_3Hmim][Br^-] completely.

Results and Discussion

Polymerization of Phenol with Sulfuric Acid Catalyst in Ionic Liquids. Chemical structures of ionic liquids used in this work are summarized in Scheme 1. Ionic liquids such as 1-hexyl-3-methylimidazolium chloride ([C_6mim][Cl^-]), 1-hexyl-3-methylimidazolium bromide ([C_6mim][Br^-]), 1-hexyl-2-methyl-3-methylimidazolium bromide ([C_6mmim][Br^-]), 1-hexyl-3-methylimidazolium iodide ([C_6mim][I^-]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([C_6mim][BF_4^-]), 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([C_6mim][$CF_3SO_3^-$]), and 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6mim][PF_6^-]) were employed as a solvent for polymerization of phenol. Brønsted acid ionic liquid ([C_4SO_3Hmim][Br^-]) was used as both solvent and catalyst for the polymerization.

In order to search optimum condition for the polymerization of phenol in ionic liquids, the effect of reaction temperature and time was first examined by using [C_6mim][Br^-] as a solvent. Results are shown in Table 1. As the reaction temperature increased, molecular weights of phenol polymer increased (runs 1 and 2). However, in the case of the reaction temperature at 130 °C, molecular weight of phenol polymer slightly decreased (run 3). Therefore, we monitored the polymerization at 100 °C. According to increasing reaction time from 1 to 3 h, molecular weights of the phenol polymer obtained became larger (runs 2 and 4). As the reaction time became longer (run 5), molecular weight of the phenol polymer increased but polydispersity also became larger. From these observations, we concluded that polymerization at 100 °C for 3 h (run 2) was optimum condition for synthesis of phenol polymer in ionic liquids.

Table 2. Effect of the Kinds of Ionic Liquids on Polymerization of Phenol[a]

run	ionic liquids	M_w	M_w/M_n	yield (%)
6	[C_6mim][Cl^-]	1100	1.3	trace
2	[C_6mim][Br^-]	3400	1.9	58
7	[C_6mim][I^-]	–[b]	–[b]	trace[b]
8	[C_6mim][$CF_3SO_3^-$]	17 000	7.9	35
9	[C_6mim][BF_4^-]	41 500	13.5	38
10	[C_6mim][PF_6^-]	2300[c]	3.2[c]	19[c]
11	[C_6mmim][Br^-]	1900	1.6	19
12	1-ethoxyethanol[d]	18 000	10.7	61
13	acetic acid[d]	–[e]	–[e]	76[e]

[a] Phenol (5 mmol), paraformaldehyde (5 mmol), catalytic sulfuric acid (0.2 mL), and ionic liquid (3.75 mL) were used for polymerization. Polymerizations were carried out at 100 °C for 3 h. [b] Decomposition of [C_6mim][I^-] by H_2SO_4 took place. [c] Precipitation of phenol polymer occurred during the reaction due to low solubility of phenol polymer in [C_6mim][PF_6^-]. [d] As a control experiment, typical solvents for polymerization of phenol were employed. [e] Gelation took place during the reaction. Only insoluble gel formed.

Under the optimum conditions, the polymerization in various ionic liquids was performed (Table 2). By using [C_6mim][Cl^-] as a solvent (run 6), the trace solid was obtained, indicating that almost phenol monomer did not react with paraformaldehyde. In [C_6mim][Br^-] (run 2), polycondensation of phenol with paraformaldehyde proceeded, and oligomeric phenol polymer with narrow polydispersity was obtained. On the other hand, in the case of [C_6mim][$CF_3SO_3^-$] and [C_6mim][BF_4^-] (runs 8 and 9), phenol polymers with high molecular weight were obtained without any gelation. These observations indicate that molecular weight of phenol polymer increases with decreasing polarity of ionic liquids employed. By using [C_6mmim][Br^-] (run 11), in which proton at C2 position of [C_6mim][Br^-] (run 2) replaced by a methyl group, polymerization did not proceed efficiently, and low molecular weight of phenol polymer was obtained. These results are attributed to decreasing H-bond acidity of ionic liquid (α value) by the replacement of C2-proton by methyl group. The H-bond acidity of ionic liquids effects on acidity of the reaction media. Because reactive species generally activate in acidic conditions,[23] high acidity of reaction media should give phenol polymer with high molecular weight. The α values of H-bond acidities in ionic liquids were calculated by the Kamlet–Taft method.[30–32] Changing from the cation from [C_6mim] to [C_6mmim] lowers the α value.[30] Low H-bond acidity in [C_6mmim][Br^-] results in low reactivity of phenol monomer in the reaction medium.

As a control experiment, analogous polymerizations of phenol in 1-ethoxyethanol and acetic acid were carried out. Molecular weights of the phenol polymers prepared in hydrophobic ionic liquids (runs 8 and 9) were large compared with that in conventional solvent of 1-ethoxyethanol (run 12). By using acetic acid as a solvent, gel formed during the reaction (run 13). Generally, high molecular weight phenol polymer is obtained by using acids as solvent due to high reactivity of phenol monomer in acids.[23] However, in this condition, the reactivity of phenol is too high to control polymerization of phenol. From these results, ionic liquids are useful candidate solvent for polymerization of phenol.

Interaction between Phenol and Ionic Liquids. To investigate change in molecular weights of the phenol polymers depended on the polarity of ionic liquids, we examined

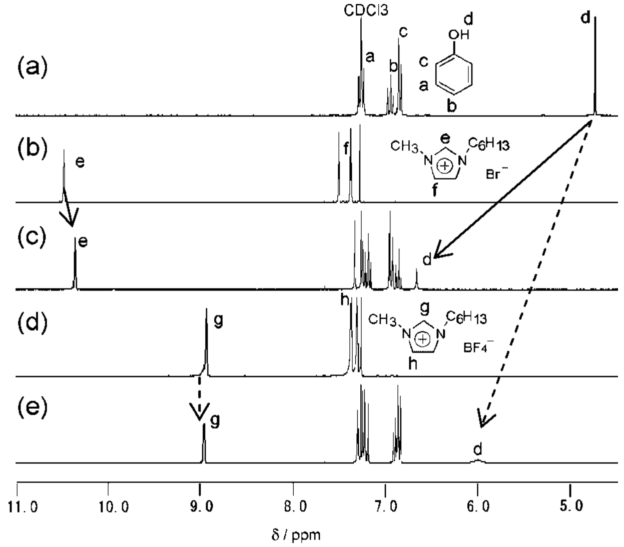

Figure 2. ^{1}H NMR spectra of (a) phenol, (b) [C$_6$mim][Br$^-$], (c) the mixture of phenol and [C$_6$mim][Br$^-$], (d) [C$_6$mim][BF$_4^-$], and (e) the mixture of phenol and [C$_6$mim][BF$_4^-$] in CDCl$_3$ at 25 °C; [ionic liquids] = [phenol] = 20 mM.

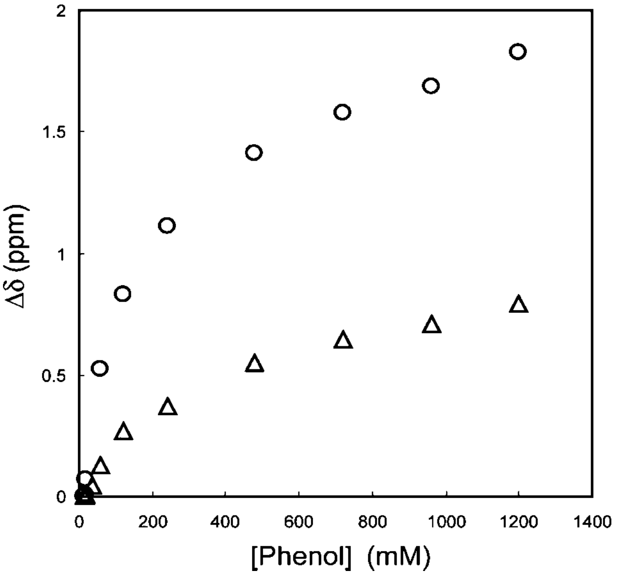

Figure 3. Peak shift of the resonance band attributed to the C2-position of imidazolium proton of [C$_6$mim][Br$^-$] (square) and [C$_6$mim][BF$_4^-$] (triangle) with varying concentration of phenol; [ionic liquids] = 20 mM, [phenol] = 0−1200 mM.

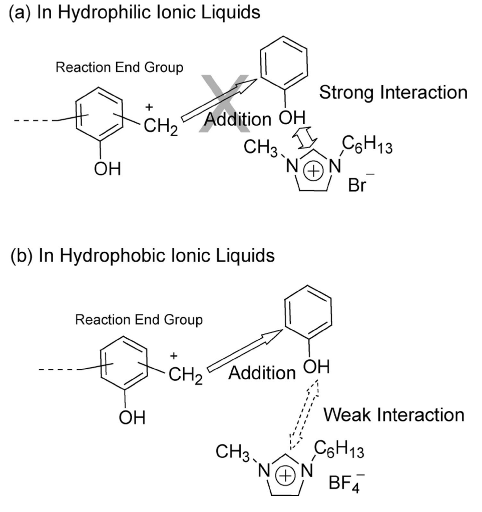

Figure 4. Interaction of phenol with (a) hydrophilic ionic liquid, [C$_6$mim][Br$^-$], and (b) hydrophobic ionic liquid, [C$_6$mim][BF$_4^-$].

interaction between phenol (monomer) and ionic liquids by ^{1}H NMR. The ^{1}H NMR measurements were carried out in nonpolar and aprotic solvent of CDCl$_3$ to eliminate interaction between phenol monomer and solvent. When phenol was mixed with hydrophilic ionic liquid of [C$_6$mim][Br$^-$] (Figure 2c), the proton of phenol (peak d) and C2-position of imidazolium moiety (peak e) showed large upper and downfield shifts, respectively, indicating interaction from electron-rich phenol to electron-poor imidazolium cation. In contrast, in the mixture of phenol and hydrophobic ionic liquid of [C$_6$mim][BF$_4^-$] (Figure 2e), small peak shifts were observed (peaks d and g). Values of the peak shift of the C2 position of imidazolium proton (peak of e in [C$_6$mim][Br$^-$] and g in [C$_6$mim][BF$_4^-$]) by adding phenol are shown in Figure 3. In the case of hydrophilic ionic liquid of [C$_6$mim][Br$^-$], even with a small amount of phenol, a large peak shift was quickly observed (Figure 3, square). On the other hand, in [C$_6$mim][BF$_4^-$], the values of the peak shift were gradually increased with phenol (Figure 3, triangle). These data indicate that the interaction of phenol with hydrophilic ionic liquid, [C$_6$mim][Br$^-$], is stronger than that with hydrophobic ionic liquid, [C$_6$mim][BF$_4^-$]. From the Kamlet−Taft method, hydrogen accepting ability (β value) depending on anion for a series of [C$_6$mim]cation-based ionic liquids was calculated. The hydrogen accepting ability of the β values increases in the following order: [C$_6$mim][BF$_4^-$] (0.61) ≈ [C$_6$mim][CF$_3$SO$_3^-$] (0.60) ≪ [C$_6$mim][Br$^-$] (0.90) < [C$_6$mim][Cl$^-$] (0.97).[31,32] High hydrogen accepting ability of [C$_6$mim][Br$^-$] results in the strong interaction between phenol monomer and [C$_6$mim][Br$^-$]. The data also indicate that the interaction of phenol monomer with [C$_6$mim][Br$^-$] is stronger than that with [C$_6$mim][BF$_4^-$]. Formation of the strong interaction of phenol monomer with [C$_6$mim][Br$^-$] should reduce electron density of phenol and increase steric hindrance of phenol. Thus, phenol reactivity with reactive end group of carbocation decreased and oligomeric phenol polymers were synthesized in hydrophilic ionic liquids such as [C$_6$mim][Br$^-$] (Figure 4a). In hydrophobic ionic liquids of [C$_6$mim][BF$_4^-$], because of the weak interaction between phenol monomer and [C$_6$mim][BF$_4^-$], electron density of phenol was not decreased and caused low steric hindrance of phenol. Therefore, addition of carbocation group was not suppressed, and thus high molecular weight phenol polymers were obtained (Figure 4b).

Polymerization of Phenol without Sulfuric Acid Catalyst in Brønsted Acid Ionic Liquid. To aim volatile acid free polymerization of phenol, we first tried to polymerize phenol without catalytic sulfuric acid in ionic liquids. However, in the absence of catalytic sulfuric acid, polymerization of phenol did not proceed even at high temperature (over 200 °C). Thus, by using nonvolatile Brønsted acid ionic liquid of [C$_4$SO$_3$Hmim][Br$^-$] as a catalyst, polymerization of phenol without catalytic sulfuric acid was examined. In [C$_6$mim][Br$^-$] with [C$_4$SO$_3$Hmim][Br$^-$], phenol polymer was obtained (run 14). The observation indicates that nonvolatile [C$_4$SO$_3$Hmim][Br$^-$] acts as a catalyst for polymerization of phenol. Furthermore, in [C$_4$SO$_3$Hmim][Br$^-$], high molecular weight phenol polymer was obtained (run 15). The data indicate that [C$_4$SO$_3$Hmim][Br$^-$] plays a role as both nonvolatile solvent and catalyst for polymerization of phenol. Volatile solvent and acid-free polymerization of phenol was accomplished by using nonvolatile Brønsted acid ionic liquid.

Isolation of Phenol Polymer and Recovery and Reuse of Ionic Liquids. Further investigation was aimed at the efficient isolation of phenol polymer and recovery of ionic liquid.

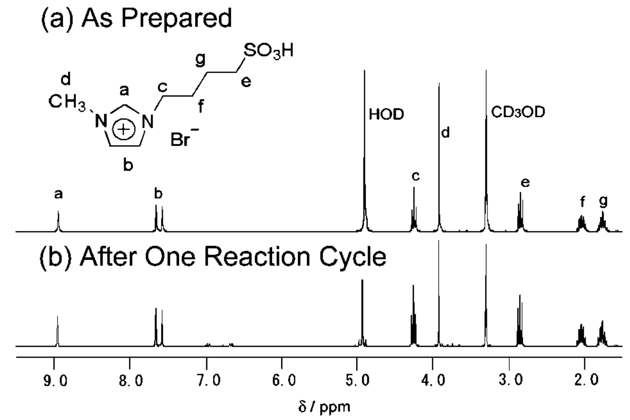

Figure 5. ^{1}H NMR spectra of [C_4SO_3Hmim][Br^-] (a) as prepared and (b) after one reaction cycle (dried under vacuum) in CD_3OD at 25 °C.

Table 3. Effect of the Kinds of Ionic Liquids on Polymerization of Phenol[a]

run	ionic liquids	M_w	M_w/M_n	yield (%)
14	[C_6mim][Br^-] + [C_4SO_3Hmim][Br^-][b]	7300	2.4	51
15	[C_4SO_3Hmim][Br^-]	120000	33.0	52

[a] Polymerization of phenol (5 mmol) was carried out in ionic liquid (2.5 g) at 100 °C for 3 h. [b] [C_6mim][Br^-] (1.25 g) and [C_4SO_3Hmim][Br^-] (1.25 g) were employed.

Because of low solubility of phenol polymer in water, phenol polymer was isolated from the reaction mixture by reprecipitation with water, avoiding completely the use of volatile organic solvents. After filtration of the precipitate, phenol polymer was easily obtained. Since the ionic liquid remaining in the filtrate was nonvolatile, the ionic liquid was easily recovered with high yield by removing water under reduced pressure (over 80%). ^{1}H NMR spectra of [C_4SO_3Hmim][Br^-] as prepared (Figure 5a) and after one reaction cycle (Figure 5b) are shown. Even after polymerization of phenol, little remaining monomer and reagents were observed (Figure 5b). Accordingly, the ionic liquid recovered is able to be reused in new polymerization cycles of phenol.

Conclusions

When phenol was polymerized in hydrophobic ionic liquids as a solvent, phenol polymers with high molecular weight were obtained. In contrast, by employing hydrophilic ionic liquids, oligomeric phenol polymers were synthesized. The interaction between electron-rich phenol monomer and electron-poor ionic liquids affected the molecular weight of phenol polymers. By choosing appropriate ionic liquids, high molecular weight and oligomeric phenol polymers were selectively obtained. Furthermore, by using Brønsted acid ionic liquid of [C_4SO_3Hmim][Br^-], phenol polymer was successfully obtained even without catalytic sulfuric acid. Isolation of phenol polymer and recovery of the ionic liquid were easily done by reprecipitation with water and removing water from the filtrate. Thus, in all process of polymerization, isolation, and recovery, it is not necessary to use volatile organic solvents. The "green" polymerization of phenol in ionic liquids is technologically and industrially important. Since phenol polymer easily forms thermally and mechanically stable phenol resin film by using additives and annealing, we now try to synthesize superior transparent ion conductive phenol resin−ionic liquid hybrid film, in which ionic liquids are dispersed in phenol resin matrix at the nanometer level. This is now under investigation.

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