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The Polymerization of Benzene Catalyzed by a Copper(I) Chloride-Aluminium Chloride-Oxygen System

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The polymerization of benzene to poly(1,4-phenylene) (PPP) has been done successfully using copper(I) chloride and aluminium chloride as catalysts under oxygen. Since copper(I) chloride and aluminium chloride form a double salt (aluminium copper(I) chloride, $AlCuCl_4$) and are soluble in benzene, a high homogeneity of the reaction system has been achieved and the polymerization reaction proceeds without any evolution of hydrogen chloride. The polymerization products contained an insoluble dark brown solid and a benzene-soluble tarry mass. The solid product has been determined to be PPP by comparison with an authentic sample. The product PPP was obtained in a yield of more than 100%, based on the molar quantity of copper(I) chloride, by controlling the quantity of aluminium chloride. For example, the treatment of benzene with aluminium chloride and copper(I) chloride (20:3:1 in molar ratio) under 1 atm of oxygen at 70 °C for 24 h gave PPP in a 187% yield, based on copper(I) chloride. This reaction could be carried out by the use of oxidants other than oxygen and by the use of low-valent metal salts other than copper(I) chloride, although a copper(I) chloride–aluminium chloride–oxygen system is most suitable for the polymerization of benzene in terms of the yield of PPP and the convenience of the reaction.

The aromatic hydrocarbon polymer is an interesting organic material in that it is thermally stable¹⁾ and can be electrically conductive upon doping with various dopants.²⁾ Poly(1,4-phenylene) (PPP) has a structure characteristic of this type of polymer. The methods of synthesizing it and its character have been investigated for a long time.¹,²⁾

Several methods for the direct synthesis of PPP from benzene have been investigated. One well-known procedure is the oxidative cationic polymerization of benzene by a Lewis acid–oxidant system reported by Kovacic et al.;³⁾

$$n\,C_6H_6 + 2n\,CuCl_2 \xrightarrow{AlCl_3} (C_6H_4)_n + 2n\,CuCl + 2n\,HCl \tag{1}$$

Usually, aluminium chloride is used as a Lewis acid, and copper(II) chloride, as an oxidant.⁴⁾ Molybdenum(V) chloride⁵⁾ and iron(III) chloride,⁶⁾ which have functions of both a Lewis acid and an oxidant, are also used. In this method, the polymerization reaction proceeds under mild conditions, and the yield of PPP is fairly high. The polymerization of alkylbenzenes, such as toluene,⁷⁾ halogenated benzenes,⁸⁾ and thiophenes,⁹⁾ has also been attempted by the use of this method. However, the vigorous evolution of a large amount of hydrogen chloride is unavoidable in this method, since the polymerization of 1 mol of benzene produces 2 mol of hydrogen chloride, according to Eq. 1. Furthermore, it is difficult to stir the reaction mixtures, even at the beginning of the reaction, because the metal salts do not dissolve in benzene, resulting in slurried conditions. Since the oxidizing metal salts are consumed during the reaction, the yield of PPP based on the oxidant is always less than 100%. Recently, the polymerization of benzene by the use of a superacid composed of aluminium chloride and copper(II) chloride was reported,¹⁰⁾ although the evolution of hydrogen chloride is unavoidable in this method also. The electrolytic polymerization of benzene in the presence of a supporting electrolyte was found to produce a film of PPP.¹¹⁾ The structure-definite PPP was synthesized by the dehalogenation of dihalogenated benzene in the presence of nickel-complex catalysts.¹²⁾

The direct polymerization of benzene by Kovacic's method does not give the PPP in so high a molecular weight. The heterogeneity of the reaction system and the insolubility of PPP in organic solvents might be the reasons for this lower molecular weight. Against this background, the methods via a soluble precusor polymer have been investigated. It has previously been reported that PPP could be synthesized by the dehydrogenation of the polymer of 1,3-cyclohexadiene.¹³⁾ However, the yield of PPP synthesized by this method was also low, and the purification of the polymer was difficult. Recently, it was also reported that the polymer of acylated 3,5-cyclohexadiene-1,2-diol, which can be synthesized by a biotechnical procedure, is thermally converted into PPP with a high molecular weight.¹⁴⁾ By this method, it is possible to make films at the stage of the precusor polymer.

The present authors have now tried to polymerize benzene to PPP by taking advantage of aluminium copper(I) chloride ($AlCuCl_4$), which is known to be soluble in various aromatic compounds¹⁵⁾ and which should be formed at the termination step in Kovacic's method. Thus, the polymerization of benzene was attempted by producing the active species (Cu(II) ion) for polymerization by using $AlCuCl_4$ and an oxidant under highly homogeneous conditions, where copper(I) chloride would be expected to work as a catalyst. The present paper reports on the synthesis of PPP in a system of aluminium chloride, copper(I) chloride, and an oxidant, where not only $AlCuCl_4$ but also excess $AlCl_3$ and an oxidant are required by the reaction. The syntheses by the use of double salts other than $AlCuCl_4$ have also been successful.

Experimental

Materials. The aluminium chloride (Kishida Chemical Co.) was purified by vacuum sublimation. The copper(I) chloride (Koso Chemical Co.) was reprecipitated from an aqueous hydrochloric acid solution by the addition of distilled water, followed by successive washing with ethanol and diethyl ether; it was then dried in vacuo at 100 °C for 24 h. The aluminium bromide, copper(I) bromide, cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride were commercially (guaranteed grades) obtained and were used without further purification.

The benzene was distilled over metallic sodium. The 1-bromopropane was distilled after drying by anhydrous magnesium sulfate.

The chloranil and potassium permanganate were commercially obtained (guaranteed and extra pure grade respectively) and were used without further purification. The 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was purified by recrystallization from acetonitrile. The oxygen was passed through columns of Molecular Sieves 3A and diphosphorus pentaoxide before use.

Analysis. The ^1H NMR spectrum was obtained with a JEOL model FX 90Q spectrometer at 89.55 MHz. The infrared absorption spectra (KBr disks and liquid film with KBr plates) were obtained with a JASCO model A-3 spectrometer. The GPC was recorded on a TOYO SODA model HLC-802UR chromatograph equipped with two TSK-GEL 2000H columns.

Polymerization of Benzene by a $CuCl-AlCl_3-O_2$ System. One gram (10.1 mmol) of copper(I) chloride, 4.04 g (30.3 mmol) of aluminium chloride, and 18.2 cm^3 (202 mmol) of benzene were placed in a 100 cm^3 Kjeldahl flask, and the mixture was stirred at room temperature for 2 h under dry nitrogen. In this stage, the copper(I) chloride was dissolved completely and a highly homogeneous solution was obtained, leaving some excess aluminium chloride. The reaction was carried out by replacing the solution atmosphere with oxygen at 60 °C for 24 h. As the reaction proceeded, the color of the reaction mixture changed from yellow to dark brown at the beginning of the reaction. At the end of the reaction, brownish black precipitates appeared at the bottom of the reaction vessel. During the reaction, no evolution of hydrogen chloride was observed. Polymerization was terminated by adding an 18% hydrochloric acid solution to the reaction mixtures. After the filtration of the reaction mixtures with a sintered glass disk, the remaining solid was repeatedly washed with a boiling solution of 18% hydrochloric acid and then with boiling water. The subsequent drying of the dark brown solid product at 100 °C for 24 h, yielded 0.458 g (119% yield based on the charged copper(I) chloride) of PPP. The filtrate was extracted by benzene, and the benzene solution was also washed several times with an 18% hydrochloric acid solution and water. After the evaporation of the benzene under reduced pressure and then drying for 24 h, 0.177 g (46.0% yield based on charged CuCl) of a reddish brown, tarry product was obtained.

The solid product was quite insoluble in various organic solvents. The elemental analysis data are shown in Table 3. The IR spectra of the solid product showed bands at 800 (C–H out-of-plane vibration of a para-disubstituted benzene ring), 1000 (C–H in-plane vibration of the same species), and 1480 cm^{-1} (C=C skeletal in-plane vibration).

The results of the elemental analysis of the benzene-soluble product were: C, 85.4; H, 6.3; Cl, 3.2%. Thus, the C/H ratio is 1.14, between the calculated values of $(C_6H_4)_n$ (1.50) and $(C_6H_6)_n$ (1.00). The IR spectrum has bands at 700, 760, 800, 1450, 1500, 1600, 2870, 2950, 3040, and 3070 cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ shows its peaks at δ 1.25, 5.4—5.5, and 7.2—7.3 (refer to TMS).

Polymerization of Benzene by the Use of Other Metal Salts and Oxidants. In the case of using other metal salts, polymerization was carried out by the procedure described above. Polymerization by the use of copper(II) chloride was carried out according to Kovacic's method.[4]

When potassium permanganate was used as an oxidant, the reaction was carried out in the presence of 18-crown-6, thus enabling this oxidant to dissolve in benzene. When chloranil was used as an oxidant, unreactive chloranil was removed from the solid product by extraction with benzene using a Soxhlet extractor. The experimental conditions are shown in Tables 4 and 5, as well as the yield of polymers.

Alkylation of PPP. The alkylation of PPP was achieved by 1-bromopropane according to the method in the literature.[16]

Elemental analysis:

Alkylated PPP prepared by the $CuCl-AlCl_3-O_2$ method:

Found: C, 87.9; H, 9.9; Cl, 0.7% (C/H ratio, 0.75).

Calcd for $[C_6H_2(C_3H_7)_2]_n$: C, 89.9; H, 10.1% (C/H ratio, 0.75).

Alkylated PPP prepared by Kovacic's method:

Found: C, 84.8; H, 9.0; Cl, 0.6% (C/H ratio, 0.79).

Calcd for $[C_6H_{2.5}(C_3H_7)_{1.5}]_n$: C, 90.6; H, 9.5% (C/H ratio, 0.81).

Results and Discussion

Synthesis of PPP by the Use of the $CuCl-AlCl_3$-Oxygen System. The direct polymerization of benzene to PPP by a copper(II)–aluminium chloride ($CuCl_2-AlCl_3$) system, as reported by Kovacic et al., is one of the best known methods. However, this method has some problems: (1) the vigorous evolution of hydrogen chloride, (2) difficulty in stirring the slurried reaction mixtures caused by the insolubility of the metal salts in benzene, and (3) the limited yield of PPP based on $CuCl_2$ because of the consumption of the $CuCl_2$ used as a reagent. As copper(I) chloride (CuCl) is a by-product of the preparation of PPP from benzene in this method, it is considered that polymerization can be continued if this CuCl is oxidized to Cu(II) species again. Thus, copper chloride is thought to be able to participate repeatedly in the polymerization as a catalyst. On the other hand, it is known that $AlCl_3$ and CuCl can form a double salt of aluminium copper(I) chloride ($AlCuCl_4$), which is soluble in benzene by the coordination of benzene to the salt.[15] From this point of view, the polymerization of benzene might proceed efficiently because of the homogeneity of the reaction system.[17]

Table 1 shows the results of polymerization using CuCl-AlCl$_3$ (1:1 in charged molar ratio) and adding various oxidants. Though oxygen, iodine, and potassium permanganate (KMnO$_4$) were added as oxidants, polymerization did not occur. Even when CuCl$_2$ was added, PPP was not obtained at all. These results indicate that AlCl$_3$ loses its activity as a Lewis-acid catalyst by forming the double salt AlCuCl$_4$.

The polymerization was successfully attempted by the addition of an excess of AlCl$_3$ with respect to the CuCl under oxygen. The results are shown in Table 2. The addition of the excess AlCl$_3$ caused benzene to polymerize smoothly, resulting in a dark brown solid. The structure of this solid product has been proved by IR spectral measurements to be almost identical with that of the PPP synthesized by Kovacic's method. However, under nitrogen, no reaction at all occurred in spite of the use of an excess of AlCl$_3$ relative to CuCl. These results indicate that oxygen is required for polymerization. When more than twice as much AlCl$_3$ as CuCl was used, PPP was obtained in a yield of more than 100%, based on the CuCl. This result clearly indicates that CuCl works as a catalyst.

On the other hand, when AlCl$_3$ and benzene (3:20 in charged molar ratio) were treated at 60 °C under oxygen without CuCl, the yield of PPP was only about 1% of that in the presence of CuCl. This result demonstrates that the polymerization is not achieved by only AlCl$_3$ and oxygen, but that it is greatly promoted by copper(I) species in cooperation with oxygen in this reaction system. The necessity of oxygen for polymerization is well supported by the consumption of oxygen during polymerization. For example, when 258 mmol of benzene was polymerized by the use of 12.8 mmol of CuCl and 38.6 mmol of AlCl$_3$ at 70 °C for 24 h, at the beginning of the reaction no appreciable amount of oxygen was consumed, but as the reaction proceeded further, the uptake of oxygen gradually increased, in all, about 12 mmol of oxygen was consumed, resulting in PPP. The yield of PPP (16.5 mmol) nearly corresponds to twice amount of oxygen consumed. The time course of the oxygen uptake is comparable to the change in

Table 1. Polymerization of Benzene by Aluminium Copper(I) Chloride with Various Oxidants[a]

Run	Charged molar ratio[b]		Yield/%
	AlCuCl$_4$	Oxidant	
1	1.0	— (O$_2$)[c]	0
2	0.5	0.25 (I$_2$)	0
3	0.5	0.1 (KMnO$_4$)	0
4	1.0	0.5 (CuCl$_2$)	0

a) Reaction time=2 h; reaction temperature=40 °C. b) Benzene=10.0. c) Under 1 atm of oxygen.

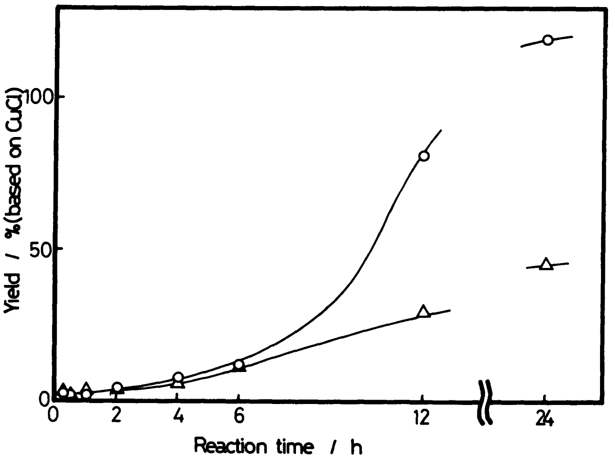


Fig. 1. Changes in the yields of PPP, insoluble (O) and soluble (Δ) portions in benzene, with reaction time by a CuCl-AlCl$_3$-O$_2$ method. Charged molar ratio of CuCl-AlCl$_3$-benzene was 1:3:20 and reaction temperature was 60 °C.

Table 2. Polymerization of Benzene Catalyzed by Copper(I) Chloride-Aluminium Chloride under Oxygen[a]

Run	Charged molar ratio[b]		Temp	Yield/%[c]		
	AlCuCl$_4$	Excess AlCl$_3$	°C	Insoluble[d]	Soluble[d]	Total
5[e]	1.0	2.0	50	0	0	0
6	1.0	2.0	40	5	4	9
7	1.0	2.0	50	43	22	65
8	1.0	2.0	60	119(3.0)[g]	46(1.1)	165(4.1)
9	1.0	2.0	70	187	41	228
10	1.0	1.0	60	56	11	67
11	0.5	1.0	60	111	47	158
12	2.0	4.0	60	139	51	190
13	1.0	2.0+3.8[f]	60	649	154	803
14	0.0	3.0	60	—(0.04)[g]	—(0.05)	—(0.09)

a) Reaction time=24 h except Run 13. b) Benzene=20.0. c) Based on CuCl. d) The products are insoluble or soluble in benzene. e) Reaction under nitrogen. f) After the reaction with a 2.0 excess (molar ratio) of aluminium chloride for 24 h, a 3.8 excess (molar ratio) of aluminium chloride was added, after which the reaction was continued for a further 24 h. g) The % values shown in parentheses are calculated based on the charged amount of benzene.

the yield of PPP with the reaction time (Fig. 1).

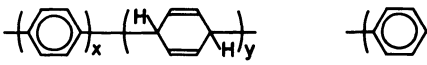
The yield of PPP was strongly influenced by the quantity of the excess $AlCl_3$; that is, the more the quantity of excess $AlCl_3$ used, the higher the yield of PPP. Furthermore, the yield increased up to 803% by the extra addition of a 3.8-fold quantity of $AlCl_3$ after a 24-h reaction and continuous stirring for another 24 h. These results indicate that excess $AlCl_3$ is consumed during the reaction. $AlCl_3$ is considered to be deactivated by water generated from oxygen and protons which will be eliminated from benzene in the course of the reaction.

The yield of PPP rose drastically with a rise in the reaction temperature. In contrast, the molar ratio of benzene to CuCl had little influence on the yield of PPP. The reaction under dry air also gave PPP, but the yield was remarkably low in comparison with that obtained by the reaction under pure oxygen. The yield of PPP also increased with a lengthening of the reaction time. In the initial stage of the reaction, however, a few hours' induction period was observed (Fig. 1).

Structure of PPP. Table 3 shows the results of the elemental analyses of the various polymerization products prepared by a $CuCl-AlCl_3-O_2$ system as well as a $CuCl_2-AlCl_3$ system. The C/H ratio of the PPP prepared at 50 °C was 1.50, identical with that of an ideal PPP structure, $(C_6H_4)_n$. The C/H ratios of the other products were also near to that of PPP. The contamination of chlorine may be due to the partial chlorination of the aromatic rings of the polymers. The C/H ratio and the content of chlorine atoms increased as the reaction temperature rose.

In the present polymerization reaction, a product which was soluble in benzene was obtained as well as an insoluble solid product. In the IR spectrum, remarkable peaks located at 700 and 760 cm^{-1} were observed; they were attributed to the C–H in-plane vibration of a mono-substituted benzene ring. From the IR spectrum, the molecular weight of this benzene-soluble product was proved to be very low. On the other hand, the peaks located at 2870 and 2950 cm^{-1} indicated that the benzene-soluble product was not completely aromatized, for these peaks were attributable to the C–H stretching vibration of alkanes. This consideration was also supported by the ^{1}H NMR spectroscopy, that is, the peaks assigned to nonaromatic and vinyl protons were observed around δ 1.25 and 5.4—5.5 respectively. The proposed structure for the soluble product is shown in Fig. 2 as well as that for the insoluble product. This structure of the soluble product is also supported by the experimental result that the soluble product could be rearomatized by oxidation with the $CuCl-AlCl_3-O_2$ system in carbon tetrachloride, producing insoluble PPP.

Molecular Weight of PPP. PPP exhibits characteristic infrared absorptions around 650—900 cm^{-1} corresponding to the C–H out-of-plane vibration of a benzene ring. These absorptions involve the peaks at 760 and 800 cm^{-1}, as for a monosubstituted and a para-disubstituted benzene ring respectively. The former peak arises from the end phenyl units of PPP, and the latter, from the internal phenylene units. By a comparison of the ratios of the two peak intensities, it



(1) (2)

Fig. 2. The proposed structure for the soluble (1) and insoluble (2) product of PPP.

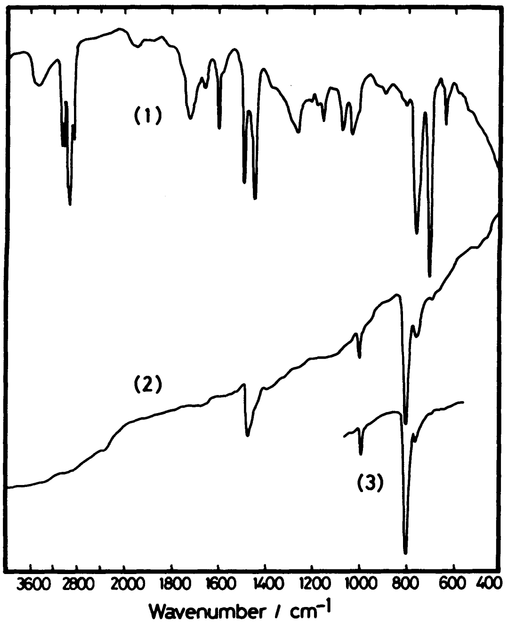


Fig. 3. Infrared spectra of PPP prepared by a $CuCl-AlCl_3-O_2$ method (soluble portion (1) and insoluble portion (2) in benzene) and by a Kovacic's method (3).

Table 3. The Elemental Analysis Data of Solid PPP Prepared by Various Methods

Method	Temp	Weight/%			C/H
	°C	C	H	Cl	Atomic ratio
$CuCl_2-AlCl_3$	40	92.90	5.25	1.24	1.48
$CuCl-AlCl_3-O_2$	50	90.70	5.08	0.86	1.50
$CuCl-AlCl_3-O_2$	60	92.70	5.02	1.08	1.55
$CuBr-AlBr_3-O_2$	50	86.65	4.44	5.17(Br)	1.64
Calcd for $(C_6H_4)_n$		94.70	5.30	0.00	1.50

is possible to estimate the molecular weight of PPP.[16] As is depicted in Fig. 3, the PPP prepared by using $CuCl-AlCl_3-O_2$ shows a little stronger absorption at 760 cm^{-1} than that prepared by using $CuCl_2-AlCl_3$, suggesting that the molecular weight of the former PPP is a little lower than that of the latter PPP.

The Friedel-Crafts alkylation of these PPPs by 1-bromopropane resulted in the dissolution in organic solvents. In either case, the alkylated PPP showed a light brown color and could be dissolved in various organic solvents. It was estimated, on the basis of the results of the elemental analyses, that the number of alkyl groups introduced to benzene rings of PPP prepared by the $CuCl-AlCl_3-O_2$ method was 2 per benzene ring, in contrast with 1.5 per ring in the case of Kovacic's PPP, where the degree of polymerization was 15.[16] Figure 4 shows some typical GPC spectra of the alkylated PPPs. From these GPC spectra, it has become apparent that the PPP prepared by the $CuCl-AlCl_3-O_2$ method has a somewhat lower molecular weight than does Kovacic's PPP.

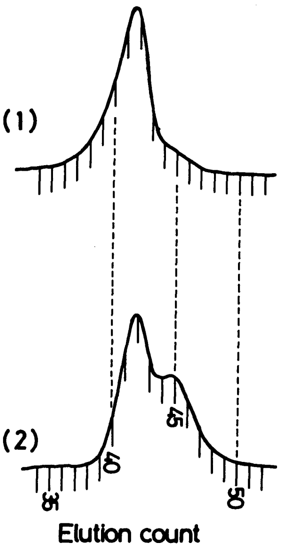


Fig. 4. Gel permeation chromatograms (chloroform as a carrier) of PPP alkylated by 1-bromopropane in the presence of $AlCl_3$. The original PPP were prepared by a Kovacic's method (1) and a $CuCl-AlCl_3-O_2$ method (2).

Syntheses of PPP by CuCl and $AlCl_3$ Using Other Oxidants. The successful preparation of PPP by the use of excess $AlCl_3$ with respect to CuCl under oxygen as an oxidant suggested that PPP could also be prepared using other oxidants under the same conditions. Table 4 shows the results of the polymerization of benzene using $KMnO_4$, chloranil, iodine, and so on as oxidants. When $KMnO_4$ was used instead of oxygen, polymerization occurred without CuCl. However, the yield of PPP got higher in the presence of CuCl. That is to say, the combination of CuCl and $KMnO_4$ influenced the acceleration of the polymerization reaction. When chloranil was used instead of oxygen, the acceleration of the reaction by a combination of CuCl and chloranil was not observed, since the 44% yield based on chloranil was achieved only with $AlCl_3$ in Kovacic's method.[18] This result indicates that the polymerization of benzene occurs independently in the absence of $AlCuCl_4$ when chloranil is used. In the case of iodine as an oxidant, the yield of the insoluble solid product was high. However, the content of iodine in the product was also very high (86.1%).

The polymerization using chloranil or iodine as an oxidant is supposed not to be suitable for the synthesis of PPP because of the difficulty of removing the oxidant from the polymer. When sodium periodate was used instead of oxygen, only a little PPP was obtained.

Syntheses of PPP by Other Metal Salts under Oxygen. It has become possible to polymerize benzene to PPP catalytically by the use of low-valent copper(I) chloride, $AlCl_3$, and oxygen. Low-valent metal salts other than CuCl were examined for the polymerization of benzene. Table 5 shows the results of these examinations. When cobalt(II) chloride ($CoCl_2$) and nickel(II) chloride ($NiCl_2$) were stirred with an excess of $AlCl_3$ in benzene, the color of the solution turned green[19] and deep yellow respectively, resulting in the formation of double salts with $AlCl_3$ and a consequent dissolution in benzene. By the use of these metal salts instead of CuCl, benzene could be polymerized to produce PPP. However, the yield of a benzene-soluble product was relatively high in

Table 4. Polymerization of Benzene Catalyzed by a Copper(I) Chloride-Aluminium Chloride-Oxidant System[a)]

Run	Charged molar ratio[b)]			Temp	Yield/%[c)]	
	CuCl	$AlCl_3$	Oxidant	°C	Insoluble	Soluble
15	1.0	3.0	— (O_2)[d)]	27	4	5
16	1.0	3.0	0.4 ($KMnO_4$)	27	112 (56)	2 (1)
17	0.0	3.0	0.4 ($KMnO_4$)	27	— (21)	— (1)
18	0.5	1.5	2.0 (Chloranil)	27	132 (33)	— (—)
19	0.8	2.4	1.0 (I_2)	50	168 (84)	— (—)
20	0.9	2.7	0.5 ($NaIO_4$)	50	2 (2)	— (—)

a) Reaction time=24 h. b) Benzene=20.0. c) Based on CuCl. The values shown in parentheses are calculated based on the charged oxidants. d) Under 1 atm of oxygen.

Table 5. Polymerization of Benzene by Various Metal Salts under Oxygen[a]

Run	Charged molar ratio[b]			Yield/%[c]	
	Salt A	Salt B	B/A	Insoluble	Soluble
20	$CoCl_2$	$AlCl_3$	4.0	25	45
21	$NiCl_2$	$AlCl_3$	4.0	19	20
6	CuCl	$AlCl_3$	2.0	43	22
22	CuCl	$AlBr_3$	2.0	21	21
23	CuBr	$AlBr_3$	2.0	19	20

a) Reactions were carried out at 50 °C under 1 atm of oxygen for 24 h. b) Salt A: benzene=1 : 20. c) Based on salt A.

comparison with the case of $AlCuCl_4$, even though the yield of a benzene-insoluble product was not changed. In these reactions, the solubility of these salts in benzene is less than that of $AlCuCl_4$, resulting in less effective polymerization. The use of aluminium bromide ($AlBr_3$) instead of $AlCl_3$ made the double salts much more soluble in benzene than in the case of $AlCl_3$. The yield of benzene-insoluble PPP, however, was lower than that when $AlCl_3$ was used. The rearomatization of the polymeric precursor is thought to take place inefficiently in the case of $AlBr_3$ because the oxidation power of the copper ion is lowered by an increase in the charge density on copper caused by the lower electronegativity of bromine than chlorine. As is shown in Table 3, the PPPs prepared by metal bromides are highly contaminated with bromine atoms and give a high C/H ratio because of the bromination of the benzene rings.

Mechanism for Polymerization. In the polymerization of benzene by using $CuCl_2$ and $AlCl_3$, Kovacic et al. proposed that the polymerization was initiated by the generation of the benzene-cation radical,[20] propagated by the coordination of an appreciable number of benzene nuclei as stair-steps, and terminated by rearomatization by means of the oxidative elimination of protons by $CuCl_2$ from the delocalized stair-step cation radical (stair-step mechanism).[21]

In the method reported here, the polymerization has occurred under oxygen by the use of excess $AlCl_3$ with respect to CuCl, in contrast to no polymerization under nitrogen in spite of the presence of excess $AlCl_3$. Thus, the present reaction is described by Eq. 2, not by Eq. 1 as in the case of the Kovacic reaction:

$$2n\,C_6H_6 + n\,O_2 \xrightarrow{AlCl_3/CuCl} 2\,(C_6H_4)_n + 2n\,H_2O \qquad (2)$$

Furthermore, when the molar ratio of $AlCl_3$ to CuCl was unity in the present system, benzene did not polymerize at all, not even under oxygen. These results suggest that the cooperation of excess $AlCl_3$ and the oxygenated copper(I) ion produces the cation radical species and initiates the polymerization. The induction period of only a few hours in this reaction is thought to be due to the lowering of the initiation activity of the benzene-cation radicals because of the interaction of the radicals with $AlCl_3$.

By the ESR experiments in the present system, the cation radical has been proved to be produced before the reaction atmosphere is replaced by oxygen. Thus, the signal observed under nitrogen with excess $AlCl_3$ (g=2.0025) has been identified as an organic radical. After the reaction under oxygen for 24 h, no additional signal was observed except that for the organic radical (g=2.0026). This result indicates that the copper(II) species do not take part in the polymerization reaction. Presumably, the oxygen activated by $AlCuCl_4$ participates in the reaction to withdraw hydrogen in the rearomatization step. The fact that a considerable amount of the benzene-soluble product was obtained in the present reaction is attributable to the weaker oxidative power of the activated oxygen than $CuCl_2$ in Kovacic's method.

As has been described before, the yield of PPP can be raised by increasing the quantity of excess $AlCl_3$ or by the addition of extra $AlCl_3$ in the course of the reaction. These results suggest the generation of water, by which $AlCl_3$ is consumed during the reaction. That is to say, the water is considered to be produced by oxygen and protons eliminated from the dihydropolymer in the termination stage.

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