July, 1989] *Bull. Chem. Soc. Jpn.*, ***62***, *2201—2207 (1989)*

The Polymerization of Toluene and Its Analogs Catalyzed by a Copper(I) Chloride-Aluminum Chloride-Oxygen System

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(Received December 26, 1988)

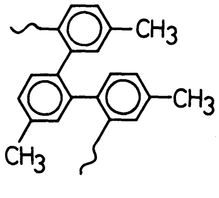
The polymerization of aromatic compounds other than benzene (such as toluene, xylene, ethylbenzene, mesitylene, and biphenyl) was performed by using a copper(I) chloride–aluminum chloride–oxygen system which caused benzene to polymerize. Excess aluminum chloride, with respect to copper(I) chloride, was required for these compounds to polymerize, as was also true for benzene. For example, the treatment of toluene with aluminum chloride and copper(I) chloride (15:3:1 in molar ratio) under 1 atm of oxygen at 50 °C for 24 h gave toluene polymer in 204% yield based on copper(I) chloride. This fact suggests that copper(I) chloride also worked as a catalyst in the case of the polymerization of toluene. The toluene polymer was obtained as both solid and liquid products, both of which were soluble in various organic solvents. The solid product has a complicated, crosslinked and "quinonoid-like" structure. On the other hand, the liquid product has a structure that is nearly identical with that of methylated poly(1,4-phenylene). Other alkylbenzenes gave the only liquid polymerization products, except for *o*-xylene which gave a small amount of solid products. The polymerization of biphenyl gave a low-molecular-weight poly(1,4-phenylene).

It is well-known that the aromatic hydrocarbon polymer is thermally stable[1] and becomes electrically conductive upon doping with various dopants.[2] In particular, an investigation of poly(1,4-phenylene) (PPP), the polymer of benzene, has been intensively carried out while considering synthetic methods and properties.

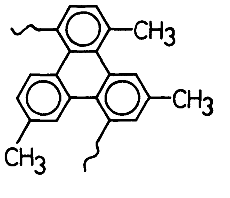
A number of methods for synthesizing PPP have been invented, such as the electrolytic polymerization of benzene,[3] the dehalogenation from dihalogenated benzene in the presence of nickel complex catalysts,[4] the dehydrogenation from poly(1,3-cyclohexadiene)[5] and so on. On the other hand, for a direct synthesis of PPP from benzene, a well-known procedure is the oxidative cationic polymerization of benzene by a Lewis acid–oxidant system reported by Kovacic et al.[6] In this method, aluminum chloride and copper(II) chloride are used as a Lewis acid and an oxidant, respectively, and are most effectively used for polymerization:[7]

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

In this method, however, the polymerization of 1 mol of benzene produces 2 mol of hydrogen chloride. Since the reaction mixtures are occupied by many insoluble metal salts which result in slurried conditions, it is difficult to stir them. Since copper(II) chloride is consumed during the reaction, the yield of PPP based on the oxidant is always less than 100%, i.e., copper(II) chloride does not work as a catalyst. The polymerization of toluene by this method gives a toluene polymer which has mainly a 1,2-phenylene backbone (**1**). Especially, by using carbon disulfide as a solvent, polynuclear polymer (**2**) is obtained which is insoluble in organic solvent.[8] In contrast, by the use of the same reagents, the other group reported that the polymerization reaction also occurs at the benzyl position of toluene molecules.[9] The polymerization of biphenyl by the Kovacic's method was also investigated.[10]



(**1**)



(**2**)

Recently, the present authors have reported that the polymerization of benzene is possible using copper(I) chloride (a low-valence metal salt), aluminum chloride, and oxygen as an oxidant.[11] In this method the polymerization can be performed under considerably homogeneous conditions as copper(I) chloride becomes soluble in benzene by forming a double salt with aluminum chloride ($AlCuCl_4$);[12] no evolution of a hydrogen chloride gas occurs. Furthermore, it becomes possible to polymerize benzene in over 100% yield based on copper(I) chloride.

Since the PPP obtained in this manner is entirely insoluble in organic solvents and does not melt upon a heat treatment, it is a poor material for processing. It is expected that the introduction of alkyl groups into a highly rigid PPP molecule causes its solubility in an organic solvent to be higher while making the processing of this type polymer easy. As one method to make this kind of modification, we tried to polymerize toluene and its analogs by taking advantage of a copper(I) chloride–aluminum chloride–oxygen system. In the present paper we report on the results of

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the polymerization of toluene and other alkylbenzenes as well as those of biphenyl, which was found to polymerize resulting in a PPP oligomer.

Experimental

Materials. The aluminum 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 toluene, *o*-xylene, *p*-xylene, ethylbenzene, and mesitylene were distilled over metallic sodium. The biphenyl was purified by recrystallization from petroleum ether.

The oxygen was dried by being passed through columns of Molecular Sieves 3A and diphosphorus pentaoxide before use.

Analysis. The ^{1}H NMR spectrum measurement was carried out with JEOL models FX90Q and GX400 spectrometers at 89.55 and 399.6 MHz, respectively. The infrared absorption spectra were measured with a JASCO model A-3 spectrometer by a KBr disk method. The GPC was recorded on a TOYO SODA model HLC-802UR chromatograph equipped with TSK-GEL G7000H, G5000H, and G3000H columns.

Polymerization of Toluene by a CuCl-AlCl$_3$-O$_2$ System. Copper(I) chloride (0.835 g, 8.43 mmol), aluminum chloride (3.38 g, 25.3 mmol), and toluene (13.5 cm^3, 127 mmol) were placed in a 100 cm^3 Kjeldahl flask, and the mixtures were stirred at room temperature for 2 h under dry nitrogen. During this stage the copper(I) chloride was completely dissolved and a highly homogeneous solution was obtained, leaving some excess aluminum chloride. The polymerization reaction was carried out by replacing the reaction atmosphere with oxygen and stirring the mixtures at 60 °C for 24 h. As the reaction proceeded, the color of the reaction mixtures changed from green to black at the end of the reaction. Polymerization was terminated by adding an 18% hydrochloric acid solution to the reaction mixtures. After the filtration of the reaction mixtures with a membrane filter (Nippon Millipore Kogyo, an SC type, pore size=8.0 μm), the remaining solid was repeatedly washed with a boiling solution of 18% hydrochloric acid and then with boiling water. The subsequent drying of the brownish black solid product at 100 °C for 24 h yielded 0.170 g (44.8% yield based on the charged copper(I) chloride) of the toluene polymer. The toluene solution was also washed several times with an 18% hydrochloric acid solution and water. After the evaporation of the toluene under reduced pressure, followed by drying for 24 h at room temperature, 0.603 g (159% yield based on the charged copper(I) chloride) of a reddish-brown oily product was obtained, which was soluble in toluene. The solid product was insoluble in benzene, acetone, and petroleum ether, though soluble in chloroform, THF, and DMF.

The results of the elemental analysis of the solid product were: C, 87.1; H, 6.3; Cl, 1.3%. Thus, the C/H ratio is 1.42, which is much higher than 1.17, the calculated value of that for $(C_6H_3(CH_3))_n$. The IR spectrum of the solid product showed bands at 810, 860 (C–H out-of-plane bending vibration of a para-disubstituted benzene ring), 1375 (C–H bending vibration of a methyl group), 1510, 1600 (C=C stretching vibration of a benzene ring), and 2920 cm^{-1} (C–H stretching vibration of a methyl group). The ^{1}H NMR spectrum in CDCl$_3$ (Fig. 2) shows peaks at δ 7.0—7.5 (m; aromatic protons), 2.2—2.5 (m; aliphatic protons of a methyl group substituted on a benzene ring), 1.25, 0.88 (m; aliphatic protons) (vide infra).

The results of the elemental analysis of the liquid product were: C, 90.2; H, 7.0; Cl, 0.6%. Thus, the C/H ratio is 1.09, which is nearly identical with the calculated value of that for $H(C_6H_3(CH_3))_4H$, 1.08. The IR spectrum has bands at 700, 730, 770 (C–H out-of-plane bending vibration of a 1,2- and 1,3-disubstituted benzene ring), 810, 890 (C–H out-of-plane bending vibration of the same species and a 1,2,4-trisubstituted benzene ring), 1375 (C–H bending vibration of a methyl group), 1510, 1600 (C=C stretching vibration of a benzene ring), 2860, 2920 (C–H stretching vibration of a methyl group), and 3020 cm^{-1} (C–H stretching vibration of a benzene ring). The ^{1}H NMR spectrum in CDCl$_3$ (Fig. 3) shows the peaks at δ 7.0—7.4 (m; aromatic protons) and 2.2—2.5 (m; aliphatic protons of a methyl group substituted on a benzene ring).

Polymerization of Biphenyl by a CuCl-AlCl$_3$-O$_2$ System. Copper(I) chloride (0.95 g, 9.60 mmol), aluminum chloride (3.85 g, 28.9 mmol), and biphenyl (14.8 g, 96.2 mmol) were placed in a 100 cm^3 Kjeldahl flask, and stirred at 80 °C for 2 h under dry nitrogen, resulting in a reddish-brown solution. Replacing the solution atmosphere with oxygen started the reaction at the same temperature for 24 h. At the end of the reaction, the color of the mixtures was purple. Reaction was terminated by the addition of an 18% hydrochloric acid solution into the reaction mixtures. The obtained solid was repeatedly washed with boiling petroleum ether, an 18% hydrochloric acid solution, and water. It was then dried at 100 °C for 24 h, resulting in 0.501 g (137% yield based on CuCl) of a brown product (poly(1,4-phenylene)).

The results of the elemental analysis for the solid product were: C, 93.1; H, 4.7; Cl, 1.2%. Thus, the C/H ratio is 1.65, while the calculated value of $(C_6H_4)_n$ is 1.50. The IR spectrum showed bands at 815 (C–H out-of-plane bending vibration of a para-disubstituted benzene ring), 1000 (C–H in-plane bending vibration of the same species), and 1480 cm^{-1} (C=C skeletal in-plane vibration).

Results and Discussion

Polymerization of Toluene by the Use of the CuCl-AlCl$_3$-Oxygen System. Table 1 shows the results of the polymerization of toluene by a copper(I) chloride–aluminum chloride–oxygen (CuCl–AlCl$_3$–O$_2$) system using excess AlCl$_3$ with respect to CuCl. Under these conditions, upon replacing the solution atmosphere by oxygen the polymerization of toluene occurred smoothly, and the toluene polymer was obtained. For example, when a threefold quantity of AlCl$_3$ with respect to that of CuCl was used and the polymerization reaction was carried out at 50 °C for 24 h, a solid polymer of toluene and liquid one were obtained in a yield of 44.8 and 159%, respectively, and no evolution of HCl was observed (run 2). In contrast

Table 1. Polymerization of Toluene Catalyzed by Copper(I) Chloride and Aluminum Chloride under Oxygen[a]

Run	Charged molar ratio[b]		Temperature /°C	Yield/%[c]		
	$AlCuCl_4$	Excess $AlCl_3$		Solid	Liquid	Total
1	1.0	2.0	15	19	52	71
2	1.0	2.0	50	45	159	204
3	1.0	2.0	91	45	369	414
4	1.0	4.5	50	192	367	559
5	2.0	4.0	50	31	155	186
6	4.0	8.0	50	86	69	155
7	1.0	2.0+2.5[d]	50	199	287	486

a) Reaction time, 24 h. b) Toluene=15.0. c) Based on CuCl. d) After the reaction with 2.0 excess molar ratio of aluminum chloride for 12 h, then adding further 2.5 excess molar ratio of aluminum chloride, the reaction was continued for further 12 h.

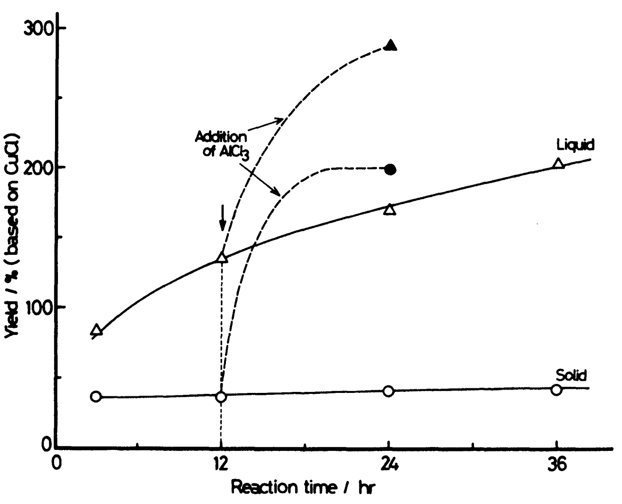
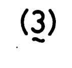


Fig. 1. Changes with the reaction time in the yields of the solid (O) and liquid (Δ) products of the toluene polymer by a $CuCl-AlCl_3-O_2$ system. The charged molar ratio of $CuCl/AlCl_3$/toluene was 1:3:15 and the reaction temperature was 50 °C. Closed circles and triangles show the yields of the toluene polymer in the case of the extra addition of 2.5 excess molar ratio of $AlCl_3$ to CuCl after the reaction for 12 h using 3 fold of $AlCl_3$ to CuCl.

with the Kovacic's method in which $CuCl_2$ works as a reagent, it becomes apparent that toluene polymerizes catalytically with respect to CuCl in the present method.

The yield of the toluene polymer generally increased with the reaction time. The yield of the solid product, however, became saturated within a few hours in contrast with that of the liquid one (Fig. 1). This result indicates that the formation mechanisms of the solid and liquid product are different from each other (vide infra). The yield of the toluene polymer was also influenced by the reaction temperature and the quantity of excess $AlCl_3$. As shown in Table 1, the yield of the toluene polymer became higher upon raising the reaction temperature (run 3) or increasing the quantity of excess $AlCl_3$ (run 4). Furthermore, a drastic increase in the yield could be achieved by an extra addition of $AlCl_3$ in the middle of the reaction and continuous stirring for another 12 h (run 7), as shown by dashed lines in Fig. 1 (the yields of the solid and the liquid products are 199 and 287% respectively at reaction temperature of 50 °C). These results indicate that the excess $AlCl_3$ is consumed during the reaction. In fact, when a half molar ratio of water to $AlCl_3$ was added to the reaction system, the polymerization reaction could be suppressed and the yield of the toluene polymer decreased by half. In addition, oxygen was consumed during the polymerization reaction. In a previous paper,[11] we reported on the result of oxygen uptake during the polymerization of benzene. In this case, the uptake of oxygen nearly corresponded to a one-half molar amount of the yield of poly(1,4-phenylene). Therefore, the deactivation of $AlCl_3$ during the reaction is considered to be due to the hydrate formation of $AlCl_3$ with the water generated by the reaction between oxygen and protons which is eliminated from toluene. On the other hand, the polymer yield increases upon rising the reaction temperature.

Structure of Toluene Polymer. Analytical data of the polymers of toluene are shown in Table 2. If the polymerization product has a disubstituted toluene structure in its polymer chain, i.e., an ideal "polytoluene" structure (**3**), the C/H ratio of the polymer given from elemental analysis should be 1.17.



(**3**)

The observed value for the solid polymers, however, is about 1.4, which is higher than 1.17. This result suggests that a considerable intramolecular crosslinkage would occur after the addition reaction of toluene, instead of rearomatization by dehydrogenation. This consideration is supported by the results of a ^1H NMR spectral measurement. In the case of the solid product, the areal ratio of peaks of the aromatic protons to those

Table 2. Analytical Data of the Toluene-Polymer Prepared by a Copper(I) Chloride-Aluminum Chloride-Oxygen System

	Anal.	^{1}H NMR		IR/cm^{-1}	GPC$^{b)}$	UV
	C/H	Ar$\underline{H}$:C$\underline{H}_3$	C-C$\underline{H}_3$$^{a)}$		count	λ_{max}/nm
Solid product	1.42	8:15	yes	810, 860, 1370, 1510, 1600, 2920	85	450
Liquid product	1.06	1;1	no	700, 730, 770, 810, 890, 1375, 1510, 1600, 2860, 2920, 3020	90	360

a) Peaks at δ 0.88 and 1.24. b) Conditions: columns, TSK-GEL G7000H+G5000H+G3000H; eluent, $CHCl_3$; temperature, 30 °C.

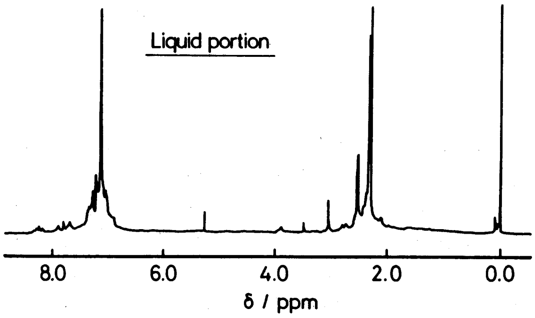
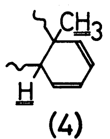
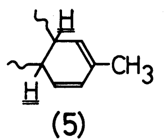


Fig. 2. ^{1}H NMR spectrum of the solid product of the toluene polymer prepared by a $CuCl-AlCl_3-O_2$ method (in $CDCl_3$ at 55 °C with a JNM GX-400 spectrometer).

of the methyl protons is 8:15, which fairly deviates from the ideal ratio 1:1. This means that a sufficient amount of aromatic protons isn't included in this polymer structure. Furthermore, as shown in Fig. 2, unexpected peaks from the wholly aromatized toluene polymer structure, such as **1**, **2**, or **3**, were observed at δ 0.88 and 1.24 in the NMR spectra of the toluene polymer. These peaks were not found in the spectra of Kovacic's toluene polymer.[8] Since the peaks at these positions are attributed to aliphatic protons, these observations suggest that the solid polymer obtained in the present investigations arises from a nonaromatized "quinonoid-like" structure like **4**, **5**, and **6**.


(4)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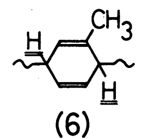

(6)

Therefore, the solid product is considered to have the following components in its chemical structure: (a) a highly crosslinked structure between aromatic rings, and (b) a nonaromatized "quinonoid-like" structure. Based on these considerations, an example of the structure **7** which is consistent with the observed analytical data might be depicted in order to estimate the structure of the solid toluene polymer.

On the other hand, the C/H ratio of the liquid product calculated from the elemental analytical data is about 1.1, which is near to the value of the ideal toluene polymer ($(C_6H_3(CH_3))_n$). The peaks at a high magnetic field in the ^{1}H NMR spectrum, which were observed for the solid polymer, were not found in the liquid polymer (cf. Fig. 3). The areal ratio of the peaks of the aromatic and the methyl protons is almost 1:1. Therefore, the liquid product can be proved to have the ideal "polytoluene" structure (**1** or **3**), in which the framework of toluene is held in the polymer chain. The molecular weight of the toluene polymer was investigated by GPC. In the case of the liquid product, although the peaks of GPC spectrum appeared nearly at the limit of the detection area, the main component could be an oligomer, perhaps a tetramer of toluene.

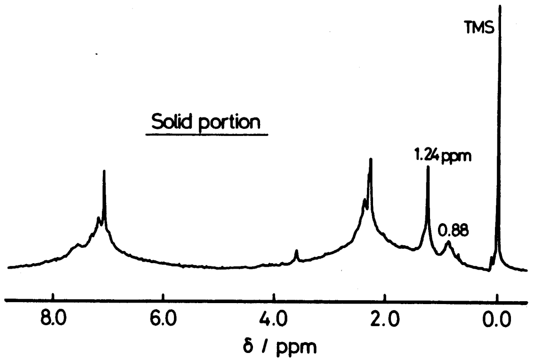
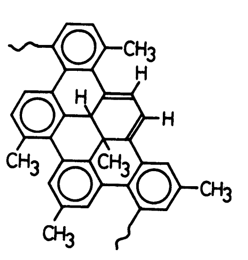


Fig. 3. ^{1}H NMR spectrum of the liquid product of the toluene polymer prepared by a $CuCl-AlCl_3-O_2$ method (in $CDCl_3$ at 25 °C with a JNM FX-90Q spectrometer).


(7)

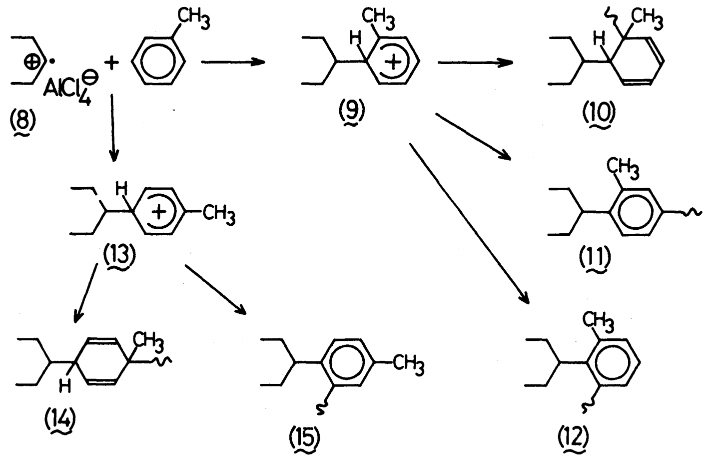
C/H=1.42
Ar$\underline{H}$:C$\underline{H}_3$=8:15

It was reported that, by the use of a Kovacic's method, the polymerization reaction also occurs at the benzyl position of a toluene molecule.[9] In the present method, however, the reaction probably doesn't occur at the benzyl position because neither the liquid product nor the solid product has any peak around δ 4 in the ^{1}H NMR spectrum assigned to methylene protons connected by two phenylene groups.

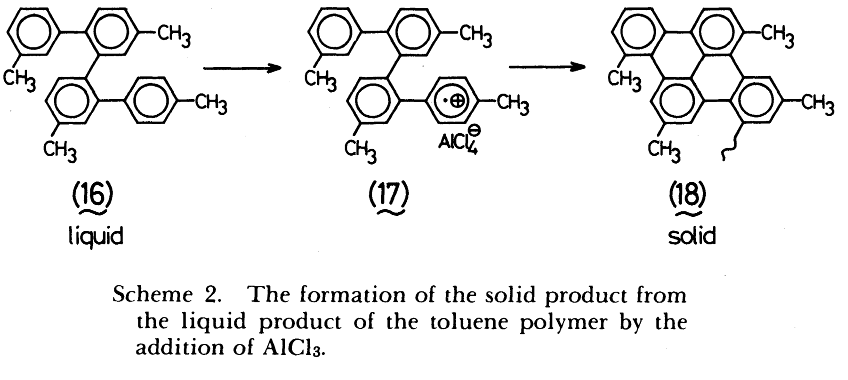
Polymerization Mechanism of Toluene. (a) Formation Mechanism of the Solid Product: The solid polymer of toluene obtained by the CuCl-AlCl$_3$-O$_2$ system has characteristic aliphatic protons due to a "quinonoid-like" structure. The formation of such protons requires the existence of a ring structure which is connected to another benzene ring of toluene at the carbon atom which substituted by a methyl group. In order to form this kind of structure, a cation radical on a benzene ring of toluene must attack another toluene molecule in an electrophilic way, resulting in cationic polymerization. The possible mechanism is illustrated in Scheme 1. Since the benzene ring of toluene is favorably attacked by electrophiles at the ortho- and para-positions, the toluene molecules attacked by the cation radical of toluene (**8**) would produce species **9** and **13**. When species **9** and **13** are attacked by the next toluene molecule, species **10**, **11**, **12**, **14**, and **15** could be considered to be produced, respectively, on the basis of the orientation of toluene in the substitution reaction. That is to say, the "quinonoid-like" structures (**10** and **14**) are considered to be formed by an extension of the polymer chain from the carbon atoms attached to a methyl group, since the density in positive charge on these carbon atoms is high due to the methyl group.

(b) Formation Mechanism of Liquid Product: In the polymerization of benzene using CuCl$_2$ and AlCl$_3$, Kovacic et al. already proposed a "stair-step" mechanism.[13] That is to say, it now appears the benzene cation radicals serve as the sites for coordination with an appreciable number of benzene nuclei in a propagative manner as stair steps, ranging from straight to spiral. When the chain buildup reaches a certain stage, the radical cation character on the terminal members become too small to induce further propagation. Covalent bond formation and the elimination of protons and electrons then lead to poly(1,4-phenylene). As to the mechanism for the formation of the liquid toluene polymer obtained by the present method, the "stair-step" mechanism is thought to be reasonable. This mechanism is supported by the absence of the peaks at δ 0.88 and 1.24, which appear in the solid product, in the ^{1}H NMR spectrum of the liquid product. This result is considered to be due to a small possibility for the formation of the aliphatic methyl group on the basis of the "quinonoid-like" structure. This is because it is almost impossible by a steric hindrance upon connecting with the stair steps that a toluene molecule can attack the carbon atom attached to a methyl group.

(c) The Effect of the Addition of Excess AlCl$_3$ in the



Scheme 1. The proposed mechanism for the solid toluene polymer.



Scheme 2. The formation of the solid product from the liquid product of the toluene polymer by the addition of AlCl$_3$.

Course of the Reaction: The extra addition of excess $AlCl_3$ in the course of the reaction and further stirring of the reaction mixtures greatly increased the yield of the toluene polymer based on CuCl. When the reaction was carried out for the same period by adding the excess amount of $AlCl_3$ at once (at the beginning of the reaction), the yield of the polymer was also high. The structure of the latter polymer, however, was different from that of the polymer obtained in the former manner. The intensity of the peaks at δ 0.88 and 1.24 in the ^{1}H NMR spectrum of the former polymer was lower than that of the latter one. In the former case, the liquid product which formed before the extra addition of $AlCl_3$ is considered to give rise to intramolecular crosslinking and to initiate cationic polymerization again after the extra addition of $AlCl_3$, resulting in the solid product (Scheme 2). In the beginning, the liquid product does not involve the "quinonoid-like" structure. If this liquid product is crosslinked and forms a part of the solid product, the intensity of the ^{1}H NMR peaks at δ 0.88 and 1.24 would be relatively low in comparison with the solid product directly obtained. In fact, the treatment of the isolated liquid product by $AlCl_3$ in nitrobenzene gave the crosslinked insoluble solid product, indicating that the crosslinking reaction occurred as the result of the extra addition of $AlCl_3$ to the liquid toluene polymer and also that the liquid product had a 1,2-phenylene backbone which could be easily crosslinked (cf. **16** in Scheme 2). As shown in Fig. 1, the yield of the solid product doesn't increase with the reaction time, although the yield of the liquid product does. The reason for this is considered to be due to the deactivation of $AlCl_3$ by hydrate formation with water, since only free $AlCl_3$ could serve as a crosslinking reagent.

Table 3. Polymerization of Various Kinds of Benzene Derivatives Catalyzed by Copper(I) Chloride–Aluminum Chloride under Oxygen[a]

Aromatic compound	Yield/%[b]
o-Xylene	106[c]
p-Xylene	140
Ethylbenzene	91
Mesitylene	81

a) Reaction time, 24 h. Reaction temperature, 50 °C. CuCl : $AlCl_3$: Aromatic compound=1 : 3 : 20. b) Based on the aromatic compound. c) The total yield involving the solid product (5%).

Polymerization of Other Benzene Derivatives. The polymerization of xylenes, ethylbenzene, and mesitylene was attempted by using the present system. Every monomer gave the corresponding polymerization product. The yields of these product are summarized in Table 3. A solid product was obtained only in the case of *o*-xylene. However, no particular difference in the IR spectra was observed between the solid and liquid products of the *o*-xylene polymer. As can be seen in Table 3, the catalytic effectiveness for the present system decreases in the case of polymerizations of xylenes compared with toluene, in spite of the higher solubility of the reaction product. For the polymerization of toluene, the catalytic effectiveness is higher than that for the polymerization of benzene. Thus, the yields of the benzene polymer and the toluene polymer are 65 and 210%, respectively, at a reaction temperature of 50 °C. The decrease in the yield of the xylene polymer is thought to be the result of a steric hindrance of substituted groups. The ^{1}H NMR spectra showed intense peaks at higher magnetic fields (about δ 1—1.5), suggesting the existence of the "quinonoid-like" structure in these cases as well. These liquid polymerization products are thought to contain both liquid and solid products which correspond to those in the case of the polymerization of toluene, since the other benzene derivatives have many, or long, alkyl groups and the degree of polymerization would be low in these derivatives.

In the case of biphenyl, the polymerization product by the present method exhibited a lighter brown color than that of benzene. The IR spectrum suggested that the polymer involves only mono- and disubstituted benzene rings, not trisubstituted ones. The intensity ratio of the absorption peaks at 700 and 760 cm^{-1}, which were attributable to the C–H vibration of a monosubstituted benzene ring, to that at around 800 cm^{-1} (which was attributable to the C–H vibration of a para-disubstituted benzene ring), was stronger than that of poly(1,4-phenylene). These facts indicate that the polymer obtained from biphenyl is a kind of poly(1,4-phenylene), though its molecular weight is lower than that obtained from benzene. Furthermore,

Table 4. The IR Peak Attributed to the C–H Vibration of a para-Disubstituted Benzene Ring of 1,4-Phenylene Oligomers

p-Phenylene compound	Wavenumber/cm^{-1}	Reference
p-Terphenyl	842	14
p-Quaterphenyl	830	14
p-Quinquephenyl	820	14
p-Sexiphenyl	815	14
Poly(1,4-phenylene)	800	7, 11
Biphenyl-polymer	815	Present work

the peak based on the C–H vibration of a para-disubstituted benzene ring was detected at a higher-wavenumber position (815 cm^{-1}) in this polymer than that in the usual poly(1,4-phenylene) from benzene (800 cm^{-1}). It is reported that the absorption band at this area in poly(1,4-phenylene) shifts to a lower wavenumber by increasing the number of para-disubstituted benzene rings.[14] The absorption band at 815 cm^{-1} is quite similar to that reported for *p*-sexiphenyl (Table 4). Thus, the main part of the biphenyl polymer obtained in the present catalytic system is thought to be a trimer of biphenyl (a hexamer with respect to phenylene unit).

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