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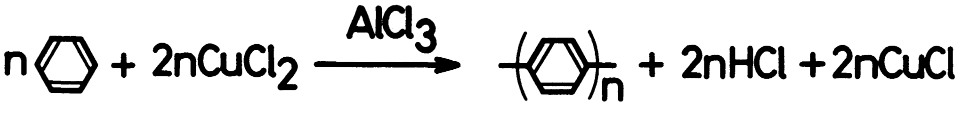
Polymerization of Benzene Catalyzed by Aluminium Chloride-Copper(I) Chloride under Oxygen

Hidefumi HIRAI,† Naoki TOSHIMA,* Keiichi KANAKA, and Atsunori KOSHIRAI
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Polymerization of benzene to poly(1,4-phenylene) has been succeeded under oxygen using an aluminium chloride-copper(I) chloride catalyst. Treatment of benzene with aluminium chloride / copper(I) chloride (3 / 1 molar ratio) under oxygen at 70 °C gave poly(1,4-phenylene) in 187% yield based on the molar quantity of copper(I) chloride. Extra addition of aluminium chloride in the course of the reaction increased the yield dramatically from 187% to more than 600%.

Poly(1,4-phenylene) (PPP) is an interesting material from the viewpoint of conjugated polymer which is thermally resistant1) and can be electrically conductive by doping with dopants such as arsenic(V) fluoride.2) PPP can be synthesized with various kinds of methods. The reported examples are dehalogenation of dihalogenated benzene by nickel complex catalysts,3) conversion of precusor polymer (such as poly-1,3-cyclohexadiene,4) and its derivative5)), polymerization of benzene by solid superacid,6) and electrolytic oxidative polymerization of benzene.7) One of well-known procedures is the polymerization of benzene by a Lewis acid-oxidant system reported by Kovacic et al. In this method, an aluminium chloride-copper(II) chloride system8) and iron(III) chloride9) were chosen as catalysts for effective polymerization. However, the oxidizing metal salts are consumed during the reaction, and the yield of PPP based on the metal salt is always less than 100%. Furthermore, as the metal salts does not dissolved in benzene and results in slurried conditions, it is difficult to stir the reaction mixtures even at the beginning of the reaction. Since polymerization of 1 mol of benzene in this reaction produces 2 mol of hydrogen chloride (Eq. 1), vigorous evolution of a large amount of hydrogen chloride cannot avoidable.



(1)

It is known that aluminium chloride and copper(I) chloride can form a double

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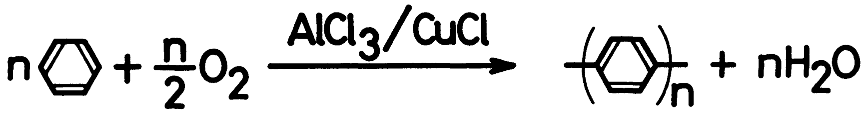
†Present address: Department of Industrial Chemistry, Faculty of Engineering, The Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162.

salt of aluminium copper(I) chloride ($AlCuCl_4$), which is soluble in benzene by coordination of benzene to the salt.10) Copper(I) chloride is by-product in the preparation of PPP from benzene according to the Kovacic's method, and is known to be easily re-oxidized by an oxidant like an oxygen gas to copper(II) chloride.11) Under these background, we have tried to polymerize benzene in the presence of aluminium chloride, copper(I) chloride, and dioxygen (Eq. 2). Under these conditions, the polymerization is expected to undergo efficiently because of homogeneity of the reaction system. PPP can be expected to be obtained in more than 100% yield based on copper(I) chloride.



(2)

The starting materials were purified by usual manners. Benzene was distilled over metallic sodium. Copper(I) chloride was reprecipitated from an aqueous hydrochloric acid solution by addition of water, and was dried in vacuo at 80 °C for 24 h. Aluminium chloride was purified by sublimation.

Polymerization of benzene was carried out as follows. First, copper(I) chloride and aluminium chloride were stirred in benzene at room temperature for 2 h under nitrogen. If the molar quantity of aluminium chloride a little exceeded that of copper(I) chloride, the mixtures became homogeneous. However, if large excess of aluminium chloride was used, some parts of aluminium chloride could not dissolved in the solution. Replacing the reaction atmosphere with oxygen made the reaction start. When the reaction mixtures were incubated at prescribed temperature, smooth polymerization was occurred without the evolution of hydrogen chloride. As the reaction proceeded, the color of the reaction mixtures became dark brown, and the dispersed precipitates were produced. Polymerization was terminated by adding 18% hydrochloric acid into the reaction mixtures. After filtration, the remaining solid was repeatedly washed with a hot solution of 18% hydrochloric acid, and then with hot water. Drying of the product at 100 °C for 12 h resulted in dark brown fine powder. The filtrate was extracted by benzene and the benzene solution was also washed with a 18% hydrochloric acid solution and water. Evaporation of benzene under reduced pressure gave a reddish brown viscous mass. IR spectra were measured with a JASCO model A-3 spectrometer.

Table 1 shows the charged molar ratios of each component, reaction temperature, and yields of PPP. When the reaction was carried out using benzene solution of $AlCuCl_4$ under oxygen, PPP was not obtained at all (run 1). Incidentally, when the reaction was carried out using another oxidant such as iodine, potassium permanganate, iron(III) chloride, and even copper(II) chloride instead of oxygen, PPP was not obtained at all.12)

In contrast, addition of excess aluminium chloride with respect to copper(I) chloride made benzene polymerize smoothly (runs 2-8). For examples, when copper(I) chloride, aluminium chloride, and benzene (1:3:20 in molar ratio) were treated at 60 °C under oxygen (run 4), the insoluble solid product and benzene-soluble viscous mass were obtained. Elemental analyses of these insoluble polymers were near to that of PPP (in the case of run 4, Found : C, 92.7; H, 5.0;

Table 1. Polymerization of benzene catalyzed by aluminium chloride-copper(I) chloride under oxygen[a)]

Run	Charged molar ratio[b)]		Temperature	Yield / %[c)]		
	$AlCuCl_4$	excess $AlCl_3$	°C	Insoluble[d)]	Soluble[d)]	Total
1	2.0	0	50	0	0	0
2	1.0	2.0	40	5	4	9
3	1.0	2.0	50	43	22	65
4	1.0	2.0	60	119	46	165
5	1.0	2.0	70	187	41	228
6	0.5	1.0	60	111	47	158
7	1.0	1.0	60	56	11	67
8	2.0	4.0	60	139	51	190
9	1.0	2.0+3.8[e)]	60	649	154	803

a) Reaction time : 24 h except run 9. b) Benzene=20.0. c) Based on CuCl. d) Insoluble or soluble in benzene. e) After the reaction with 2.0 excess molar ratio of aluminium chloride for 24 h, adding further 3.8 excess molar ratio of aluminium chloride, then, reaction was continued for further 24 h.

Cl, 1.1%. Calcd for C_6H_4 : C, 94.7; H, 5.3%). The contamination of chlorine may be due to the partial chlorination of the aromatic rings of polymers. Infrared spectra of the polymers were identical with those of PPP prepared by using a aluminium chloride-copper(II) chloride system (Kovacic's method).[7)] The typical absorption band for PPP were observed at 800 cm^{-1}, 1000 cm^{-1}, and 1480 cm^{-1}, which are attributable to the C-H out-of-plane, and in-plane vibration of para disubstituted benzene ring, and C=C skeletal in-plane vibration, respectively. The yield of insoluble PPP, prepared under the condition of run 4, was 119 % based on copper(I) chloride.

The yield of PPP was strongly influenced by the quantity of the excess aluminium chloride. As mentioned above, when 3 fold aluminium chloride to copper(I) chloride was used, PPP was obtained in the yield more than 100%. This result clearly indicates that copper(I) chloride works as a catalyst. When twice aluminium chloride to copper(I) chloride was used, however, the yield of PPP didn't exceed 100% (run 7). In contrast, the yield increased up to 803% by extra addition of 3.8 fold aluminium chloride with continueous stirring for further 24 h after the reaction carried out with 3 fold aluminium chloride for 24 h (run 9). This result indicates that excess aluminium chloride is consumed during the reaction. Aluminium chloride is considered to be deactivated by water generated from oxygen and protons eliminated from benzene.

The yield of PPP rose drastically with rising reaction temperature (runs 2-5). The rising of reaction temperature, however, tends to increase the content of chlorine in the product. The molar ratio of benzene to copper(I) chloride, in contrast, exerts little influence on the yield of PPP (runs 4, 6, and 8).

Because of insolubility of PPP, molecular weight of PPP was indirectly determinated by the GPC measurement (using two TSK-GEL G 2000H columns, and chloroform as eluent) of the alkylated PPP produced by the reaction with 1-bromopropane.13) In the case of PPP prepared by the Kovacic's method, the peak of GPC spectrum was around 42 in elution count. In the present case, the GPC spectrum consisted of the main peak at 42 and a shoulder peak at 45 in the elution count. Thus, the PPP prepared by the present method contained the lower molecular weight portions than the one prepared by the Kovacic's method. This result is consistent with the formation of considerable amounts of benzene-soluble portion14) in the present case.

A detailed study on the reaction mechanism is currently under way.

References

1) Reviews : J. G. Speight, P. Kovacic, and F. W. Koch, Rev. Makromol. Chem., 6, 295 (1971); G. K. Noren and J. K. Stille, J. Polym. Sci., Macromol. Revs., 5, 385 (1971); Y. Imai, Yuki Gosei Kagaku Kyokai Shi, 42, 1061 (1984).

2) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys., 71, 1506 (1979).

3) T. Yamamoto, Y. Hayashi, and A. Yamamoto, Bull. Chem. Soc. Jpn., 51, 2091 (1978).

4) C. S. Marvel and G. E. Hartzell, J. Am. Chem. Soc., 81, 448 (1959).

5) D. G. H. Ballard, A. Courtis, I. M. Shirley, and S. C. Taylor, J. Chem. Soc., Chem. Commun., 1983, 954.

6) N. Kitajima, Y. Hakone, and Y. Ono, Chem. Lett., 1982, 871.

7) I. Rubinstein, J. Electrochem. Soc., 130, 1506 (1983); M. Tabata, M. Satoh, K. Kaneto, and K. Yoshino, J. Phys. Soc. Jpn., 55, 1305 (1986).

8) P. Kovacic and A. Kyriakis, J. Am. Chem. Soc., 85, 454 (1963).

9) P. Kovacic and F. W. Koch, J. Org. Chem., 28, 1864 (1963).

10) R. W. Turner and E. L. Amma, J. Am. Chem. Soc., 88, 1877 (1966).

11) In fact, the catalytic polymerization of benzene in a heterogeneous state catalyzed by $CuCl_2$-$AlCl_3$ under O_2 was reported. However, the reaction also vigorously evolves hydrogen chloride (K. Oomae and M. Hirabayashi, Japan Patent 42 2280 (1967); Chem. Abstr., 67, 44288n (1967)).

12) As reported, $CuCl_2$ and $AlCl_3$ in benzene give PPP. However, the present result indicates that the addition of CuCl to this system, forming the double salt, $AlCuCl_4$, inhibits the polymerization.

13) M. B. Jones, P. Kovacic, and D. Lanska, J. Polym. Sci., Polym. Chem. Ed., 19, 89 (1981).

14) Molecular weight of benzene-soluble portion of PPP was roughly in the range of 100 to 3000 (calibrated with polystyrene standard).

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