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POLYMERIZATION OF BENZENE WITH $Cu(AlCl_4)_2$

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$Cu(AlCl_4)_2$ reacts with benzene to give poly(1,4-phenylene). When 2.5 mmol of benzene was reacted with 2.5 mmol of $Cu(AlCl_4)_2$ at 20°C for 2 h, poly(1,4-phenylene) was obtained in 92 % yield, which is higher than that obtained with the conventional system, $AlCl_3$-$CuCl_2$ mixture, under the same conditions.

Benzene is polymerized to poly(1,4-phenylene) on treatment of benzene with Lewis acid-oxidant systems, in the most cases in the presence of water.1) The mixture of aluminum chloride and copper(II) chloride2-3) was reported to be particularly effective for the polymerization under mild conditions, while several other effective systems include $AlCl_3$-NO_2,4) $AlBr_3$-$CuBr_2$,3) $SbCl_5$-$CuCl_2$,3) $MoCl_5$5) and $FeCl_3$.6)

Recently, the mixture of aluminum chloride and copper(II) chloride, especially when kneaded, was found to be an active catalyst for the isomerization of pentane under ambient conditions, though each of the components is not active at all.7-8) By heating the mixture, the present authors isolated a novel 2:1 complex of aluminum chloride and copper(II) chloride, $Cu(AlCl_4)_2$, and attributed the synergism to the formation of the complex in the mixture, since the complex has very high activity for the isomerization.9-10) The crystal structure of $Cu(AlCl_4)_2$ has been determined by a single-crystal X-ray analysis.11) The study on the isomerization mechanism over $Cu(AlCl_4)_2$ suggested that $Cu(AlCl_4)_2$ has both properties as a Lewis acid and an oxidant.12) Therefore, it was predicted that the polymerization of benzene should proceed on treatment of $Cu(AlCl_4)_2$. Herein, we report that this is indeed the case.

$Cu(AlCl_4)_2$ was prepared by heating a mixture of 2.0 g of aluminum chloride and 1.0 g of copper(II) chloride at 240°C for 10 h in a glass ampule. The formation of $Cu(AlCl_4)_2$ was confirmed by the X-ray diffraction pattern of the heated mixture. Aluminum chloride was purified by sublimation from the eutectic of aluminum chloride and sodium chloride with a small amount of aluminum powder. Copper(II) chloride was prepared by dehydrating $CuCl_2$ $2H_2O$ in air at 250°C for 3 h and then under vacuum at 250°C for 2 h. The reaction procedures are as follows: $Cu(AlCl_4)_2$ was placed under nitrogen in a reaction vessel with a volume of 40 ml. The vessel, connected to a vacuum system with a dead volume of 200 ml, was evacuated and cooled with liquid nitrogen. Benzene was then distilled into the reactor and the temperature of the reactor was warmed to the ambient. Gas was evolved and its amount was monitorred with time by manometric measurements of the pressure. After the reaction, iospropyl alchool was introduced into the vessel in order to dissolve inorganic materials. Then, the remaining solid was separated by filtration, treated with boiling concentrated hydrochloric acid to eliminate the remaining metal halides, and washed with distilled water till chlorine ion was not detected in the filtrate, and finally dried under vacuum at 120°C for 5 h.

When 2.5 mmol of benzene was reacted with 2.5 mmol of $Cu(AlCl_4)_2$ for 2 h at 20°C, 0.087 g of the resinous solid of brownish black was obtained. The elemental analyses of the solid were almost in agreement with those of poly-phenylene, although a small amount of chlorine was also contained. (Calcd:C, 94.74; H, 5.26. Found:C, 93.88; H, 4.73; Cl, 1.39) The chlorine may be due to remaining metal chlorides or partial chlorination of the aromatic rings of the polymer. The infrared spectrum and the X-ray diffraction pattern of the polymer were essentially same as those of poly(1,4-phenylene) reported by Kovacic et al..2) Thus, the principal absorption band, characteristic of para substituents, was observed at 805 cm^{-1}. The less intense absorption bands at 767 and 692 cm^{-1} attributable to monosubstituted benzene ring were also observed. The X-ray diffraction pattern, which demonstrated that the polymer was highly crystalline, gave values of 4.53, 3.99 and 3.20 Å for the d-spacings in decreasing order of intensity. Since the intensity of d-spacing at 4.53 Å corresponding to a phenyl unit is strong, the polymer obtained has essentially all para structure.

During the reaction, evolution of gas observed. As shown in Fig. 1, the evolution is fast for the first 20 min, but almost ceases after 1.5 h. The most part of the gas (>99 %) was hydrogen chloride and a small amount of $C_1 \sim C_5$ hydro-

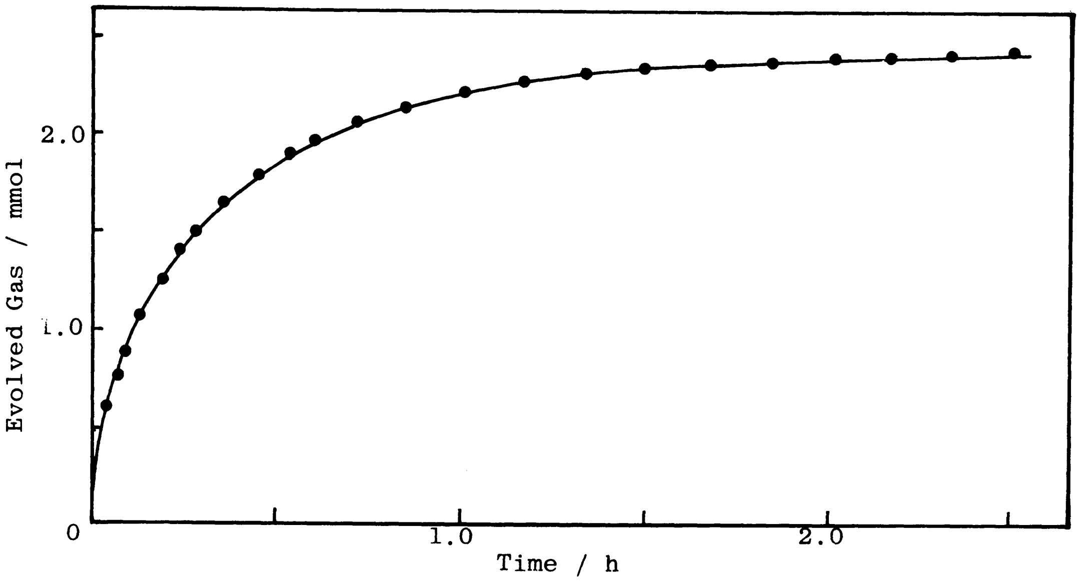


Fig. 1. Time Course of Benzene Polymerization

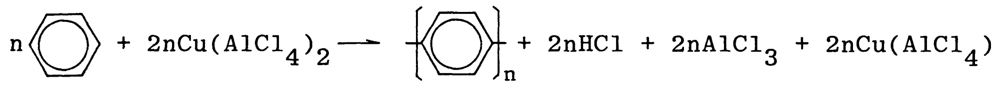
Benzene; 2.5 mmol, $Cu(AlCl_4)_2$; 2.5 mmol
Reaction Temperature 20°C

Table 1. Polymerization of Benzene with Various Metal Halides.

Reagent	Yield wt./g	Yield %*
$AlCl_3$(2.5 mmol)-$CuCl_2$(2.5 mmol) no kneaded	0.043	45.0
$AlCl_3$(2.5 mmol)-$CuCl_2$(2.5 mmol) kneaded	0.068	71.4
$Cu(AlCl_4)_2$(2.5 mmol)	0.087	92.4
$GaCl_3$(5.0 mmol)-$CuCl_2$(5.0 mmol) kneaded	0.075	39.6

2.5 mmol of benzene was reacted for 2 h at 20°C. *Cu base mol%

carbons, mainly isobutane, were detected by gas chromatography. The molar amount of hydrogen chloride evolved in 2 h is almost equal to that of the complex and twice of benzene reacted. These quantitative relations always held for varing starting ratios of benzene and $Cu(AlCl_4)_2$. The reduction of copper(II) ion was confirmed by ESR on addition of benzene to $Cu(AlCl_4)_2$. At the same time, a singlet absorption of appreciable intensity (g = 2.0023) was observed, though the assignment is not made yet. Therefore, the reaction could be expressed by the following equation.



Here, $Cu(AlCl_4)_2$ probably exists as a stable complex with unreacted benzene.[13)]

The activities of $Cu(AlCl_4)_2$ and $AlCl_3$-$CuCl_2$ mixture were compared by the yield after 2 h reaction under the same reaction conditions. The mixture was either prepared by simply mixing two substances in the reactor as in the works by Kovacic and coworkers,[14-15] or by kneading two substances in a porcelain mortar for 5 min. They are designated as a mixture of $AlCl_3$-$CuCl_2$ and a kneaded mixture of $AlCl_3$-$CuCl_2$, respectively. As described earlier, previous works revealed the presence of $Cu(AlCl_4)_2$ in the kneaded mixture of $AlCl_3$-$CuCl_2$. As shown in Table 1, the reaction was almost quantitative with $Cu(AlCl_4)_2$, while the mixtures gave lower yields. Between the two types of mixtures, the kneaded $AlCl_3$-$CuCl_2$ gave higher yield than the $AlCl_3$-$CuCl_2$ mixture. These trends for benzene polymerization are in complete agreement with those for pentane isomerization, indicating that the reactive species for benzene polymerization in the mixtures is also $Cu(AlCl_4)_2$ formed from the two components.

The kneaded mixture of gallium chloride and copper(II) chloride is also an active catalyst for pentane isomerization, and forms partly a new compound, $Cu(GaCl_4)_2$. Thus, the kneaded mixture of $GaCl_3$-$CuCl_2$ was used as a reagent for benzene polymerization. As shown in Table 1, the mixture polymerizes benzene, though the yield is lower than that obtained with $AlCl_3$-$CuCl_2$ mixture.

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