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# Preparation of Poly(1,4-phenylene) by Oxidative Polymerization of Benzene with 2,3-Dichloro-5,6-dicyano-p-benzoquinone

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Oxidative polymerization of benzene with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) under strongly acidic conditions produced structure-defined poly(1,4-phenylene) (PP). Addition of $CF_3SO_3H$ prior to the stoichiometric oxidation enabled the efficient formation of the protonated $\sigma$-complex of benzene through which linear PP (degree of the polymerization was ca. 30) was produced by the subsequent addition of DDQ.

Syntheses of $\pi$-conjugated polymers has been the subject of many investigations.[1)] Poly(1,4-phenylene) (PP) deserves much attention directed toward the applications to electronic devices due to its high conductivity.[2)] PP is synthesized by electrochemical as well as chemical oxidative polymerization of benzene. Electrochemical preparation provides doped and cross-linked PP due to the oxidation at high applied potential (ca. 2.8 V vs. Ag/AgCl).[3)] Chemical polymerization using $AlCl_3$-CuCl has been developed with a view of mass production.[4)] Reductive coupling of dihalobenzene by electrolysis or with chemical reductants has also been described to avoid cross-linking.[5)] However, the product is sometimes contaminated with the oxidant and/or the reductant, and is obtained as very low-molecular-weight polymer. In addition, insolbility of PP gives rise to great difficulties in the characterization as well as in the synthesis.

Recently, much effort has been consumed to develop chemical preparation of pure PP with high conductivity for mass production. Trifluoromethanesulfonic acid has been found to promote electron transfer in the oxidative polymerization of benzene by reducing the oxidation potential to ca. 1.6 V vs. Ag/AgCl.[6)] Here we report the oxidative polymerization of benzene in strongly acidic medium for chemical preparation of pure poly(1,4-phenylene) whose structure is confirmed to be linear in comparison with the PP obtained by the conventional methods.

The polymerization was performed as follows. Trifluoromethanesulfonic acid (15.0 g, 2.0 mol $dm^{-3}$) was dissolved in nitromethane (50 $cm^3$) at 0 °C to which was added benzene (5.47 g, 1.4 mol $dm^{-3}$). The reaction mixture was stirred at 0 °C under anaerobic conditions for 1 h. DDQ (17.0 g, 1.5 mol $dm^{-3}$) was added to the solution under stirring for 20 h. By pouring the mixture into methanol to precipitate the product, and washing successively with aqueous KOH and methanol, PP was obtained as a brown powder. Yield: 95 wt%.

The polymer was obtained as an insoluble powder with empirical formula of $C_6H_4$.[7] Elemental analysis and IR spectrum confirmed that the obtained polymer was a pure PP without any detectable structural defect. 2,3-Dichloro-5,6-dicyano-p-hydroquinone (DDH) was isolated quantitatively after the polymerization. The IR spectrum clearly exhibited absorptions at 800, 760, and 690 $cm^{-1}$ that was characteristic of the phenylene chain (Fig. 1). The absorption at 800 $cm^{-1}$ was attributed to the C-H out-of-plane vibration of 1,4-disubstituted phenylene unit. No peak was observed between 900 $cm^{-1}$ and 800 $cm^{-1}$, by which branched or cross-linked structure was excluded. The absorption attributed to the C-H vibration of the monosubstituted phenyl group at the end of the polymer chain was observed at 760, and 690 $cm^{-1}$. The relationship between the degree of polymerization (DP) and the ratio of the intensity of these peaks has been reported as $DP = 2(I_{800}/I_{690}) + 2$.[8] DP of the obtained polymer thus determined was ca. 30[9] which was larger than that of the polymer by Kovacic's method (DP = 10-20).

The polymerization has been suggested to proceed through the *stair-step mechanism* as scheme 1.[10]

$$C_6H_6 \xrightarrow{-\,e^-} [C_6H_6]^{+\cdot} \xrightarrow{n\,C_6H_6} [(C_6H_6)_n]^{+\cdot} \xrightarrow[-(2n-1)\,e^-]{-2n\,H^+} (C_6H_4)_n \qquad \textbf{Scheme 1.}$$

The formation of the CT complex ($[(C_6H_6)_n]^{+\cdot}$) in a strongly acidic medium has been demonstrated by Ab initio MO calculations.[11]

Since oxidative polymerization of benzene is depressed by the insolubility of the product, attempts to facile polymerization *via* soluble derivatives of the polymer were performed. Addition of $CF_3SO_3H$ was performed under lowered temperature to promote the formation of the protonated σ-complex.

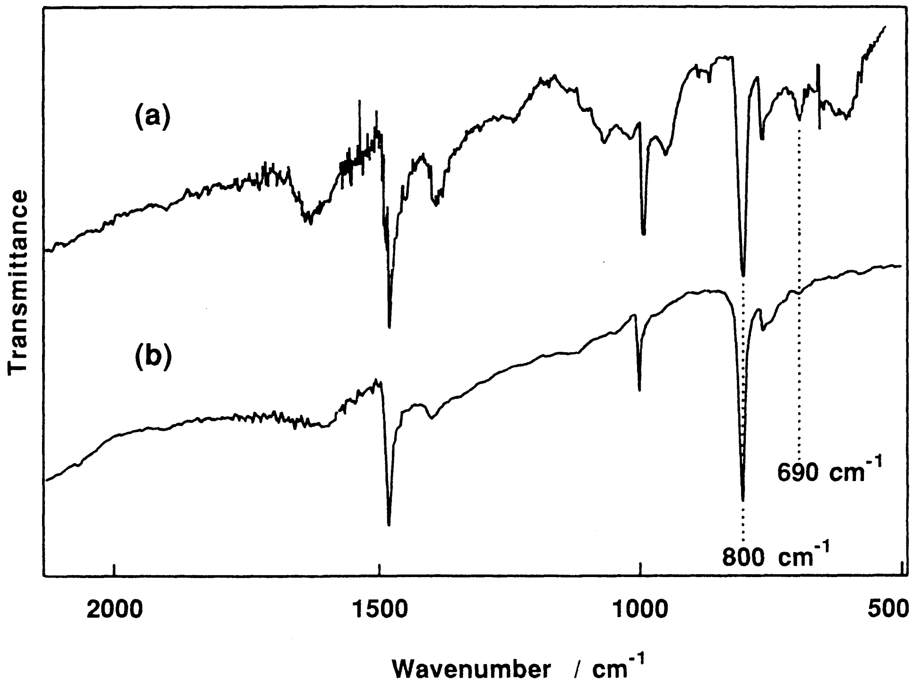

Fig. 1. IR spectra of PP by Kovacic's method (a) and the obtained polymer (b).

The propagation for the formation of the assembly of benzene as a CT complex initiated by the oxidation with the oxidant to the cation radical of benzene is promoted under the strongly acidic conditions in the earlier stage of the polymerization. Subsequently, a stoichiometric amount of DDQ oxidized the CT complex to produce PP efficiently.

The $\sigma$-complex formation was monitored by UV-vis. spectra where nitromethane was used as solvent to dissolve both benzene and acid. By the addition of $CF_3SO_3H$ (1 mol $dm^{-3}$) to deaerated nitromethane containing benzene (10 mmol $dm^{-3}$), the color of the solution turned yellow from colorless, and a new broad shoulder at longer wavelength side of the absorption band of nitromethane appeared near 420 nm that is attributed to the protonated $\sigma$-complex of benzene.[12)] The absorbance of the shoulder increased over a period of 5 hours, which suggest that the formation of the $\sigma$-complex is rather slow. These results explain the fact that addition of acid prior to the oxidation resulted in the formation of PP with high DP. Subsequent addition of DDQ (10 mmol $dm^{-3}$) to the acidic solution of benzene gives rise to a broad absorption near 460 nm that is attributable to neither DDQ[13)] nor the $\sigma$-complex and assignable to the CT-complex formation between DDQ and the $\sigma$-complex.

The CT band was also observed immediately after mixing a benzene solution of DDQ and $CF_3SO_3H$, but the spectrum changed gradually with precipitation of PP. The final spectrum exhibited a peak at 360 nm and a very weak sholder at 460 nm, which suggests that the CT complex decomposed substantially to produce phenylene chain. The formation of the $\sigma$-complex of benzene with other less strong acids as $CH_3SO_3H$ or $CF_3COOH$ was not observed spectroscopically.

The role of $CF_3SO_3H$ on this oxidative polymerization of benzene are summarized as follows. The acid suppresses nucleophilic side reactions by basic species to the cation radical produced by the one-electron oxidation of benzene. The strong acid forms a cationic $\sigma$-complex with benzene that promotes an electrophilic attack to another benzene molecule, by which the polymerization efficiency is improved. The acid also shifts the reduction potential of DDQ to positive side[14)] to facile electron transfer in the oxidation of benzene.

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