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Communications

Polymerization of Propargylpyridinium Bromide by Palladium and Platinum Chlorides

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The conjugated polymers having ionic nature were scarce and restricted to some cases as follows: the solid-state polymerization of propiolic salts by γ -irradiation,¹ water-soluble polyene polymers by quarterization of poly(6-bromo-1-hexyne),² and the synthesis of mono- and di- substituted ionic polyacetylene by the activation of the acetylene bond in ethynylpyridine by introduction of a strong electron withdrawing substituents in conjugation to it.³⁻⁵ Due to their extensive conjugation and ionic nature, these polymers have potential as materials for mixed ionic and electronic conductivity, energy storage devices, and permselective membrane.

In recent years, novel conjugated ionic polyelectrolytes were prepared by the polymerization of dipropargyl ammonium salts having bromide and tosylate as counter anions by the metathesis catalysts.⁶ Now we report the synthesis of a novel conjugated polyelectrolyte by the polymerization of a propargyl bromide salt having the pyridyl substituent, propargyl pyridinium bromide (PPB) by PdCl₂ and PtCl₂ as catalyst.

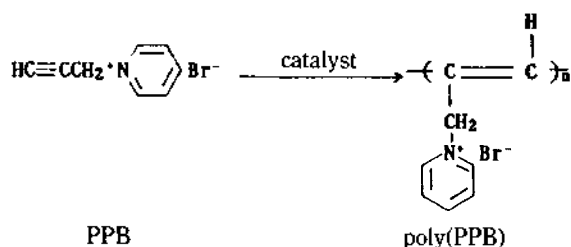


Table 1. Polymerization of PPB by Palladium and Platinum Chlorides^a

Exp. no.	Catalyst	M/C ^b	[M] ₀ ^c	Solvent	Yield ^d (%)	η_{inh} ^e (dl/g)
1	PdCl ₂	30	0.5	DMF	59	0.10
2	PdCl ₂	30	0.5	Pyridine	68	0.11
3	PdCl ₂	50	0.5	Pyridine	51	0.10
4	PdCl ₂	30	1.0	Pyridine	79	0.12
5	PdCl ₂	30	0.5	Formic acid	45	0.07
6	PdCl ₂	30	0.5	Nitrobenzene	34	0.08
7	PtCl ₂	30	0.5	DMF	45	0.09
8	PtCl ₂	30	0.5	Pyridine	53	0.11

^aPolymerization was carried out at 90°C for 48 h. ^bMonomer-to-catalyst mole ratio. ^cInitial monomer concentration ([M]₀). ^dEthyl ether-insoluble polymer. ^eMeasured at a concentration of 0.5 g/dl in methanol at 30°C.

All procedures for the preparation of PPB and catalyst system, and the polymerization was carried out under dry nitrogen atmosphere, because PPB is very hygroscopic and the active species of catalysts are sensitive to moisture and oxygen. The polymerization was carried out as described earlier.^{7,8} The resulting polymer was precipitated into excess ethyl ether.

Table 1 shows the results for the polymerization of PPB by palladium and platinum chlorides. PdCl₂ effectively polymerized PPB under various reaction conditions to give a moderate yield of polymer. Four typical solvents (DMF, pyridine, formic acid, and nitrobenzene) were used for the present polymerization. The polymerization in the solvents of DMF and pyridine proceeded better than those in the solvents of formic acid and nitrobenzene. The polymer yield was increased as the monomer to catalyst mole ratio (M/C) is decreased and the initial monomer concentration ([M]₀) is increased (exp. no., 2, 3, 4). PtCl₂ showed a similar catalytic activity to that of PdCl₂. The resulting poly(PPB)s were black powder and soluble in polar solvents such as methanol, DMF, DMSO, acetone, and formic acid, but insoluble in the nonpolar aromatic and hydrocarbon solvents such as chlorobenzene, toluene, ethyl ether, *n*-hexane etc. In most cases,

a small amount of insoluble polymer was formed during polymerization. The insoluble product may be originated from the cross-linking by the activated allyl protons of polymer. The inherent viscosities were in the range of 0.07-0.12 dl/g. These low viscosities indicate that the poly(PPB) had a relatively low molecular weight.

The resulting poly(PPB) was also hygroscopic as like with that of monomer PPB. The IR spectrum of poly(PPB) showed neither the acetylenic carbon-carbon stretching frequency (2125 cm^{-1}) nor the acetylenic $\equiv\text{C-H}$ stretching frequency (3225 cm^{-1}). Instead the carbon-carbon double bond stretching frequency in the polymer backbone was observed at 1627 cm^{-1} with the characteristic peaks of pyridine moiety. The UV-visible spectrum of poly(PPB) exhibited the characteristic broad absorption peak (up to 600 nm) which is originated from the $\pi\rightarrow\pi^*$ transition of the conjugated polyene. $^1\text{H-NMR}$ spectrum of poly(PPB) showed the pyridyl and vinyl protons at 6.8-10.1 ppm and the methylene protons at about 5.3 ppm. The $^{13}\text{C-NMR}$ spectrum of poly(PPB) did not show the acetylenic carbon peaks (63, 82 ppm), instead the carbon-carbon double bond and pyridyl peaks in the polymer were observed at 121-147 ppm.

In conclusion, a new conjugated polyelectrolyte having pyridine moiety was synthesized in a moderate yield by palladium and platinum chlorides. A more description of poly(PPB) and other derivatives on electrical and gas permeation properties will be discussed elsewhere.

References

- Davidov, B. E.; Krentsel, B. A.; Kchutareva, G. V. *J. Polym. Sci., Part C* 1967, 16, 1365.
- Kawasaki, M.; Masuda, T.; Higashimura, T. *Polymer J.* 1983, 15, 767.
- Subramanyam, A.; Blumstein, A. *Macromolecules* 1991, 24, 2668.
- Subramanyam, A.; Blumstein, A.; Li, K-P. *Macromolecules* 1992, 25, 2065.
- Subramanyam, A.; Blumstein, A. *U. S. Patent* 1991, 5,037, 916.
- Kang, K. L.; Cho, H. N.; Choi, K. Y.; Choi, S. K. *Macromolecules* 1993, 26, 4539.
- Gal, Y. S.; Jung, B.; Lee, W. C.; Choi, S. K. *Polymer (Korea)*, 1992, 16, 191.
- Gal, Y. S.; Choi, S. K. *J. Polym. Sci. Polym. Chem. Ed.* 1993, 31, 345.

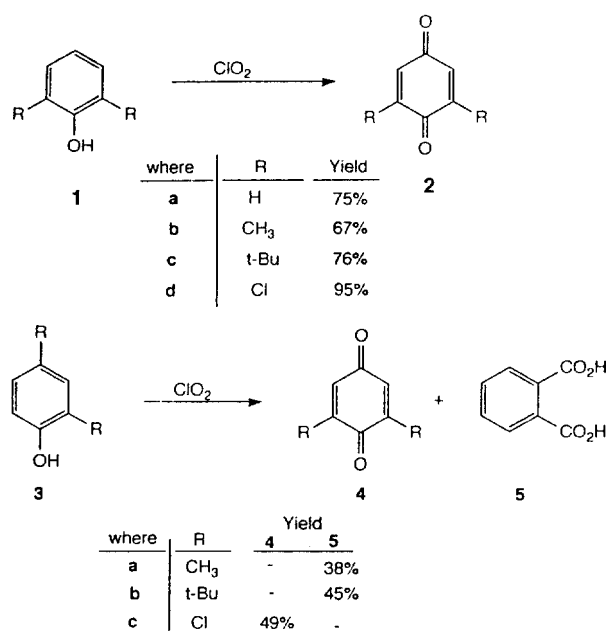
Oxidation of Phenols and Naphthols with Chlorine Dioxide

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Quinones are versatile starting materials in the synthesis



Scheme 1. Oxidation of phenols with chlorine dioxide.

of many important natural products and are particularly useful as dienophiles in Diels-Alder reactions. Quinones may be produced in high yield by the oxidation of phenols and aromatic amines with Fremy's salt¹ or various oxidants². Even though *o*-arylhydroxylamines are easily oxidized to the corresponding quinones, preparation of *o*-hydroxyamines meet a difficulty of contamination of side products. As a consequence, many *o*-arylhydroxylamines are not always readily available as starting materials.

On the other hand aromatic phenols are readily available and are usually quite inexpensive. However the two best reagents (*i.e.*, Fremy's salt and thallium nitrate) for the oxidation of these substrates are relatively expensive and those oxidants are only soluble in aqueous or semiaqueous solution. Even though some successful attempts³ to oxidize hydrophobic phenols to quinones with Fremy's salt in a two-phase ether-water mixture using phase transfer catalysts are reported, most oxidations are only carried out in aqueous solution.

We report here a simple method for the oxidation of phenols and naphthols to the corresponding quinones and the various interesting products such as phthalic acid and 2-carboxycinnamic acid by chlorine dioxide. Chlorine dioxide has been used as a germicide for drinking water,⁴ and has found extensive use in the destruction⁵ of certain chemicals including phenols, but has not been studied extensively on the oxidation of phenols and naphthols. Chlorine dioxide is a yellow gas radical which is produced⁶ by the reaction of aqueous potassium persulfate and aqueous sodium chlorite. Air or nitrogen passed through the solution to carry the generated chlorine dioxide to the point of use. Oxidations are carried out in organic solvents⁷ such as chloroform and THF as well as semiaqueous solution. pH effects on the oxidation are investigated using buffer in semiaqueous solution.

2,6-Disubstituted phenols such as 2,6-dimethyl, 2,6-di-*tert*-butyl, and 2,6-dichlorophenol as well as phenol as shown in Scheme 1 are oxidized into the corresponding quinones