Mechanism of Charge-transfer Polymerizations: Polymerization of *N*-Vinylcarbazole with Tetrachloro-*p*-benzoquinone in Benzene

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IT has been reported that *p*-chloranil (tetrachloro-*p*-benzoquinone) can polymerize *N*-vinylcarbazole in a typical charge-transfer polymerization.[1] We report that with pure *p*-chloranil almost no polymerization occurs in the dark or below room temperature. The polymerization of *N*-vinylcarbazole by *p*-chloranil, therefore, appears to be mainly a cationic one initiated by acidic impurities.

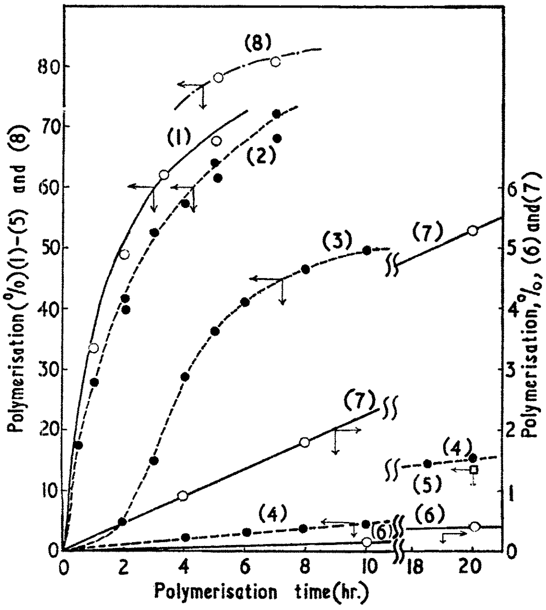

FIGURE. *Polymerization of* N-*vinylcarbazole by* p-*chloranil.* ([M] = Monomer concentration, moles/litre, [A] = chloranil concentration, mole %/monomer.) 1, Toluene, 80°, [M] = 0·5, [A] = 2·4; 2—5, benzene, 80°, [M] = 0·5, [A] = 4·0; 6 and 7, benzene 5—6°, [M] = 0·5, [A] = 4·0; 8, benzene, 80°; [M] = 0·5; [2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone] = 2×10^{-3} mole/l.

Curve 1 (Figure) represents an example of the reported polymerization.[2] Curve 2 and 3 are our results with *p*-chloranil, purified by one and three recrystallizations from benzene, respectively.[3] Trace acidic impurities in *p*-chloranil are tenaciously retained and only repeated recrystallization from benzene combined with repeated fractional sublimations *in vacuo* gave the pure compound: with this, the polymerization of *N*-vinylcarbazole was very slow (Curves 4 and 6).

Chromatography (benzene–calcium carbonate) followed by sublimation under reduced pressure also gave pure material (curve 5). The absorption spectra of the material adsorbed on the column were similar to that of 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone and it is suggested that this, or similar compounds (*e.g.* trichlorohydroxy-*p*-benzoquinone), are the acidic impurities in *p*-chloranil. A trace of this acid was sufficient to polymerize *N*-vinylcarbazole (Curve 8).

In the copolymerization of *N*-vinylcarbazole with dibromo-*N*-vinylcarbazole[4] or with isobutyl vinyl ether[5] with *p*-chloranil as an initiator the propagation was found to be cationic, as expected if the main part of the polymerization is initiated by acidic impurities.

An increase in the polymer yield occurred when the solution was irradiated in the charge-transfer band (500w Xenon lamp, Curve 7), which indicates that some polymerization by a mechanism involving a charge-transfer complex is operative.

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[2] L. P. Ellinger, *Polymer*, 1964, **5**, 559.

[3] T. Natsuume, S. Kusabayashi, and H. Mikawa, 16th Symposium on Macromolecular Chemistry, Fukuoka, Japan, October, 1967, Abstract IB-04.

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[5] M. Fujimatsu, Y. Akana, T. Natsuume, H. Hirata, S. Kusabayashi, and H. Mikawa, 21st Meeting of the Chemical Society of Japan, Osaka, April, 1968, Abstract 17212.