

A RADICAL-CATION INITIATED POLYMERIZATION OF N-VINYLCARBAZOLE

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It has been reported recently that nitroalkanes catalyze a cationic polymerization of N-vinylcarbazole at or above its m.p., and it is postulated that initiation involves proton transfer from catalyst to monomer¹. We have found that a solution polymerization with somewhat similar characteristics can be effected instantly at or below room temperature by addition of traces or more of compounds hitherto unknown to catalyze addition polymerization. The following compounds were most effective: p-chloranil, o-chloranil, p-bromanil, 2,3-dichloro-5,6-dicyanobenzoquinone, 1,4,5,8-tetrachloroanthraquinone, 7,7,8,8-tetracyanoquinodimethane, tetracyanoethylene, chlorine, bromine, iodine, nitrogendioxide, and the bromide salts of the Wurster ions of 1,4-diaminodurene and 1,6-diaminopyrene. Longer induction periods were encountered with trichloroacetonitrile, pyromellitic anhydride, p-iodanil, and p-benzoquinone. We believe this to be the first reported example of a polymerization initiated by a radical-cation.

A 90% yield of poly(N-vinylcarbazole) was recovered by filtering off precipitate formed at room temperature by adding 3 ml. Eastman reagent grade 1,1,2,2-tetrachloroethane (contains elemental chlorine) to 1 g. N-vinylcarbazole dissolved in 10 ml. spectroquality acetonitrile. The infrared spectrum of the polymer was the same as that of thermally polymerized N-vinylcarbazole. Polyvinylcarbazole remained dissolved when prepared in methylene chloride, chloroform, benzene, ethylether,

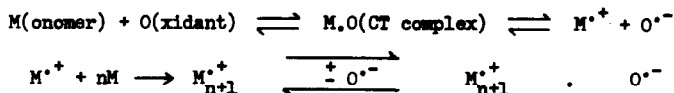
thiophene, or styrene. Polymers prepared at room temperature with 2,3-dichloro-5,6-dicyanobenzoquinone in acetonitrile, with trichloroacetonitrile in acetonitrile, with chlorine (as above) in 1:1 acetonitrile-methylenechloride, and with chlorine (as above) in methylenechloride at -40°C , had molecular weights^{2,3} of 4350, 3890, 4830 and 18100 (18700) respectively. Their elemental content corresponded to theory^{2,4}.

A dark material, presumed to be charge-transfer complex⁵, was observed to form on the surface of a pinch of powdered p-chloranil or tetracyanoquinodimethane gently dropped into a solution of N-vinylcarbazole. Streams of powdery polymer were observed to rise up from such surfaces or those of Wurster salts when acetonitrile was used as the solvent. The polymerization was qualitatively unaffected by the presence of comparatively large amounts of thiophene, a potent retarder of conventional cationic propagation⁶, acrylonitrile, a radical or anionically readily polymerized monomer, and styrene, a monomer readily polymerized by all known mechanisms⁷. Polymerization was retarded or inhibited by addition of small amounts of water, aniline, N,N-dimethylaniline, triethylamine, N-methylquinolinium chloride or lithium chloride (dissolved in acetonitrile). No polymerization occurred in reagent grade methanol, acetone, tetrahydrofuran, or N,N-dimethylformamide.

The effects of water and amines¹ indicate that the polymerization catalyzed by nitroalkanes and the compounds we describe involve a cationic mechanism. It seems unlikely, however, that proton transfer is involved in the initiation of the polymerization we have observed because most of the catalysts do not contain hydrogen and they are probably too electrophilic to serve as transfer agents for protons from other possible sources.

We suggest that this is a cationic polymerization initiated by

a Wurster radical-cation formed by oxidation of N-vinylcarbazole. The proposed scheme for a polymerization catalyzed by a compound known to form charge-transfer complexes is shown below.



This scheme is consistent with the known formation of Wurster ions as secondary products following formation of charge-transfer complexes of amines with quinones⁸. Many of the catalysts are known to form charge-transfer complexes with aromatic amines. The halogens and Wurster salts are the main exceptions⁹. Halogens, however, are known to react with aromatic amines to yield Wurster ions as principal products¹⁰. A Wurster ion of an amine other than monomer probably initiates polymerization by adding to monomer or exchanging an electron with monomer to form the Wurster ion of N-vinylcarbazole.

The initiation and propagation probably do not involve intermediates with independent radical and ionic functions such as those formed in polymerizations involving reduced monomers¹¹. It is reasonable to assume that the positive charge of the Wurster ion of N-vinylcarbazole is concentrated about the nitrogen atom and that a separation of ionic and radical functions would involve a quaternarization of the nitrogen atom and consequently a deactivation of the reactivity of the cationic function of the radical-cation (e.g. $\text{>N}^{\bullet+}\text{-CH=CH}_2 \rightarrow \text{>N}^+\text{-CH-CH}_2^{\bullet}$). In polymerizations of N-vinylcarbazole in styrene and acrylonitrile, the environment of the radical-cation consists almost entirely of molecules which are susceptible to free radical initiated polymerization. The inertness of these solvents indicates the absence of an intermediate with a localized carbon-radical function. This also suggests that no separation of radical and ionic functions of the Wurster ion occurs,

and it is consistent with the properties of known Wurster ions¹².

The similarity of polymerizations induced by differently constituted catalysts suggest that in the course of propagation and termination no interaction other than ionic association occurs between the cation consisting of the polymeric adduct of Wurster ion with monomer and the anion representing reduced catalyst. This is reasonable, even for cases likely to involve radical-anions such as those formed by reduction of quinones, since anions of this type are known to be capable of co-existing with a Wurster ion for a time¹³ much longer than that required to complete a polymerization. Addition of chloride ion probably results in the formation of an ion-pair involving this anion regardless of the oxidant used to produce the Wurster ion, and the retarding effect of methylquinolinium and lithium chloride on the polymerization may be due to common ion suppression of dissociation of this ion-pair at an early stage of polymerization.

The scope and mechanism of this polymerization are being studied in more detail. One might expect monomers which are not as readily oxidized as aromatic amines to be less susceptible to the polymerization we have described. N-vinyl-2-pyrrolidone and N-vinyl-phthalimide were polymerized by chlorine and quinones, but not as readily as N-vinylcarbazole. The application of oxidative catalysis does not appear to be limited to the polymerization of N-vinylated monomers. A polymer of 4-vinylpyridine in the form of a charge-transfer complex with p-chloranil was obtained from the reaction of monomer with this quinone.

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- 2 Single determinations after Soxhlet extraction with methanol.
- 3 Mechrolab Vapor Pressure Osmometer. Analytical accuracy decreases for $\bar{M}_n > 5000$.
- 4 Chlorine contents were 0.46, 0.37, 0.58 and 0.33% respectively. Lack of quantitative correlation with molecular weight is probably due to experimental errors involved in determining chlorine content by a standard procedure.
- 5 The formation of complex on the surface of solid p-chloranil has been identified with 1,4-diaminodurene in solution. See H. Scott, H. Ur, and M. M. Labes, Nature 197, 375 (1963).
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- 7 These compounds were the only solvents present. No absorptions other than those of poly(N-vinylcarbazole) were detected in the infrared spectra of methanol precipitated products.
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- 9 The only other exception is nitrogendioxide which can be safely assumed to be capable of oxidizing most aromatic amines to their Wurster ions. We have prepared charge transfer complexes of trichloroacetonitrile with aromatic amines in unpublished work.
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- 12 Although known Wurster ions do not contain a polymerizable double bond, it is interesting to note that they are monomeric under comparable conditions, i.e. they are paramagnetic in solution. To account for the diamagnetism of most solid Wurster salts, Michaelis (ref. 10) postulated that Wurster ions undergo dimerization in the solid state, although he recognized that this could not involve a normal covalent bond. H. M. McConnell and R. Lynden-Bell, J. Chem. Phys. 36, 2393 (1962), have recently explained the sharp decrease in the magnetic susceptibility of solid Wurster salts in terms of a spin-pairing phenomena which does not involve the formation of a valence bond.

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