Mechanism of Charge-transfer Polymerization: Selective Excitation of the Charge-transfer Band in the Polymerization of *N*-Vinylcarbazole by *p*-Quinoid Compounds

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Summary Selective excitation of the charge-transfer bands of the charge-transfer complexes formed in the ground state between *N*-vinylcarbazole and *p*-quinoid compounds initiates the cationic polymerization of *N*-vinylcarbazole.

EXAMPLES of photosensitized charge-transfer polymerization of *N*-vinylcarbazole (VCZ) have been reported, where the monomer is directly involved in the charge-transfer process as a donor molecule to induce the polymerization.[1,2] However, the primary process of the initiation in the polymerization has not been elucidated.

Photosensitized charge-transfer polymerizations of N-*vinylcarbazole by* p-*quinoid compounds*

[VCZ] = 0·5 M; [Acceptor] = $1·2 \times 10^{-2}$ M; in benzene at 5—6°

No.	Acceptor	Light (nm)	Polym. time (h)	Yield (%)
1.	*p*-Bromanil	>420	8, 15, 20	5·5, 16·9, 33·4
2.	*p*-Bromanil	>500	20	9·9
3.	*p*-Bromanil	>320	8, 12	26·7, 32·6
4.	*p*-Chloranil	>420	8, 20, 30, 50	1·4, 2·9, 6·7, 9·6
5.	*p*-Chloranil	>500	20	<1·0
6.	*p*-Chloranil	>320	8, 20, 50	2·9, 5·4, 13·6
7.	2,6-DQ	>420	12, 15, 20	10·8, 14·7, 20·0
8.	2,6-DQ	>500	20	4·1
9.	2,5-DQ	>420	10, 20	3·5, 15·8
10.	2,5-DQ	>500	20	4·1

We now report clear-cut evidence that selective excitation of the charge-transfer band of the charge-transfer complex formed in the ground state initiates the polymerization, and discuss the primary process of the initiation in the photosensitized charge-transfer polymerization.

Systems containing VCZ and *p*-quinoid compounds such as *p*-bromanil, *p*-chloranil, and 2,6- and 2,5-dichloroquinone (DQ) exhibit distinct, broad charge-transfer bands, separated from the absorptions of each component (λ_{CT}max in CCl_4: 509, 506, 462, and 452 nm, respectively), and enabled us to examine the dependence of the polymerization upon the wavelength of the incident light.

Each of the monomer and acceptor solutions (0·5 M, $1·2 \times 10^{-2}$M, respectively) was evacuated at 10^{-6} mmHg, transferred into a hard-glass reaction vessel, and irradiated at 5—6° in an ice-box with 500w xenon lamp (Ushio Elec. Co., UXL-500D) through a condensing lens at about 40 cm from the lamp. Glass filters (Toshiba Elec. Co.), VY-42 ($\lambda >$420 nm, 40% transmission at 420 nm), and VY-50 ($\lambda >$500 nm, 40% transmission at 500 nm), were used to cut off the light. The polymer yield was determined gravimetrically, after precipitation with methanol. The *p*-quinoid compounds were rigorously purified as reported.[3,4]

In the dark, almost no polymerization occurred in benzene below room temperature in any of the systems studied. We have recently found that the rapid charge-transfer polymerization of VCZ ostensibly initiated by *p*-chloranil was, in fact, a conventional cationic one initiated by the acidic impurity retained in *p*-chloranil.[4] Moreover, with 2,5- or 2,6-DQ, thermal polymerization of VCZ in benzene (80°; 20 h) was not observed or was only slight. However, when the system was irradiated in the charge-transfer band ($\lambda >$420 nm) in benzene, polymerization occurred in each system† (Table). It proceeded by a cationic mechanism, as suggested by the results of additive effects‡ or copolymerization with isobutyl vinyl ether. At wavelengths >420 nm, absorption of photoenergy by the acceptors occurred to a much smaller extent although absorption by VCZ was almost negligible. But polymerization also occurred when the systems were irradiated with light of wavelength >500 nm, which only the charge-transfer complexes absorb. Thus photoexcitation of the charge-transfer complex formed in the ground state initiates the polymerization, probably *via* ionization.

Illumination with light including near-u.v. light ($\lambda >$320 nm), which both the monomer and the acceptors—as well as the charge-transfer complexes—absorb, resulted in a distinct increase in the polymer yield§ (Nos. 3 and 6, Table) It is suggested that in this case the uncomplexed monomer or the acceptor is excited in addition to the charge-transfer complex, and that the polymerization initiated by the charge-transfer interaction in the excited state of either the monomer (donor) or the acceptor, probably electron transfer, (which we call here "exciplex mechanism" as distinct from "charge-transfer complex excitation mechanism") is also operative and is responsible for the increase in the polymer yield. This result also suggests that in photosensitized charge-transfer polymerizations of much weaker donor–acceptor systems where the charge-transfer bands

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† Preliminary results on the VCZ–*p*-chloranil system were presented at a symposium.[5]

‡ The polymerization was not affected by the addition of DPPH but was strongly retarded or inhibited by the addition of trimethylamine (aqueous solution).

§ Photochemical radical polymerization of VCZ alone does not occur to any great extent in benzene, and is not possible in the presence of *p*-quinoid compounds.

overlap with the absorptions of components, polymerization by "exciplex mechanism" may make a considerable contribution. The photosensitized polymerization of VCZ by nitrobenzene,[1] or by maleic anhydride,[6] may fall into this category.

(*Received, July 13th*, 1970; *Com.* 1122.)

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