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MECHANISM OF CHARGE-TRANSFER POLYMERIZATION: PHOTOSENSITIZED CHARGE-TRANSFER COPOLYMERIZATIONS OF N-VINYLINDOLE WITH ELECTRON-ACCEPTING MONOMERS

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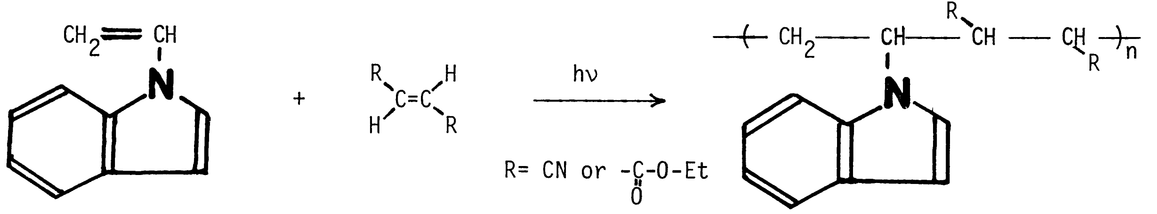
It was found for the first time that N-vinylindole was copolymerized with such electron-accepting monomers as fumaronitrile or diethyl fumarate to yield 1:1 alternating copolymers by photoirradiation. The initiation process of the photopolymerization was suggested to involve the charge-transfer or probably electron transfer from N-vinylindole to the electron-accepting monomer in the electronically excited state.

The photosensitized charge-transfer polymerization has been a topic of current interest. However, most studies in this field have been concentrated especially on N-vinylcarbazole[1] or α-methylstyrene[2]. In this communication we wish to report the photosensitized charge-transfer copolymerizations of N-vinylindole with such electron-accepting monomers as fumaronitrile or diethyl fumarate[3].



N-Vinylindole (VI) was synthesized from indole[5], dried over sodium wire, then over potassium wire and distilled from it twice in vacuo under dry nitrogen stream, and further distilled immediately before use, bp 70°C/0.3mmHg. Fumaronitrile (FN) was purified by recrystallization three times from purified benzene and fractionally sublimed twice in vacuo immediately before use. Diethyl fumarate (DEF) was dried over calcium chloride and distilled twice from calcium hydride in vacuo under dry nitrogen stream, bp 75°C/5mmHg. The reaction systems were evacuated at 10^{-2}mmHg by means of several freeze-pump-thaw cycles in a glass tube, 1.5cm in diameter, sealed off and irradiated at 23-25°C with light of wavelength longer than 310 nm at a distance of about 2cm from a 500W high pressure mercury lamp (PIH-500, Eikosha Co,Ltd.). The reaction mixture of the VI-FN system was poured into excess methanol. The precipitates were filtered, washed with methanol, dried in vacuo at room temperature for 2 days, and weighed. The analytical samples were further reprecipitated repeatedly from N,N-dimethylformamide (DMF) with methanol. Likewise, the reaction mixture of the VI-DEF system was poured into excess n-hexane. The precipitates were filtered, washed with n-hexane, and further reprecipitated from carbon tetrachloride with n-hexane, dried in vacuo at room temperature for 2 days, and weighed.

When VI only was irradiated in a benzene solution, no photochemical reaction occurred. However, when a solution of equimolar amounts of VI and the electron-accepting monomer such as FN or DEF was irradiated, radical copolymerization between VI and the electron-accepting monomer took place, although in low conversions. The copolymers were obtained as white powders. The copolymer formation was confirmed by their solubility behaviors, elementary analyses, and infrared and ultrviolet absorption spectra. The VI-FN copolymer was easily soluble in dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), DMF or pyridine, soluble in tetrahydrofuran (THF), but insoluble in benzene in which poly-VI was easily soluble. The VI-DEF copolymer was easily soluble in benzene, THF, DMF, DMSO, or carbon tetrachloride in which poly-VI is insoluble. The infrared specra of the VI-FN and VI-DEF copolymers show a weak C≡N absorption at 2240cm^{-1} and a strong C=O absorption at 1730cm^{-1}, respectively. The absorption bands at 965 and 975cm^{-1} due to the trans out-of-plane ${}^{H}\diagdown_{\diagup}C{=}C^{\diagup}_{\diagdown H}$ deformation vibration observed in the FN or DEF monomer and the bands at 960 and 860cm^{-1} due to the vinyl group on nitrogen observed in the VI monomer, essentially disappeared in both copolymers. It was indicated that the copolymerization proceeded at the vinyllic double bond of VI and the olefinic double bond of the electron-accepting monomer. The low molecular weight of the VI-FN copolymer (Table 1) seems to be due to the precipitation of the copolymer from the reaction system during polymerization because of its poor solubility in benzene. The copolymer composition was found to be 1:1.2 (VI:FN) for the VI-FN copolymer and 1:1.5 (VI-DEF) for the VI-DEF copolymer as determined from the nitrogen analysis. Since the FN or DEF monomer did not homopolymerize under the present reaction conditions, it was suggested that both copolymers have a 1:1 recurring unit of VI and the electron-accepting monomer in the main chain, thus being alternating copolymers, and that the addition reaction of FN or DEF at the electron rich β-carbon of the VI monomer occurred partially$^{6)}$. The results are summarized in Table 1.

Table 1. Photopolymerization of N-Vinylindole.

No.	VI mg/10ml (mol/l)	acceptor	time (hr)	yield mg	nitrogen contents(%)	MW^{*a}	softening point (°C)
1	715 (0.5)	none	10	0.0	-	-	-
2	715 (0.5)	FN 390 (0.5)	5	23.6	20.25	900	above 300
3	715 (0.5)	DEF 860 (0.5)	5	47.9	3.06	6800	108-111

*: obtained from Mechrolab VPO.

The fluorescence of VI was found to be quenched by the addition of FN or DEF as shown in Figs. 1 and 2. The Stern-Volmer plots for the fluorescence quantum yield were linear up to ca. 1×10^{-2}mol concentration of the quencher⁷⁾ with quenching constants 1.39×10^{2} and 1.85×10^{2} l/mol for the VI-FN and VI-DEF system, respectively (Fig.3). The exothermic singlet-singlet energy transfer from VI to FN or DEF is not responsible for the present fluorescence quenching and this quenching is explained by the charge-transfer or electron-transfer mechanism. The exciplex fluorescence was not detected in the present systems, although in the indole-FN system a very weak, new emmision attributable to the exciplex was observed with an isosbestic point in a non-polar solvent. Also, the VI-FN and VI-DEF systems showed a weak charge-transfer interaction even in their ground states at relatively high concentrations of each component as evidenced from the electronic absorption spectra. The absorption spectra of the VI-FN and VI-DEF systems shifted to the red region as compared with the sum of the absorptions of each component of the same concentration as shown in Fig.4. Thus, the ground state charge-transfer complex as well as the free VI are the photoabsorbing species in the present systems.

These results together with the absence of any photoreactions of VI only strongly suggest that the present photosensitized copolymerizations were initiated by the charge-transfer or probably electron-transfer from VI to the electron-accepting monomer in the excited state as schematically shown below.

$$\begin{tikzcd}
\mathrm{VI} + \mathrm{FN} \arrow[r, shift left] \arrow[dr, "h\nu"'] & (\mathrm{VI\text{-}FN}) \arrow[l, shift left] \arrow[r, shift left, "h\nu"] & (\mathrm{VI\text{-}FN})^{*} \arrow[l, shift left] \arrow[r] \arrow[dl, shift left] & {[\,(\mathrm{VI}^{+}\ \mathrm{FN}^{-})} \arrow[r, shift left] & \mathrm{VI}^{\dot{+}} + \mathrm{FN}^{\dot{-}}\,] \arrow[l, shift left] \arrow[dl, squiggly] \\
 & {}^{1}\mathrm{VI}^{*} + \mathrm{FN} \arrow[ur, shift left] & & \text{Copolymerization} &
\end{tikzcd}$$

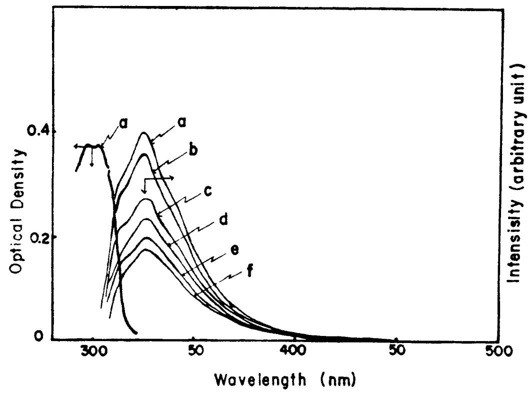


Fig. 1. Absorption spectrum and fluorescence spectra of VI and the system VI-FN in benzene at room temperature. [VI]=1.0×10^{-4}mol/l. [FN]: (a); none, (b); 1.0×10^{-3}mol/l, (c);3.0×10^{-3} mol/l, (d); 5.0×10^{-3}mol/l, (e); 7.0×10^{-3}mol/l, (f); 1.0×10^{-2}mol/l.

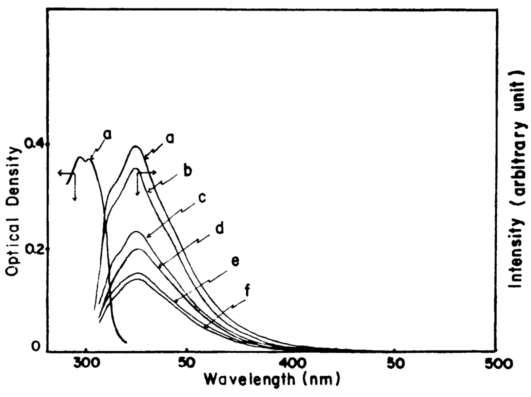


Fig. 2. Absorption spectrum and fluorescence spectra of VI and the system VI-DEF in benzene at room temperature. [VI]=1.0×10^{-4}mol/l. [FN]: (a); none, (b); 1.0×10^{-3}mol/l, (c); 3.4×10^{-3} mol/l, (d); 5.0×10^{-3}mol/l, (e); 8.6×10^{-3}mol/l, (f); 1.0×10^{-2}mol/l.

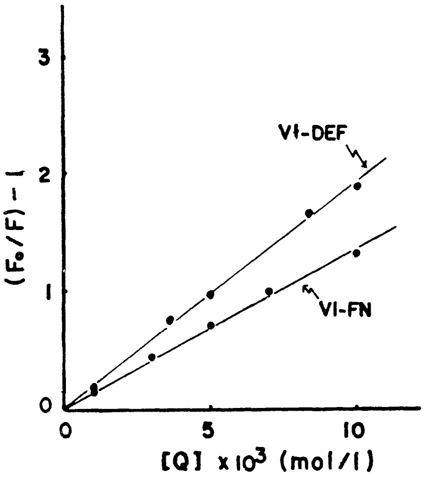


Fig. 3. Stern-Volmer plots for the quenching of VI fluorescence by FN or DEF in benzene solution at room temperature. [VI]=1.0×10^{-4} mol/l, [FN]; from 1.0×10^{-3} to 1.0×10^{-2}mol/l, [DEF]: from 1.0×10^{-3}mol/l to 1.0×10^{-2}mol/l.

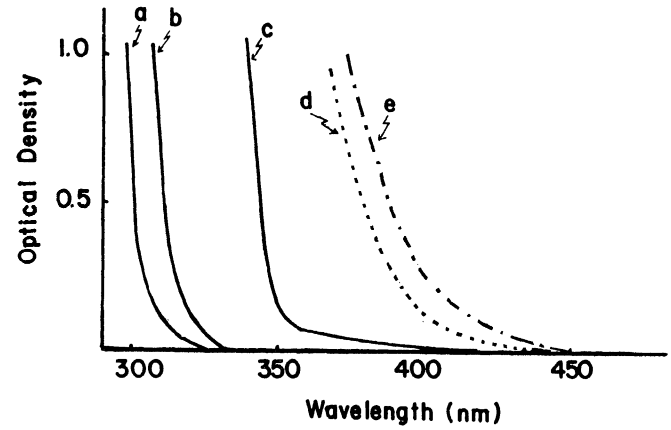


Fig. 4. Absorption spectra of the systems VI-electron acceptors in benzene at room temperature. (a): [FN]=0.05mol/l, (b): [DEF]=0.05mol/l, (c): [VI]=0.5mol/l, (d): [VI]+[DEF], [VI]=0.5mol/l and [DEF]=0.05mol/l. (e): [VI]+[FN], [VI]=0.5mol/l and [FN]=0.05mol/l.

References

1) K.Tada, Y.Shirota, and H.Mikawa, Macromolecules, 6, 9 (1973), and references cited therein.

2) M.Irie, S.Tomimoto, and K.Hayashi, J.Polym.Sci., A-1, 10, 3243 (1972).

3) Photochemical behavior of N-vinylindole was unknown to date. Moreover, only few studies have been made on the copolymerization of N-vinylindole$^{4)}$.

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5) H.Nomori, M.Hatano, and S.Kambara, Polym.letters, 4, 623 (1966).

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7) Above 5×10^{-2}mol the electron-accepting monomer (FN or DEF) absorbs the photoenergy of the exciting light 300nm.

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