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Cyclodimerization, Polymerization, and Copolymerization of *N*-Vinylcarbazole Photoinduced by Rhodamine 6G

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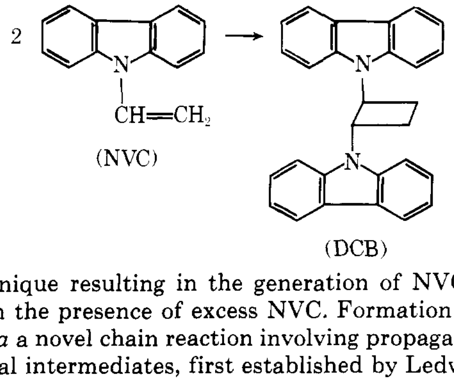
ABSTRACT: Rhodamine 6G is shown to be a highly efficient photosensitizer for cyclodimerization of *N*-vinylcarbazole (NVC) in alcohols and in benzene, provided that a suitable co-oxidant such as dissolved oxygen, copper(II) heptanoate, or chloranil is present in the system. In the absence of co-oxidant, poly(*N*-vinylcarbazole) is produced by a free radical mechanism. Copolymerization of NVC with MMA occurs simultaneously with cyclodimerization of NVC in appropriate reaction mixtures containing dissolved oxygen. However, it is shown that the quantum efficiency for initiation of copolymerization is less than 1% of that for the concurrent cyclodimerization. The effects of additives (and NVC) on the fluorescence of Rhodamine 6G correlate with retardation effects on the cyclodimerization of NVC and it is concluded that the latter process is initiated by an overall electron transfer from NVC to the singlet excited dye molecule. In contrast, it is suggested that the comparatively inefficient initiation process leading to radical polymerizations arises from a competing pathway involving the triplet excited dye molecule. Whereas both *cis*- and *trans*-*N*-propenylcarbazoles are efficient quenchers of the fluorescence of Rhodamine 6G and have similar ionization potentials, only the trans form is reactive in photoinduced cyclodimerization or polymerizations; molecular models indicate that *cis*-*N*-propenylcarbazole is nonplanar. These observations suggest that quenching of fluorescence of Rhodamine 6G occurs *via* an encounter complex which must undergo an appropriate relaxation or solvent reorganization before yielding a fully oxidized and reduced reactant pair.

Formation of the cyclodimer of *N*-vinylcarbazole (NVC) was first reported independently by Ellinger[1] from photolysis of NVC in methanol in the presence of chloranil, and by Breitenbach, *et al.*,[2] from the electrolysis of solutions of NVC in acetonitrile containing mercury(II) cyanide. Shortly afterwards, Ledwith, *et al.*,[3] reported that the same dimer was even more readily produced by reaction of NVC with iron(III) nitrate in methanol. In all these studies the dimer was produced during attempted polymerizations of NVC and its structure was finally established as *trans*-1,2-dicarbazylcylobutane (DCB) by Ellinger, Feeney, and Ledwith[4] following detailed nmr investigation. It is now clear that the cyclodimer of NVC may be produced by almost any technique resulting in the generation of NVC cation radical in the presence of excess NVC. Formation of DCB occurs *via* a novel chain reaction involving propagating cation radical intermediates, first established by Ledwith and collaborators[5,6] from detailed investigations of the photoinduced reactions, and this accounts for its ready formation by almost all types of oxidation procedures including thermal (metal catalyzed),[7] electrochemical (anodic),[2,8] photochemical,[9,10] and by pulse radiolysis.[11] The dimer may also be produced by direct irradiation of NVC in solvents such as methanol or acetone,[12,13] provided oxygen is present in the system, although initiation in these cases may be a biphotonic process[14] and is certainly orders of magnitude less efficient than in the photosensitized reactions.[6]



(NVC) (DCB)

The photoinduced cyclodimerization of NVC is of particular interest for the following reasons. (I) The reactions may be quantitative, if irradiation is prolonged, and are photoinduced by a very wide range of sensitizers many of which have triplet state (and even singlet state) energies lower than those of carbazole derivatives. (II) For many sensitizers photolysis in the absence of dissolved oxygen does not produce cyclodimer but may yield poly(*N*-vinylcarbazole). (III) In some cases, photoinduced reactions of NVC yield both polymer and cyclodimer simultaneously. Mikawa and collaborators[12,15] have recently reported extensively on the competing cyclodimerization, polymerization, and copolymerization pathways in photoinduced reactions of NVC and have explained formation of the various products in terms of specific solvent effects on the reactivity of the initially formed NVC cation radical. However, a true picture of the relative efficiencies of competing cyclodimerization and polymerization cannot be drawn from these studies largely because of a lack of information as to the quantum efficiencies of the respective initiation processes.

We have attempted to clarify these matters by studies of well-defined systems where relative efficiencies in polymerization and cyclodimerization are easily separated. It is the purpose of the present paper to give detailed experimental results from a study of the reactions of NVC in mainly alcoholic solvents photoinduced by the strongly fluorescing dye Rhodamine 6G (Rh6G). This particular sensitizer was selected because of its efficiency in photocatalyzing reactions of NVC, because its singlet state and triplet state energies are below those of NVC and hence the normal energy transfer processes can be ignored, and because its interactions with all components in the system are readily monitored by concurrent study of absorption and emission spectra. Choice of alcohols as solvents prevents any contribution to polymerization of NVC by cationic process. This is especially important since the relative specific rates for propagation by free cationic and free radical intermediates[16] differ by approximately 10^5. Thus a very low concentration of propagating cationic intermediates, perhaps produced by electron transfer from initially formed free radical species,[17] would result in a serious distortion of the relative yields of polymer and dimer produced under any given set of conditions. NVC is not particularly reactive as a monomer in free radical polymerization and so, in appropriate cases, free radical activity was further tested by inclusion of methyl methacrylate and chacterization of the resulting copolymers.

Experimental Section

Materials. *N*-Vinylcarbazole (Koch-Light) was recrystallized twice from methanol at a temperature of 40°, dried in a vacuum oven, and stored *in vacuo* in the dark (mp 64–65°).

Rhodamine 6G was purified according to the method of Ramette and Sandell.[18] As obtained commercially the dye contains chloride as counterion. This material is readily soluble in alcohol and polar solvents but is insoluble in benzene. For the latter purpose the dye was converted to its tetrachlorogallate salt ($GaCl_4^-$) as described by Greenwood[19] for the preparation of triphenyl methyl tetrachlorogallate. Rhodamine 6G tetrachlorogallate slowly absorbs atmospheric moisture to produce a *cationic* initiator for polymerization of NVC and hence must be used freshly prepared.

Ferrocene was purified by vacuum sublimation at 50° (mp 170–173°). Chloranil was recrystallized from benzene and dried under vacuum (mp 289–290°).

Methyl methacrylate was washed twice with aqueous 5% sodium hydroxide to remove inhibitor, followed by two washings with water. After drying with sodium sulfate the monomer was distilled from calcium hydrate at reduced pressure under nitrogen through a 4-ft packed column. The middle fraction (bp 24° (50 mm)) was used as freshly distilled.

Copper(II) heptanoate was prepared by addition of copper(II) nitrate to an aqueous solution of sodium heptanoate (from sodium bicarbonate and heptanoic acid). The green copper soap was filtered, dissolved in ether, and refiltered to remove copper(II) carbonate, and the mother solution was dried over sodium sulfate before evaporation. The blue green residue was recrystallized from benzene containing a trace of heptanoic acid. Solvents such as the various alcohols, benzene, acetone, and 1,4-diazabicyclo[2.2.2]octane (used as a quencher) were all reagent grade materials, distilled before use with good middle fractions taken in all cases.

Carbazole derivatives used as quenchers, and not specifically listed below, were either commercial samples recrystallized from mainly alcoholic solvents to appropriate constant melting points or, alternatively, were available from other work.[20]

***trans*-*N*-Propenylcarbazole.** *trans*-*N*-Propenylcarbazole was prepared by a method due to Bruck.[21] Carbazole (33 g) and 28 g of potassium hydroxide were refluxed in 350 ml of dimethoxyethane for 40 min. Solvent (50 ml) was then distilled off and 47 g of 2-chloro-*N*,*N*-dimethylaminopropane hydrochloride (Aldrich) was added over a period of 30 min to the refluxing mixture. Refluxing was continued for 18 hr. The cooled solution was poured into 1 l. of water and extracted with ether. The ether extracts were in turn extracted with 2*N* hydrochloric acid to separate unreacted carbazole; these acid extracts were made alkaline by addition of 50 g of sodium hydroxide in 200 ml of water. The oil which separated was taken into ether; the extracts were dried with potassium carbonate and, after solvent removal, vacuum distillation yielded 25 g of 1-(*N*-carbazolyl)-2-dimethylaminopropane (golden-yellow oil). This was dissolved in 350 ml of ether and 32 g of methyl iodide added; precipitation of the methiodide commenced immediately. Crystallization was induced by using benzene as solvent, and retreating with methyl iodide. The combined crops weighed 37 g. The methiodide was dissolved in 1200 ml of 50:50 methanol–water and treated with 50 g of silver oxide; the filtrate was concentrated leaving a brown residue which was heated for 6 hr at 90°. Water and ether were then added; the ethereal extracts were dried before evaporation leaving a yellow oil. This was recrystallized from 60–80° petroleum ether to yield 8 g (19.5%) of almost colorless prisms: mp 53–54°.

***N*-Allylcarbazole.** Preparation was effected in the manner described by Heller, *et al.*[22] Carbazole-*N*-potassium salt (Eastman Chemicals) (18.6 g) was refluxed with 12 g of freshly distilled allyl bromide (B.D.H.) (using the fraction collected at 71°) in 200 ml of tetrahydrofuran, previously distilled from calcium hydride. Refluxing was continued overnight; water (500 ml) was then added and ether was extracted. The extracts were dried over anhydrous magnesium sulfate and the residue after evaporation was recrystallized from methanol. A pale brown solid (11.5 g, 61%) was obtained of mp 52–54°. Vacuum sublimation (100° (0.2 mm)) produced a white product of mp 54–55°.

***cis*-*N*-Propenylcarbazole.** A successful preparation of this compound was achieved using an isomerization technique due to Hubert.[23] Potassium metal (1.2 g) was added to 50 ml of liquid ammonia at −40° under nitrogen. An intense blue color developed instantly. On addition of a small crystal of ferric nitrate, the blue color was destroyed, leaving a solution of potassium amide. Basic alumina (20 g) was added, and the nitrogen stream was increased to evaporate excess liquid ammonia. Initial attempts to isomerize *N*-allylcarbazole, prepared as already described, using the dried catalyst were unsuccessful. Acting on a suggestion due to Hubert,[24] 15 g of *N*-allylcarbazole in 200 ml of *n*-hexane was added under nitrogen to the freshly prepared catalyst, *still damp with the final traces of liquid ammonia.* Reaction was immediate upon contact with the catalyst. After 1 hr in contact with the catalyst, the solution was filtered, and removal of solvent left a colorless slightly opaque oil. The cis isomer is a liquid.

Nmr analysis showed two doublets at τ 8.69 and 9.01 due to =CH, CH_3 in the trans and cis isomer, respectively; the individual intensities suggested an 80:20 cis–trans mixture. The infrared spectrum of the product oil showed no trace of allylic absorptions; a high conversion had therefore been achieved. Coupling constants between the methyl group and the β-olefinic proton were measured to be $J(\beta_{\mathrm{trans}})$ = 6.2 Hz and $J(\beta_{\mathrm{cis}})$ = 7.0 Hz, and with the α-olefinic proton $J(\alpha_{\mathrm{cis}})$ = 1.4 Hz. These are in good agreement with the previously reported values of $J(\beta_{\mathrm{trans}})$ = 6.5 Hz and $J(\alpha_{\mathrm{trans}})$ = 1.5 Hz and $J(\alpha_{\mathrm{trans}})$ = 1.5 Hz and $J(\alpha_{\mathrm{cis}})$ = 1.7 Hz.[23]

Spectra. Spectra in the uv and visible regions were measured by means of Unicam S.P. 500 or Unicam S.P. 800 spectrophotometers. Infrared spectra were measured on a Unicam S.P. 200 spectrophotometer. Fluorescence spectra and quenching constants were measured on a Perkin-Elmer 203 spectrofluorimeter with the cell housing maintained at 25° by means of a current of air. Nmr spectra were recorded on a Varian A60 spectrometer. Analyses by gas–liquid chromatography were carried out on a Perkin-Elmer F11 Chromatograph (Flame ionization type). Molecular weights of nonpolymeric materials were determined in a Mechrolab vapor pressure osmometer (Model 307A).

Kinetic Measurements. Photolyses were carried out with irradiation from a 500-W Tungsten lamp projector focussed on a lollipop-shaped reaction vessel contained in a constant temperature water bath with flat glass windows. Two methods of analysis were employed for measurements of rates of cyclodimerization and polymerization.

Gravimetric Method for Cyclodimer and Polymers. Here the precipitated cyclodimer or polymer was filtered at appropriate time intervals and weighed. It was necessary to correct for the residual solubility of cyclodimer in appropriate solvents (*e.g.*, in methanol DCB has a solubility of 3.7×10^{-3} *M* at 25°). The gravimetric method was used mainly where polymerization was important. For most cyclodimerizations the glc technique described below was much more accurate and convenient.

Analysis for NVC by Gas–Liquid Chromatography. This

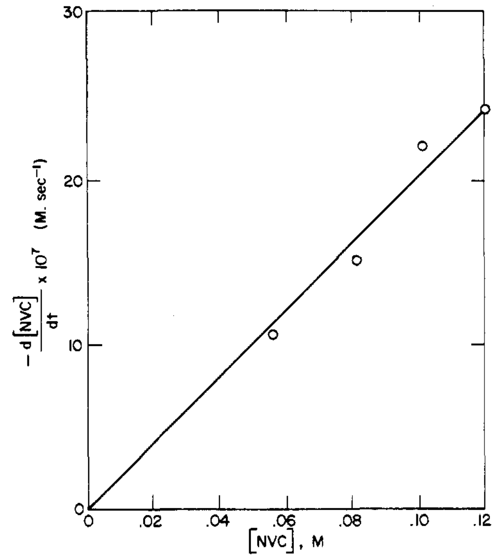


Figure 1. Cyclodimerization of NVC photoinduced by Rhodamine 6G. Variation in initial rate as a function of [NVC].

method is identical to that previously reported[25] for analysis of alkyl vinyl ethers and involves rapid hydrolysis of unreacted NVC, by means of 10% HCl in 90% aqueous methanol, to a mixture of carbazole, acetaldehyde, and 1,1-dimethoxyethane.

$$R_2NCH{=}CH_2 + H_2O \xrightarrow{H_3O^+} R_2NH + CH_3CHO$$

$$CH_3CHO + 2MeOH \xrightarrow{H_3O^+} CH_3CH(OMe)_2 + H_2O$$

The technique has been fully described[25] and it was shown that carbazole, DCB, and Rhodamine 6G did not interfere. Methyl ethyl ketone was used as internal standard for the glc analysis and the amount of NVC used after appropriate time intervals was readily obtained.

Separation of reaction products into cyclodimer and homopolymer of NVC (or copolymers of NVC with methyl methacrylate) was readily achieved by controlled partial precipitations of polymeric solutions. Polymers were precipitated and after filtration, subsequent evaporation of mother liquor yielded cyclodimer. Cyclodimer and polymers were readily distinguished by infrared analysis where the former exhibits a characteristic pair of sharp doublets at 1210 and 1230 cm.$^{-1}$

Results

Cyclodimerization and Homopolymerization of NVC Photocatalyzed by Rhodamine 6G. Rhodamine 6G was a particularly effective photocatalyst for cyclodimerization of NVC in methanol and use of wavelength filters established that the sensitizer (λ_{max} 523 nm) was the important light absorbing species. The kinetic results detailed below were, accordingly, obtained by irradiation of appropriate reaction mixtures with unfiltered light from a 500-W tungsten filament lamp as detailed in the Experimental Section.

It needs to be stressed at the outset that cyclodimer was obtained in Rhodamine 6G sensitized reactions only when oxygen was present in the reaction mixtures, otherwise poly(*N*-vinylcarbazole) was produced. A further point of general significance was that photobleaching of the red colored dye always accompanied homopolymerization of NVC but not cyclodimerization. Control experiments with azobisisobutyronitrile (AIBN), as thermal free radical initiator, established that bleaching of Rhodamine 6G occurs in free radical homopolymerization of NVC. The dye color was not restored on admission of oxygen to the reaction system and the polymer was not colored after reprecipitation into methanol.

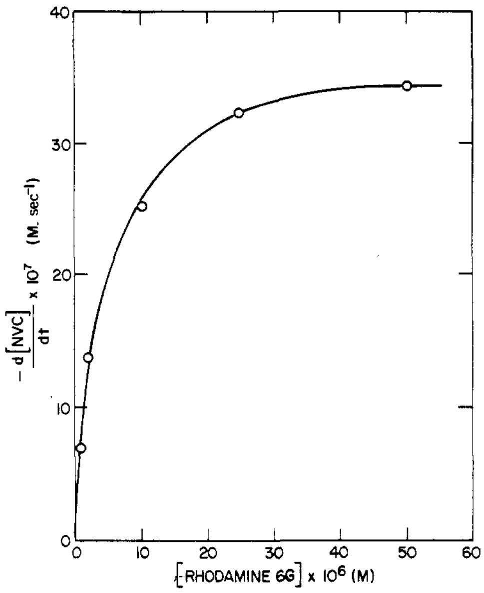


Figure 2. Cyclodimerization of NVC photoinduced by Rhodamine 6G. Variation in initial rate as a function of [Rhodamine 6G].

Table I
Cyclodimerization of NVC Photoinduced by Rhodamine 6G in Methanol[a] at 25°

Additive[b]	Rel rate	Additive[b]	Rel rate
None	1.00	Cl$^-$	1.00
Ferrocene	0.04	DABCO	1.00
I$^-$	0.16	Cu(II) heptanoate	1.00
Br$^-$	1.00	Cu(II) heptanoate[c]	0.95

[a] Reaction mixtures contained NVC (0.12 *M*) and Rhodamine 6G (5 × 10^{-6} *M*) and were photolyzed in air. [b] Additives were present at 10^{-3} *M* and the halide ions were used as the sodium or potassium salts. [c] Reaction under nitrogen.

Rates of cyclodimerization of NVC in air-saturated methanol solutions were measured as a function of olefin and dye concentrations, respectively, and the results are shown in Figures 1 and 2.

Cyclodimerization is apparently first order in [NVC] and first order in [Rh6G] up to approximately 5 × 10^{-6} *M* Rh6G after which self quenching of the excited dye molecules predominates and the reaction rates eventually become independent of dye concentration.

Reaction rates measured under standard conditions ([NVC] = 0.10 *M*, [Rh6G] = 10^{-5} *M*) in methanol at 25 and 50° yielded an apparent activation energy for cyclodimerization of 4 kcal mol^{-1}.

Effect of Additives on Cyclodimerization in Methanol. Preliminary experiments established that ferrocene and sodium iodide were extremely efficient quenchers for the Rhodamine 6G catalyzed reactions of NVC, quenching both cyclodimerization in air, and homopolymerization under nitrogen. 1,4-Diazabicyclo[2.2.2.]octane (DABCO), an efficient quencher of reactions of NVC photocatalyzed by other sensitizers,[6] was without effect in the Rhodamine 6G catalyzed processes. In contrast, copper(II) heptanoate which had no effect on the Rhodamine 6G sensitized reaction in the presence of air, catalyzed formation of cyclodimer in the nitrogen saturated systems. Quantitative effects of the additives used are indicated in Table I.

The effect of copper(II) heptanoate in apparently substituting for oxygen in the Rhodamine 6G sensitized reaction prompted a further experiment with a wholly organic cooxidant, chloranil. Chloranil is an effective photocatalyst for cyclodimerization of NVC[6] but, in methanol solutions, must be activated by light of wavelength less than 450 nm, corresponding to the long wavelength limit of the absorption spectrum of chloranil.[26] A solution of NVC (0.1 *M*), Rhodamine 6G (10^{-4} *M*), and chloranil (10^{-3} *M*) in methanol was irradiated in the absence of oxygen with light of wavelength 480–585 nm transmitted by a Wratten Filter. Cyclodimer formed at a rate only slightly less than that typically observed for Rhodamine 6G sensitized reactions in air.

Effects of Solvent on Cyclodimerization and Homopolymerization of NVC. The solvents methanol, ethanol, 2-propanol, and *tert*-butyl alcohol gave almost identical results in that cyclodimer was produced in air saturated solutions and homopolymer in solutions flushed with nitrogen. Raising the temperature of the reaction mixtures to the boiling points of the various alcohols appeared to promote formation of homopolymer at the expense of cyclodimer. However, these results should be ascribed to the very poor solubility of oxygen in the alcohols at elevated temperatures, rather than to a real differential temperature effect on the two processes, as confirmed by the observations that addition of copper(II) heptanoate (5×10^{-3} *M*) caused exclusive formation of dimer, in all the alcohol solvents, irrespective of temperature or the presence of oxygen.

A further point of mechanistic value is that use of the more viscous alcoholic solvents, benzyl alcohol, α,α'-dimethylbenzyl alcohol, and ethylene glycol drastically reduced quenching of the fluorescence of the Rhodamine 6G by NVC (*vide infra*) and, under standard cyclodimerization conditions, gave only homopolymer of NVC on photolysis in air or in nitrogen.

Although cyclodimerization of NVC is readily achieved in alcohol or acetone by means of a wide range of photocatalysts,[6] many sensitizers give rise to homopolymerization when corresponding reactions are carried out in nonpolar solvents such as benzene. Accordingly, Rhodamine 6G (normally the chloride ion salt) was converted into its benzene soluble tetrachlorogallate ($GaCl_4^-$) derivative as described in the Experimental Section. A typical cyclodimerization experiment was performed with NVC (0.1 *M*) and Rhodamine 6G tetrachlorogallate (10^{-5} *M*) in benzene at 25°. After 3 hr irradiation the benzene was evaporated and the residue shown by ir analysis to be 100% cyclodimer. When the same reaction was performed under nitrogen, the solution became viscous indicating formation of homopolymer, the latter being readily precipitated by pouring the benzene solution into methanol.

Competition between Cyclodimerization of NVC and Free Radical Copolymerization with Methyl Methacrylate. Control experiments established that Rhodamine 6G does not photocatalyze the free radical homopolymerization of methyl methacrylate (MMA) in methanol, ethanol, 2-propanol, or *tert*-butyl alcohol. It follows therefore that hydrogen abstraction from the solvent or addition to MMA are not efficient mechanisms for formation of free radicals by photoexcited Rhodamine 6G.

The effects of the various alcohol solvents in competitive cyclodimerization and free radical polymerization were reinvestigated in the presence of 0.5 *M* MMA. Results were similiar to those previously noted for NVC alone; reactions in air at 30° gave rise to mainly dimer formation whereas reactions under nitrogen gave exclusively copolymers. Addition of hydroquinone (10^{-2} *M*) completely inhibited the photoinduced copolymerizations confirming the free radical nature of the propagating species. In an attempt to suppress the cyclodimerization in favor of free radical copolymerization, concentrations of added MMA were increased systematically as indicated in Table II for both methanol and benzene solvents.

Table II
Effect of MMA on Photoinduced Cyclodimerization of NVC in Methanol at 30°

[MMA], *M*	Atmosphere	Yield polymer,[a] %	Yield dimer,[a] %
	Air		28
	N_2	19	
0.5	Air	1.1	28
0.5	N_2	2.7	
1.0	Air	1.6	27
1.0	N_2	3.6	
2.0	Air	2.2	32
2.0	N_2	5.2	
3.0	Air	3.6	29
3.0	N_2	5.3	
4.0	Air	4.3	32
4.0	N_2	5.7	
3.0	Air	6.0[b]	81[b]
4.0	Air	5.8[b]	84[b]

[a] Photolysis for 1 hr of mixtures containing NVC (0.10 *M*) and Rhodamine 6G (10^{-5} *M*) yield based on total monomers. [b] Solvent benzene, Rhodamine 6G tetrachlorogallate (10^{-5} *M*).

The data of Table II show convincingly that (i) increasing the amount of added MMA (0.5–4.0 *M*) increases the rate of copolymerization, as expected; (ii) the rate of cyclodimerization of NVC in air is independent of the presence and concentration of added MMA, even though copolymer is formed simultaneously; (iii) the rates of copolymerization, although significantly higher under nitrogen than in air, are much lower than corresponding rates of cyclodimerization; (iv) with Rhodamine 6G as sensitizer, cyclodimerization is apparently even more favorable in benzene than in methanol.

Composition of Copolymers. A range of copolymers was prepared, purified by reprecipitation from chloroform into methanol and analyzed for elemental nitrogen. Typical concentrations were [NVC] = 0.1 *M* and [MMA] = 0.5 *M* and the reactions were stopped at about 5% conversion of total monomer. Results are given in Table III and it is clear that copolymer compositions for NVC–MMA systems are different for poor solvents such as alcohols, where the copolymers are largely insoluble, and good solvents such as tetrahydrofuran and benzene. This point has been discussed previously in the light of similiar observations for other systems.[17]

Molecular Weights of Copolymers. Three copolymers, prepared in methanol by photocatalysis by Rhodamine 6G at ratios [MMA]/[NVC] = 20, 30, and 40 and at constant [NVC] = 0.1 *M*, were carefully reprecipitated and dried and their intrinsic viscosities [η] were determined in benzene solution. Since the copolymers are very rich in MMA the Staudinger equation for *p*-MMA[28] was used in order to obtain approximate values of viscosity average molecular weights $\bar{M}_v$. For *p*-MMA, assuming a normal distribution, the viscosity average molecular weight is related to the number average molecular weight ($\bar{M}_n$) by the expression

$$\overline{M}_n = 0.525\overline{M}_v$$

and approximate values of the degree of polymerization estimated in this way are indicated in Table IV.

When [MMA]/[NVC] = 20 the data of Table II show that a typical Rhodamine 6G sensitized reaction yielded

Table III
Copolymerization of NVC and MMA[a]

Initiator	Solvent	[MMA]/[NVC] (monomers)	% N (copolymers)	[MMA]/[NVC] (exptl)	[MMA]/[NVC][27] in copolymers (calcd)
Rhodamine 6G	*i*-PrOH	5.0	2.12	4.52	10.91
Rhodamine 6G	*t*-BuOH	5.0	2.18	4.64	10.91
AIBN	*i*-PrOH	5.0	2.15	4.58	10.91
AIBN	THF	5.0	1.14	10.35	10.91
AIBN	MeOH	1.0	4.66	1.07	2.88
AIBN	MeOH	2.5	3.51	2.06	5.89
Rhodamine 6G	MeOH	40	0.71	17.8	80.9

[a] Copolymerizations were taken to 5% conversion in each case. Reactions initiated by Rhodamine 6G were photochemical at 30° and those by AIBN were thermal at 55°.

Table IV
Molecular Weights of MMA-NVC Copolymers

[MMA]/[NVC][a] (monomers)	$[\eta]$,[b] cm^3 g^{-1}	$\overline{M}_v$	$\overline{M}_n$	$\overline{DP}$
20	29.3	80,900	42,500	406
30	36.3	106,200	55,800	541
40	42.8	131,200	68,900	674

[a] Polymers prepared at constant [NVC] = 0.1 *M*, [Rhodamine 6G] = 10^{-5} *M*. [b] Determined in benzene at 25°.

(after 1 hr of photolysis in air at 30°) 0.312 g of cyclodimer and 0.238 g of copolymer. Hence we can estimate the number of moles of cyclodimer formed as 0.312/386 = 8.1×10^{-4}, and the number of moles of (average) polymer as 0.238/42500 = 5.6×10^{-6}. Thus if the same intermediates are responsible for both cyclodimerization and copolymerization then only approximately 5.6/810 or 0.7% are diverted from dimer formation by the presence of a 20 *M* excess of the much more reactive (toward free radicals) MMA.

Photoreactions of *cis*- and *trans*-*N*-Propenylcarbazole. Rhodamine 6G sensitized photolysis of *trans*-*N*-propenylcarbazole in air saturated methanol solutions gave rise to slow formation of the all-trans head to head cyclodimer identical to that obtained by a corresponding iron(III) catalyzed reaction.[3] However, under standard conditions, the rate of cyclodimerization of *trans*-*N*-propenylcarbazole was only approximately one tenth of that of NVC. Surprisingly, corresponding reactions of *cis*-*N*-propenylcarbazole failed to yield any photoproduct in air or in nitrogen, the olefin being recovered unchanged after 24 hr of photolysis. It is interesting to note that the cis isomer is similiarly unreactive in iron(III) catalyzed reactions. Likewise whereas the trans isomer could be used to cosensitize copolymerization with methyl methacrylate by photolysis in the presence of Rhodamine 6G in nitrogen (the copolymer is very rich in MMA), corresponding reactions involving the cis isomer failed to produce any product.

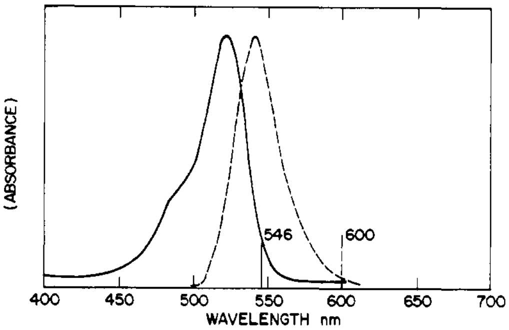


Figure 3. Absorption (——) and fluorescence emission (- - -) spectra of Rhodamine 6G in methanol. The vertical lines indicate wavelengths used for excitation and observation of emission, respectively.

Fluorescence Quenching Experiments. Rhodamine 6G is a particularly powerful fluorescing dye molecule and an immediate observation at the start of the present work was the dramatic effect of added NVC, and other carbazole derivatives, on the fluorescence intensity. Absorption and (uncorrected) emission spectra for Rhodamine 6G are shown in Figure 3, which also indicates the positions of the excitation and emission wavelengths used in the quantitative Stern–Volmer quenching studies. Self quenching and reabsorption phenomena are important for Rhodamine 6G as evidenced by the apparent shift in $\lambda_{\max}$ for emission, with changing concentration. Thus maximum emission intensity was recorded at the following wavelengths for the concentrations indicated: 575 nm (10^{-3} *M*); 565 (10^{-4} *M*); 552 (10^{-5} *M*); 545 (10^{-6} *M*); 544 (10^{-7} *M*). Stern–Volmer quenching data were obtained, therefore, for solutions in which the concentration of Rhodamine 6G was fixed at 5×10^{-6} *M*. The Stern–Volmer expression for quenching of excited states may be written as

$$F_0/F = 1 + K_Q[Q]$$

where F_0 and F are the relative intensities of emission for the pure fluorescer and the quenched fluorescer, respectively. [Q] is the concentration of quencher Q required to reduce the fluorescence intensity from F_0 to F. The constant K_Q is a measure of the quenching ability of the additive Q and relates to the apparent rate constant for quenching (k_q) by $K_Q = k_q T_F$ where T_F is the fluorescence lifetime of the emitting species. For fluorescence quenching it is commonly the case that values of k_q approximate the diffusion controlled encounter rate coefficients for the particular solvents and temperature employed. A more exact analysis of the diffusional and actual quenching components of k_q has been given by Evans,[29] but the simple interpretation is sufficient for present purposes. The value of T_F for Rhodamine 6G (6.6×10^{-9} sec in ethanol[30]) and the closely related Rhodamine B (6.0×10^{-9} sec in methanol[31]) led us to adopt an estimate of 6×10^{-9} sec for the fluorescence lifetime of Rhodamine 6G in methanol. A typical Stern–Volmer quenching study is illustrated in Figure 4 for the combination *N*-ethylcarbazole–Rhodamine 6G in methanol, and representative quenching data for a series of carbazole compounds are given in Table V. The data of Table V also indicate that increasing solvent viscosity de-

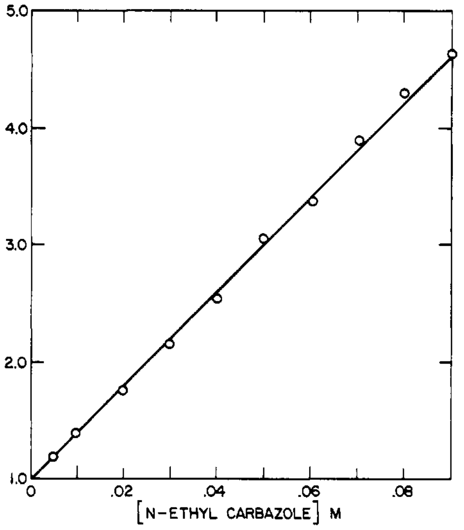


Figure 4. Stern-Volmer plot for the quenching of fluorescence of Rhodamine 6G by *N*-ethylcarbazole in methanol at 25°.

Table V
Fluorescence Quenching of Rhodamine 6G (5×10^{-6} *M*) in Methanol at 25°

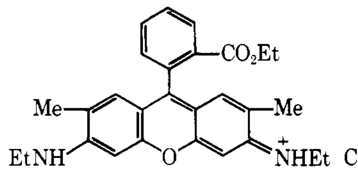
Quenchers	K_Q, M^{-1}	$10^{-9}k_q$, M^{-1} sec^{-1}
N-Vinylcarbazole	23.0	3.8
N-Vinylcarbazole[a]	13.0[a]	2.2[a]
N-Ethylcarbazole[b]	40.0[b]	6.7[b]
N-Ethylcarbazole[c]	25.0[c]	4.2[c]
N-Ethylcarbazole[d]	12.4[d]	2.1[d]
trans-*N*-Propenylcarbazole	51.2	8.5
cis-*N*-Propenylcarbazole	40.0	6.7
N-Acetylcarbazole	0.0	0.0
3-Nitro-*N*-ethylcarbazole	24.3	4.1
3-Formyl-*N*-ethylcarbazole	0.0	0.0
3-Acetyl-*N*-ethylcarbazole	7.9	1.3
3,6-Dichloro-*N*-ethylcarbazole	18.7	3.1
DABCO	8.0	1.3
Ferrocene	88.1	14.7
I^-	90.2	15.0
Br^-	0.0	0.0
Cl^-	0.0	0.0

[a] Solvent benzene, $\eta = 6.4 \times 10^{-3}$ P (Rhodamine 6G tetrachlorogallate). [b] Solvent methanol, $\eta = 5.9 \times 10^{3}$ P. [c] Solvent 2-propanol, $\eta = 23.7 \times 10^{3}$ P. [d] Solvent *tert*-butyl alcohol, $\eta = 58.8 \times 10^{3}$ P.

creases values of K_Q, as anticipated, an effect which is most marked for the viscous alcohols benzyl alcohol and ethylene glycol in which, as noted earlier, the fluorescence of Rhodamine 6G was essentially unquenched by NVC at room temperature and photolysis resulted only in the formation of low yields of homopolymer. A further point of interest, indicated by the data of Table V, is that species such as ferrocene and I^- (but not Cl^- and Br^-) which are efficient quenchers for the photoinduced reactions of NVC are also extremely effective quenchers for the fluorescence of Rhodamine 6G.

Discussion

Nature of the Interactions between Photoexcited Rhodamine 6G and NVC. Rhodamine 6G is a stable cationic dye molecule having the absorption and (very strong) fluorescing characteristics indicated in Figure 3. Independent studies have indicated[30] that the quantum yield for fluorescence of Rhodamine 6G in methanol is 0.83, leaving a maximum of 17% of excited dye molecules available as excited triplet state species (E_T = 43 kcal).



Rhodamine 6G

The lowest energy singlet state of carbazoles may be put at approximately 84 kcal and the lowest triplet state at 70 kcal.[32] It follows therefore that the conventional electron exchange (collisional overlap) mechanism of energy transfer may be completely ruled out as being too endothermic for interactions of excited Rhodamine 6G (singlet or triplet) with ground state NVC. On the other hand, quenching of the fluorescence of Rhodamine 6G by NVC and other carbazole compounds is a highly efficient process occurring at essentially diffusion controlled rates (Figure 4, Table V). Significantly the quenching efficiency of carbazole compounds toward Rhodamine 6G falls dramatically with increasing degree of substitution by electron withdrawing groups (Table V) which have the effect of raising the ionization potential,[33] and solution phase oxidation potential,[34] of the carbazole nucleus. A plausible mechanism for quenching of the fluorescence of Rhodamine 6G by carbazole compounds involves an essentially electron transfer process *via* intermediate formation of encounter complexes, or exciplexes, similiar to those now established for a wide variety of organic systems.[35] In essence, quenching *via* exciplex formation may be represented, *viz,*

$$\mathrm{Rh6G^+} \xrightarrow{h\nu} (\mathrm{Rh6G^+})^*$$

$$(\mathrm{Rh6G^+})^* + \mathrm{NVC} \longrightarrow (\mathrm{Rh6G^+})^*\text{---}\mathrm{NVC} \longrightarrow \mathrm{Rh6G} + \mathrm{NVC}$$

where the intermediate exciplex $(\mathrm{Rh6G^+})^*$- - -NVC may, perhaps, be more accurately represented by [Rh6G·, NVC·$^+$].

In support of this assumption is the fact that well-known electron donors such as ferrocene and iodide ion are even more effective quenchers of the fluorescence of Rhodamine 6G than are the various carbazole derivatives investigated (Table V), and simultaneously retard or inhibit the Rhodamine 6G sensitized reaction of NVC (Table I). Since the quantum yield for fluorescence of Rhodamine 6G is so high[30] and since fluorescence quenching by carbazole derivatives, including NVC, occurs with such high efficiencies at essentially diffusion controlled rates, it follows that for the concentrations of NVC employed ($\sim 10^{-1}$ *M*) energy wastage in excited Rhodamine 6G by emission of light, or intersystem crossing to the triplet state, can be of only minor importance.

It can be argued, therefore, that the photoreactions of NVC described in the present work, which lead mainly (and most efficiently) to the formation of its cyclobutane dimer, arise *via* interaction of singlet excited Rhodamine 6G with NVC, and that the mechanism of this interaction involves a substantial element of electron transfer from NVC to the excited dye molecule. Indeed, taken with the evidence for initiation of cyclodimerization by other processes, already outlined in the introductory section, overall electron transfer from NVC to singlet excited Rhodamine 6G must be accepted as the only reasonable process consistent with all the experimental observations.

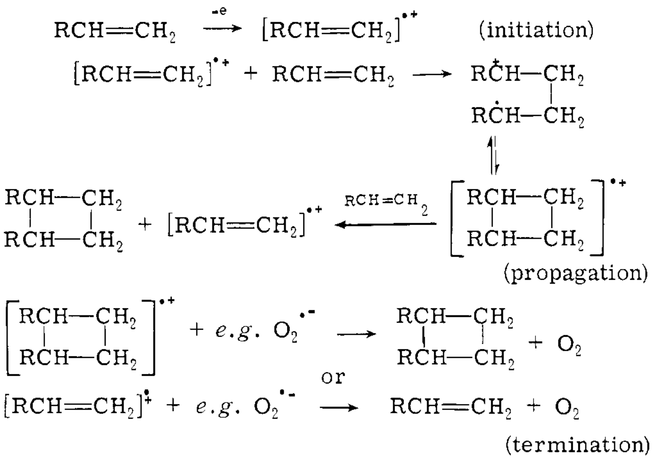
Mechanism of Cyclodimerization of NVC. Of primary significance in establishing a mechanism for the cyclodimerization of NVC was determination of quantum yields for formation of cyclodimer in the presence of a variety of sensitizers. Quantum yield, as referred to herein, may be defined as the number of moles of cyclodimer produced per mole of light photons absorbed by the sensitizer. For aromatic ketones and quinones, values of the quantum yield lie well in excess of unity and a chain reaction mechanism must, therefore, be operative.[6,26] Unfortunately the highly convenient technique of ferrioxalate actinometry[36] may not be used reliably at the wavelengths (>500 nm) absorbed by Rhodamine 6G and similiar dyes, so that direct measurement of the quantum yields was not possible. However, the longest wavelength absorbing sensitizers used in these studies, acriflavine and 2,4,6-triphenylpyrylium tetrafluoroborate, each gave values for quantum yields (measured at 405 nm) greater than unity.[9,26] From a comparison of relative light absorption properties and rates of cyclodimerization under comparable conditions, it may be assumed that quantum yields for cyclodimerization of NVC by Rhodamine 6G are at least as high as these for sensitization by acriflavine and 2,4,6-triphenylpyrylium tetrafluoroborate.

Unlike many of the aromatic ketone and quinone sensitizers, the fluorescing dye sensitizers including Rhodamine 6G do not produce cyclodimer from NVC except in the presence of air (oxygen) or other deliberately added co-oxidants. The mechanism for interaction of singlet excited dye with NVC, outlined above, may be further extended to include the oxygen effect as follows:

$$\begin{tikzcd}(\mathrm{Rh6G^+})^* + \mathrm{NVC} \arrow[r] & (\mathrm{Rh6G^+})^*\text{---}\mathrm{NVC} \arrow[d, "O_2"] \\ & \mathrm{Rh6G^+} + \mathrm{NVC}^{\cdot+},\ O_2^{\cdot-}\end{tikzcd}$$

In this way, dissolved O_2 or any other deliberately added co-oxidant may function so as to regenerate the ground state dye sensitizer and provide a comparatively stable counteranion ($O_2\cdot^-$) for the propagation process which follows. Co-oxidants, other that O_2, found to be effective for the Rhodamine 6G sensitized reactions include copper(II) heptanoate and chloranil.

The chain reaction steps, required by the high quantum yields for product formation, may then be represented generally as follows:



Other vinylated aromatic amines cyclodimerize by the same type of mechanism[7,9] and more recent work by Evans[37] and by Farid,[38] of the Eastman Kodak Laboratories, has established that the cation radical chain reaction mechanism may be applied to photoinduced cyclodimerization of phenyl vinyl ether and several indene derivatives.

Retardation of the cyclodimerization process by strong electron donors such as ferrocene and iodide ion is readily understood on the basis of competitive quenching of singlet excited Rhodamine 6G, interfering with initiation, rather than by extra termination processes involving interactions of the retarders with the propagating cation radicals, this point being reinforced by the observation that DABCO is a retarder for the cyclodimerization of NVC only when it is a more efficient quencher of the sensitizer fluorescence.[6]

Within the limited range of solvents (mainly alcohols) employed for the present work, there is no significant effect of solvent dielectric constant on rates of photoinduced cyclodimerization. Only when the alcohols are so viscous as to greatly reduce fluorescence quenching of Rhodamine 6G by NVC was an effect on rate of cyclodimerization detectable. In this case, as for quenching by ferrocene and iodide ion, it seems clear that retardation of photoinduced cyclodimerization by the more viscous alcohol solvents results from interference with the primary initiation step, *i.e.*, initial formation of the cation radical of NVC, rather than any subsequent partitioning of reaction intermediates. It is especially noteworthy in this respect that Rhodamine 6G tetrachlorogallate is a highly efficient photosenitizer for cyclodimerization of NVC in benzene, provided oxygen is present. Benzene when used as solvent for reactions of NVC, photoinduced by other neutral sensitizers, promotes formation of polymer rather than cyclodimer, a point noticed in our own studies[6,26] and in the extensive investigations of Mikawa and collaborators.[15] However, the present results are inconsistent with the conclusions of the latter workers in that solvent polarity (*e.g.*, as between benzene and various alcohols) cannot be a primary factor in determining whether intermediates (*e.g.*, $\mathrm{NVC}\cdot^+$), produced by photoexcitation of sensitizer in the presence of NVC, partition so as to produce either cyclodimer or homopolymer.

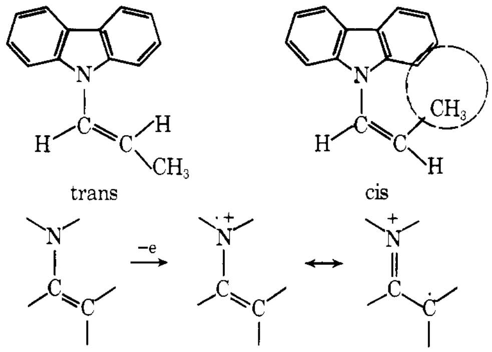
Mechanism of Homopolymerization and Copolymerization of NVC. It has already been noted in the Results section that while free radical polymerization processes are dominant when *N*-vinylcarbazole is allowed to react with photoexcited Rhodamine 6G in the absence of oxygen or other co-oxidants, the efficiencies of polymerization are significantly lower than those for corresponding cyclodimerization when air is admitted to the systems. *N*-Vinylcarbazole is not a particularly reactive monomer in free radical processes and so the efficiency of Rhodamine 6G in producing initiating free radicals was further tested by including excess quantities of methyl methacrylate in the reaction mixtures.

For the latter systems (Table II) it is clear that cyclodimerization proceeds at the same rate, irrespective of the concentrations of added methyl methacrylate, and that the quantum efficiency for *initiation* of the concurrent copolymerization of NVC and MMA is less than 1% of that for cyclodimerization of NVC. Concurrent homopolymerization of NVC and cyclodimerization would not be expected in the solvents used for the present work since, in independent work,[39] we have shown conclusively that dissolved oxygen (and other oxidants) completely inhibits free radical homopolymerization of NVC in methanol. In contrast dissolved oxygen does not inhibit homopolymerization of MMA in methanol or copolymerization of NVC with MMA in methanol. Reactivity ratios are such that, for the latter case, it is reasonable to assume that a MMA-type radical is the dominant propagating species.

We may conclude, therefore, that for Rhodamine 6G sensitized reactions of NVC in methanol or benzene, a very efficient initiation reaction leading to formation of cyclodimer is accompanied by a comparatively inefficient process leading to free radical polymerization. It then becomes necessary to consider whether these two processes arise from a common intermediate, as has been widely assumed.[12,15]

From the effects of viscous solvents which inhibited fluorescence quenching and cyclodimerization, and because the rates of cyclodimerization are essentially unaffected by very large excess concentrations of methyl methacrylate, we incline to the view that at least for sensitization by Rhodamine 6G, cyclodimerization and radical polymerizations arise from two distinct primary reaction processes. The mechanisms of initiation and propagation for the cyclodimerizations have been discussed above and a plausible explanation for the relatively inefficient polymerization would be a reaction or reactions involving the *triplet* state of the sensitizer. Whether the triplet dye molecule is produced by intersystem crossing (ϕ_{ic} for Rhodamine 6G = 0.17) or by interaction of excited singlet dye with NVC in a manner similiar to that recently established for comparable systems by Ottolenghi[40] and Mataga[41] and their respective collaborators cannot be determined at the present time. Free radical polymerization could be initiated by a totally unrelated reaction between triplet Rhodamine 6G and the monomer or solvent, or by electron transfer between NVC and triplet sensitizer. The former process appears most likely since we have already shown[6,9] that triplet sensitizers such as benzophones are highly efficient photocatalysts for the cyclodimerization of NVC.

Photosensitized Reactions of *cis*- and *trans*-*N*-Propenylcarbazole. It is very interesting that whereas *cis*- and *trans*-*N*-propenylcarbazole are highly efficient quenchers for the fluorescence of Rhodamine 6G (Table V), only the trans isomer gives either cyclodimer or copolymers with methyl methacrylate. The cis isomer is apparently completely unreactive although having an ionization potential very similiar to that of NVC and *trans*-*N*-propenylcarbazole.[33] Construction of space filling molecular models shows that *cis*-*N*-propenylcarbazole cannot easily adopt a conformation in which the nitrogen lone pair and the ethylenic π bonds are coplanar. Resonance structures of the kind required for the postulated cyclodimerization reaction would, therefore, be ruled out for steric reasons, *e.g.*



Thus we may deduce that fluorescence quenching of Rhodamine 6G by carbazoles, while it may appear to parallel known electron donor properties of the quencher, does not necessarily involve immediate formation of a redox couple. On the contrary, it seems likely that quenching arises by mere collisional interaction of carbazole derivative and photoexcited Rhodamine 6G, and that a subsequent relaxation of this encounter complex (possibly involving solvent molecules) is required for subsequent chemical processes.

S = Rhodamine 6G and D = carbazole derivative

$$S \xrightarrow{h\nu} S^*$$

$$\begin{tikzcd} S^* + D \arrow[r] & S^*\text{---}D \arrow[r] \arrow[d, shift left, "\text{encounter complex}"'] & S + D \\ \text{products} & \text{S(reduced) D(oxidized)} \arrow[l] \arrow[u, shift left] \arrow[ur] \end{tikzcd}$$

Conclusion

Cyclodimerization of NVC is efficiently photosensitized by Rhodamine 6G in several alcoholic solvents and in benzene, provided oxygen or other co-oxidants are present in the system. In the absence of co-oxidant free radical homopolymerization of NVC occurs and, for mixtures of NVC and methyl methacrylate even in the presence of oxygen, free radical copolymerization and cyclodimerization occur simultaneously. Fluorescence quenching measurements indicate that cyclodimerization results from electron transfer processes of singlet excited Rhodamine 6G with NVC leading to a cation radical chain reaction. Radical polymerizations are always much less efficiently initiated than comparable cyclodimerization and it seems likely that polymerization and cyclodimerizations do not arise from a common intermediate. Rather, for Rhodamine 6G in methanol, a minor reaction involving triplet excited sensitizer is suggested as responsible for free radical polymerizations.

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Excimer Formation by Poly(*N*-vinylcarbazole) in Solution

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ABSTRACT: Excimer formation by poly(*N*-vinylcarbazole) and its copolymers with fumaronitrile, diethyl fumarate, and diethyl maleate in solution has been investigated. The 1:1 alternating copolymers with fumaronitrile and diethyl fumarate exhibit no excimer fluorescence, while the *N*-vinylcarbazole (VCz) homopolymer and VCz-rich copolymer with diethyl maleate, both having the VCz sequence, show excimer fluorescence. These observations lead to the conclusion that in the polymers having carbazole rings as pendant groups excimer formation is possible only between two adjacent chromophores which are separated by a main chain segment of three carbon atoms.

Some aromatic vinyl polymers such as polystyrene,[2,3] poly(1-vinylnaphthalene),[3,4] poly(1-vinylpyrene),[5,6] poly(*N*-vinylcarbazole),[7-9] poly(acenaphthylene),[6,10,11] and poly(naphthyl methacrylate)[12] show excimer fluorescence in solution as well as in solid film.[13] It is characteristic of such polymers to form excimers even in dilute solution, in contrast to the behavior of small molecules. Although the excimer formation of small molecules in solution has been attributed to a diffusion mechanism,[14] the mechanism in polymers has not yet been established. That the above mentioned polymers show excimer fluorescence even in dilute solution may simply be due to the polymers having a higher local concentration of chromophores along the main chain. Since the polymers have pendant chromophores in a one dimensional arrangement along the main chain in high density, the following three possibilities are conceivable as the structure of the excimer-forming site of the polymers in solution: (i) excimer formation between adjacent chromophores, which are separated by a main chain segment of three carbon atoms; (ii) excimer formation between two far-distant chromophores, which happen to be close to each other in the same chain as a result of folding of the polymer chain; (iii) excimer formation between two chromophores belonging to different chains. Cases i and ii correspond to the intramolecular excimer formation, and case iii to the intermolecular excimer formation. Although excimer formation in polystyrene and poly(1-vinylnaphthalene) has been considered to be mainly case i,[2] there is no explicit evidence so far. In poly(acenaphthylene),[10] however, only case ii or iii is possible, since two adjacent naphthalene rings cannot be arranged with the planes of the napthalene rings parallel to each other within the distance of excimer formation. The case iii can easily be distinguished from the other two cases by diluting the solution so that no intertwining of the polymer chains can occur. A clear distinction between i and ii is difficult to achieve. If we have an alternating copolymer in which each pendant chromophore is separated along the chain by a comonomer unit which does not participate in excimer formation, the spectroscopic behavior of such polymers will provide important information for distinguishing between cases i and ii.

Among the polymers which are known to show excimer fluorescence, poly(*N*-vinylcarbazole) (PVCz) is a thoroughly investigated and practically important polymer.[6-8] The present study deals with the problem of excimer formation in this polymer, especially with the use of alternating copolymers in which each pendant carbazole chromophore is separated regularly by a comonomer unit having no conjugated π electrons. We recently found that *N*-vinylcarbazole (VCz) copolymerized with several electron accepting vinyl monomers such as fumaronitrile (FN),[15] diethyl fumarate (DEF),[16] and diethyl maleate (DEM) (Figure 1). In both FN and DEF, 1:1 alternating copolymers can be obtained regardless of the monomer feed ratios. Copolymerization with DEM yields a 1:1 alternating copolymer if the monomer feed ratio of VCz is less than 0.5, but if this ratio exceeds 0.5, the VCz contents in the copolymers increase continuously with an increase in VCz feed. In this polymer, the DEM-DEM sequence cannot exist, because DEM itself does not homopolymerize. Thus, we have succeeded in preparing several kinds of VCz copolymers. In the alternating copolymers, each VCz unit is separated regularly on both sides with comonomer units, and there are no adjacent carbazole chromophores which are separated by a main chain segment of three carbon atoms. But in random copolymers such as VCz–DEM, the sequence of VCz units is interrupted occasionally by a known amount of comonomers. The 1:1 alternating copolymers did not show excimer fluorescence, and only the VCz homopolymer and the VCz-rich copolymer with DEM, which have two adjacent carbazole chromophores, showed excimer fluorescence.

Experimental Section

VCz homopolymers were obtained by radical polymerization with 2,2′-azobis(isobutyronitrile) in benzene solution at 80°. The polymers were reprecipitated more than three times from methanol and dried *in vacuo*. The resulting polymers had a molecular weight of 8×10^3 to 8×10^4. One-to-one alternating copolymers of the VCz–FN and VCz–DEF were obtained as described before.[15,16] The VCz–DEM copolymers having various VCz contents were prepared by radical copolymerization at different monomer feed ratios, and the copolymer compositions were determined by nitrogen analysis as well as by spectroscopically using the molar extinction coefficient of the VCz homopolymer. Copolymerization of the VCz–DEM system will be reported elsewhere.[17] The lowest π–π^* absorption maxima in the VCz–FN and VCz–DEF copolymers shifted to the blue region by about 10 nm ($\lambda_{\max}$ 333 nm) and about 5 nm (338.5 nm), respectively, compared with that of the VCz ho-