branches and the formation of cross-linked polymers at temperatures below 350 °C.

In conclusion, the molecular weight increase and the decrease in the thermal degradation of PE are considered to be dependent on the rate of diffusion, in relation to the viscosity of the media, of the two radicals produced by initiation outside the cage.

Acknowledgment. We express our gratitude to Dr. Yamaguchi of Showa Denkko K.K. for supplying the LHDPE sample, to Mr. Sakane of Toyo Soda Manufacturing Co. Ltd. for GPC measurements, and to Dr. Takido of the Chemical Analysis Center of Nihon University for NMR measurements. We also thank Mr. Kanda and Mr. Hase for their assistance with the experimental work.

References and Notes

(1) Kagiya, T. *High Polymers Jpn.* **1980**, *29*, 667.
(2) Oakes, W. G.; Richards, R. B. *J. Chem. Soc.* **1949**, 2929.
(3) Grassie, N. "Chemistry of High Polymer Degradation Process"; Butterworths: London, 1956; p 68.
(4) Wall, L. A.; Madorsky, S. L.; Brown, D. W.; Straus, S.; Shimha, R. *J. Am. Chem. Soc.* **1954**, *76*, 3434.
(5) Baily, W. J.; Liotta, C. L. *Polymn. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1964**, *5*, 333.
(6) van Schooten, J.; Evenhuis, J. K. *Polymer* **1965**, *6*, 343, 561.
(7) Tsuchiya, Y.; Sumi, K. *J. Polym. Sci., Part A-1* **1968**, *6*, 415; *J. Polym. Sci., Part B* **1968**, *6*, 357.
(8) Witt, D. R.; Hogan, J. P. *J. Polym. Sci., Part A-1* **1970**, *8*, 2689.
(9) Tanaka, K.; Takakura, M.; Koshino, Y. *J. Appl. Polym. Sci.* **1974**, *18*, 1131.
(10) Holmström, A.; Sörvik, E. M. *J. Chromatogr.* **1970**, *53*, 95; *J. Appl. Polym. Sci.* **1974**, *18*, 761, 3153; *J. Polym. Sci., Polym. Symp.* **1976**, *No. 57*, 33.
(11) Kuroki, T.; Sawaguchi, T.; Niikuni, S.; Ikemura, T. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(12) Sehon, A. H.; Szwarc, M. *Proc. R. Soc. London, Ser. A* **1950**, *202*, 263.
(13) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 456.
(14) Trotman-Dikenson, A. F. "Free Radicals"; Methuen: London, 1959; p 38.
(15) Mita, I. "Aspects of degradation and Stabilization of Polymers"; Jellinek, H. H. G., Ed.; Elsevier: Amsterdam, 1978; p 247.
(16) Iida, T. A.; Honda, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1480.
(17) Ushiki, H.; Horie, K.; Okamoto, A.; Mita, I. *Polym. J.* **1979**, *11*, 691; **1980**, *12*, 35.
(18) Behzadi, A.; Borgwardt, U.; Henglein, A.; Schamberg, E.; Schnabel, W. *Ber. Bunsenges. Phys. Chem.* **1970**, *74*, 649.
(19) Arnett, R. L.; Stacy, C. *J. Polym. Eng. Sci.* **1966**, *6*, 295.

Cross-Link Formation in a Solid Photopolymer Based on the Chromophore 1,2-Diphenylcyclopropene

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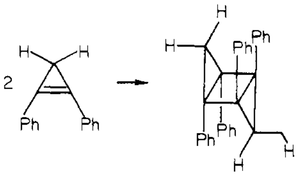
Received March 18, 1982

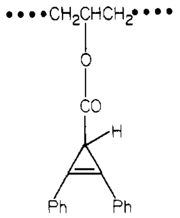
ABSTRACT: The absolute quantum yield of cross-link formation in a photopolymer based on the photoreactive chromophore 1,2-diphenylcyclopropene (CP) approaches the theoretical maximum for a single-step cross-linking process. In the matrix, only a small fraction of chromophores (~4%) are in reactive configurations, and it appears from the fluorescence behavior of the films that these are associated with excimers. Chemical analysis reveals the formation of tricyclic dimers in the irradiated films, as anticipated by DeBoer et al.,[2,3] which indicates that the primary cross-linking step is cycloaddition between the double bonds of two suitably oriented cyclopropene rings. The high initial quantum yield of the photoreaction coupled to a low concentration of reactive sites implies extensive energy migration in the system. From lifetime measurements, the migration range of the triplet excitation in the matrix is estimated at 150 Å.

In the course of work on the photochemistry of phenyl-substituted cyclopropenes[1,2] DeBoer and Breslow observed the facile dimerization of the excited triplet states of these molecules.



(2 + 2)Cycloaddition was the only reaction of the triplet state of 1,2-diphenylcyclopropene, and the corresponding tricyclic dimers were the principal products in the sensitized photolysis of 1,2,3-triphenylcyclopropene and of 1,2-diphenylcyclopropene-3-carboxylate.[2] The high quantum efficiency of the cycloaddition reaction in solution[1] suggested its use as a photo-cross-linking device. Incorporation of cyclopropene groups into suitable polymers did indeed produce highly photosensitive materials.[3-6]

We have now investigated a polymer (PCP) obtained by the partial esterification of poly(vinyl alcohol) with the acid chloride of 1,2-diphenylcyclopropene-3-carboxylic acid.



PCP

In the sample available to us 30% of the esterifiable positions were occupied by CP groups. The absolute

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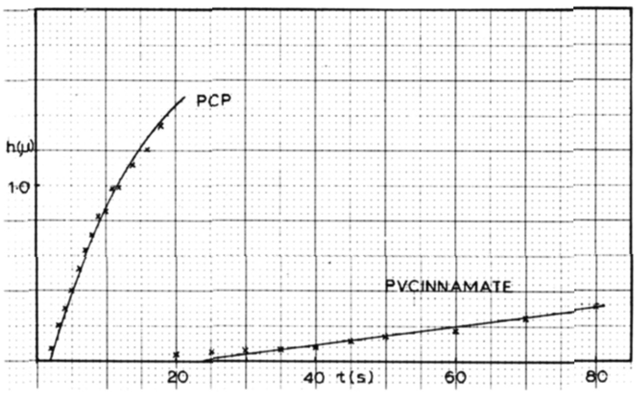
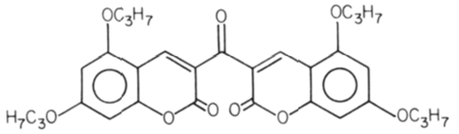


Figure 1. Gel curves of PCP and of poly(vinyl cinnamate) films sensitized with the ketocoumarin KC and irradiated at 380 nm. h = thickness of gel (μm); t = exposure time (s).

quantum yield of cross-link formation in PCP films sensitized with the ketocoumarin KC was found to approach the theoretical maximum for a single-step cross-linking process. This observation provided the incentive for a more detailed study of the mechanism by which cross-links are formed in solid films of the material.



KC

Absolute Quantum Yield of Cross-Link Formation. Cross-link formation in a solid polymer film can be monitored by exposing the film to increasing doses of radiation, removing the soluble parts of the film in a solvent, and determining the insoluble residue, or gel, remaining. A plot of the amount of gel as a function of the corresponding exposure (radiation dose E) is the gel curve of the photopolymer.[7,8] The gel curve originates at the gel point, which defines the minimum exposure (E_G) required for incipient gel formation.

Figure 1 compares the gel curves of PCP and of the standard photopolymer, poly(vinyl cinnamate). Both were sensitized with the same ketocoumarin (KC) and irradiated under the same conditions following the procedure outlined in ref 7. It can be seen from the figure that PCP is by far the more photosensitive of the two materials.

The quantum yield ϕ of cross-link formation is defined as the number of chromophores entering into crosslinks for every photon absorbed. If two chromophores are involved in the cross-link, the maximum value of ϕ achievable in the absence of a chain reaction is 2. The quantum yield so defined is related to the gel point exposure by the expression[8,9]

$$\phi = d/2.303\epsilon m M_w E_G \qquad (1)$$

Here, d is the specific gravity of the polymer film, ϵ and m are the molar extinction coefficient and the molarity of the light-absorbing species (chromophore or sensitizer), M_w is the weight-average molecular weight of the polymer, and E_G is the gel point exposure (in einstein cm^{-2}).

In applying eq 1 to the data of Figure 1, we note that the critical exposure time for incipient gel formation is t_G = 1.16 s (see Experimental Part for details). The film had been exposed at 380 nm to a monochromatic beam of intensity $I_0 = 0.88 \times 10^{-10}$ einstein cm^{-2} s^{-1}. The gel point exposure is therefore $E_G = I_0 t_G = 1.02 \times 10^{-10}$ einstein cm^{-2}. The extinction coefficient of the sensitizer at 380 nm is $\epsilon_s = 4.25 \times 10^4$ L mol^{-1} cm^{-1} and its molarity in the solid film m_s = 0.205. The weight-average molecular weight, determined by combined osmometry and gel permeation chromatography, is M_w = 287 400. With these data, the quantum yield of cross-linking in the triplet-sensitized photopolymer is found to be

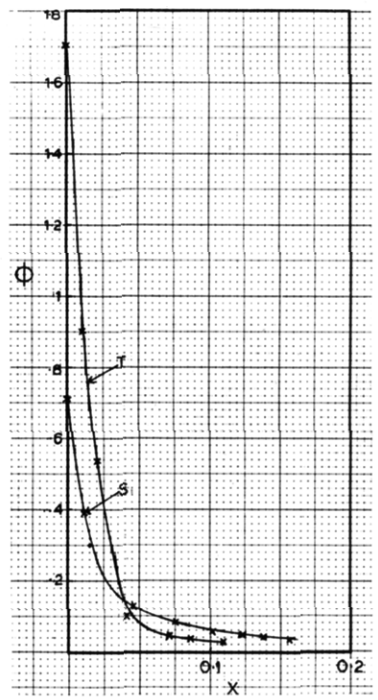


Figure 2. Quantum yield of the photoreaction as a function of the degree (x) of chromophore conversion. S = unsensitized film irradiated at 300 nm; T = triplet-sensitized film (with KC) irradiated at 380 nm.

$$\phi = 1.70 \pm 0.05$$

This is a remarkable result. It means that in triplet-sensitized PCP films the efficiency of cross-link formation has reached 85% of the theoretical maximum and that here the incident radiation is almost quantitatively converted into cross-links. This exceptionally high efficiency led us to investigate the mechanism of cross-link formation in greater detail.

Similar experiments with unsensitized PCP films exposed to monochromatic radiation at 300 nm gave a quantum yield of $\phi = 0.71 \pm 0.05$.

Quantum Yield of the Photoreaction as a Function of Chromophore Conversion. A first clue to the mechanism of cross-link formation in PCP films came from the change of quantum yield in the course of the photoreaction. For that purpose, the quantum yield may be derived from the rate of change of the optical density during exposure.

$$\phi = \frac{1}{A}\frac{\mathrm{d}D}{\mathrm{d}t}\frac{10^{-3}}{T_0 \Delta\epsilon} \qquad (2)$$

In eq 2 D is the optical density in the absorption band of the reactive chromophore, A is the fraction of light absorbed by the sensitizer, I_0 is the incident radiation flux (in einstein cm^{-2} s^{-1}), and $\Delta\epsilon$ is the difference in the molar extinction coefficients of reactant and product.

Figure 2 shows a plot of the quantum yield as a function of the degree of chromophore conversion, both for the case of the triplet-sensitized film and for that of the unsensitized material. The following points are made:

(i) The quantum yield values obtained from spectrophotometry are not very accurate at low conversion, where the change in optical density must be small. In contrast, the gel point exposure informs us about the quantum yield

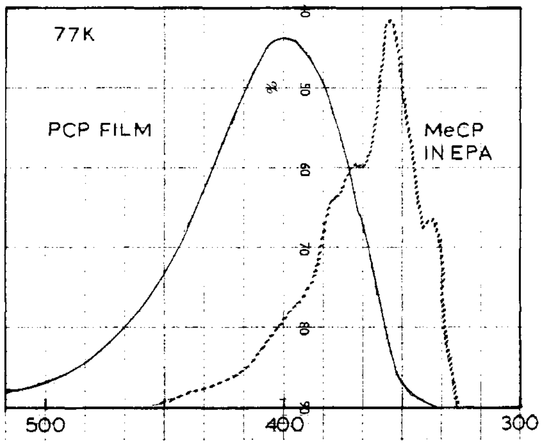


Figure 3. Fluorescence spectra at 77 K of a dilute solution of MeCP in EPA (ether–isopentane–ethanol = 5:5:2) and of a solid film of PCP.

at or near the gel point, which in PCP corresponds to a chromophore conversion of about 0.15%. The two methods are suited to different ranges of chemical conversion. In the data in Figure 2 the value of ϕ derived from the gel point provides the starting point of the quantum yield function $\phi(x)$.

(ii) The quantum yield decreases steeply as the solid-state reaction progresses and reaches very low values at a conversion of about 0.04%. This indicates that the reaction occurs efficiently only at a very small number of sites.[10]

(iii) The combination of a small number of reactive sites with a high initial quantum yield of the photoprocess strongly suggests that the excitation quanta are mobile in the film and are able to reach the reactive sites by energy migration.[11]

Information on the nature of the reactive sites may be obtained from fluorescence spectroscopy and from chemical analysis of the photoproducts.

Fluorescence Spectra and Lifetimes. Dilute solutions of PCP as well as solutions of the model compound methyl 1,2-diphenylcyclopropene-3-carboxylate (MeCP) emit the normal "monomer" fluorescence of the CP chromophore shown in Figure 3. The fluorescence of solid films of the polymer PCP is, however, considerably red shifted. This effect is attributed to the formation of an excimer. The observation of a similar red shift in saturated solutions of the model MeCP as well as a kinetic investigation supports this view.

Kinetic profiles of fluorescence were obtained at 383 nm, which is the wavelength of peak emission of the monomer, and at 470 nm, where the monomer emission is minimal. In dilute solutions, fluorescence decay was very fast at all wavelength ($\tau < 50$ ps).

In solid films of PCP, fluoresence decay was slower and could be matched satisfactorily by a biexponential function of the form[12]

$$i(t) = A_a \exp(-t/\tau_a) + A_b \exp(-t/\tau_b) \qquad (3)$$

At 383 nm the lifetimes of the two components were $\tau_a(383) = 215 \pm 20$ ps and $\tau_b(383) = 1.65 \pm 0.15$ ns, and from the ratio of the A factors it followed that more than 80% of the emission was caused by the shorter-lived species.

At 470 nm the double exponential could be fitted only with a negative preexponential factor A_a. That means that at 470 nm there was a "growing-in" of the longer-lived species after excitation. This confirms the notion of a small number of excimer sites, populated by energy migration from a large ensemble of monomeric chromophores. The lifetimes of the two components observed at 470 nm were $\tau_a(470) = 200 \pm 50$ ps and $\tau_b(470) = 1.84 \pm 0.20$ ns. We conclude that τ_b is the decay time of the excimer and τ_a is the average time taken to populate the excimer sites in the film. Figure 4 shows the fluorescence decay measured at 383 nm.

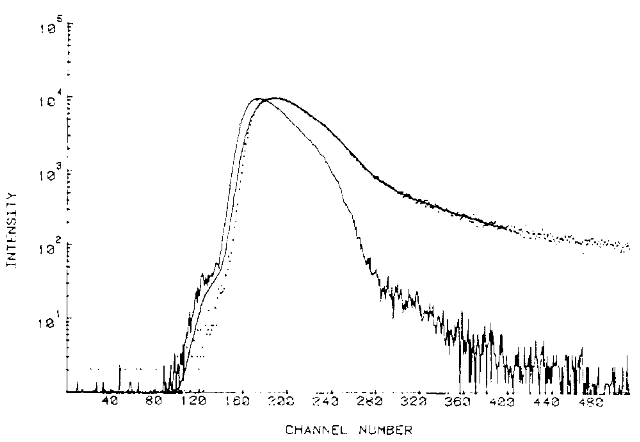


Figure 4. Fluorescence decay of PCP, recorded at 383 nm. Lower curve, laser pulse profile. Points on upper curve are experimental results and the full line is the best computer fit to the biexponential function of eq 3. 1 channel = 16 ps.

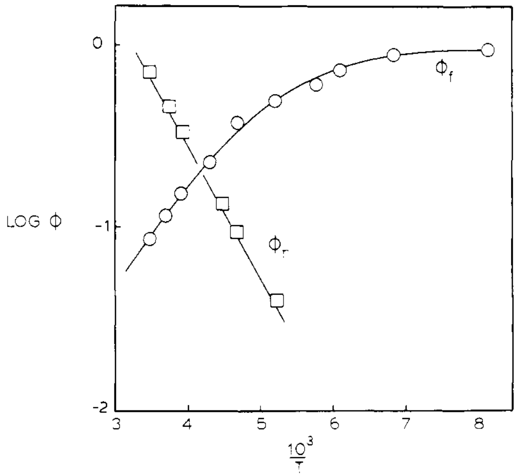


Figure 5. Temperature dependence of the quantum yield of fluorescence ϕ_f and of the quantum yield ϕ_r of the chromophore reaction (Arrhenius plot).

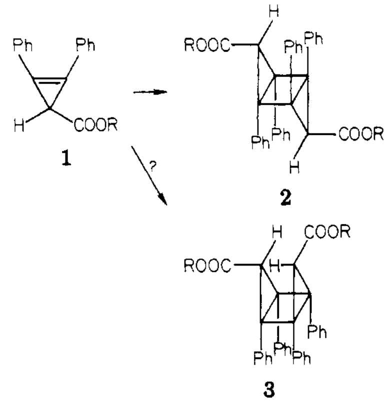
Although the spectral shift from 383 nm to 417 nm (the peak of the excimer emission) is smaller than that usually encountered in excimer-forming systems,[13] it is much too large to be caused purely by matrix immobilization.[14] In the fluorescence spectrum of a dilute solution of MeCP in a rigid polystyrene matrix, immobilization causes only a change in the occupancy of the lower vibrational levels of the ground state but no significant spectral shift. The emission centered around 410 nm is therefore associated with an excimer-type interaction between pairs of CP chromophores.

The quantum yield of fluorescence increases with falling temperature, while the quantum yield of the photoreaction decreases. The complementary nature of excimer emission and chemical reaction is demonstrated in Figure 5, which shows Arrhenius plots of ϕ_f and ϕ_r. The fluorescence quantum yield in the film is 0.085 at room temperature, and approaches a value of $\phi_f = 0.86$ below −130 °C. The quantum yield of the photoprocess (singlet pathway) decreases with falling temperature and is associated with a small activation energy of 0.63 kcal mol^{-1}.

All these experiments indicate the presence of weakly bound excimers in the PCP matrix. Furthermore, the overall fluorescence intensity decreases and the shape of the emission spectrum changes during irradiation, which suggests the involvement of excimer sites in the cross-linking process. Although the excimer sites betray their presence by singlet excimer emission, the existence of these sites and the relative configuration of the chromophores at these sites are equally relevant to the mechanisms of the triplet-state reaction in the solid polymer.[15]

Photochemistry of the Diphenylcyclopropene Chromophore in the Matrix. The triplet yield in the direct excitation of the diphenylcyclopropene chromophore is very low. Irradiation of an unsensitized film of PCP produces therefore almost exclusively singlet excited states. The photoreactions in sensitized films of PCP, on the other hand, are based entirely on the triplet excited state of the chromophore.

Singlet and triplet excited states of cyclopropene have different photochemistries.[16] The singlet excited state ring-opens to a vinyl carbene, which undergoes typical carbene reactions of addition and insertion. In the triplet excited state, the three-membered ring is preserved[1,2] and the principal reaction is (2+2)cycloaddition to a suitable double bond. In solutions of the model MeCP this leads to the tricyclic dimer 2, where the two cyclopropane rings



are connected in an anti position (chair form). Dimer 3, which is the syn isomer of 2 (boat form), is sterically less favorable and has, so far, not been reported in the literature.[16] We believe that one or both cyclodimers 2 and 3 provide the cross-links in the irradiated solid matrix. This view is based on the following experiments.

Films of PCP sensitized with thioxanthone[2] were exposed to monochromatic radiation at 380 nm, which is only absorbed by the triplet sensitizer. After exposure, the cross-linked films were hydrolyzed, the free acids were separated and remethylated, and the mixture of esters was submitted to HPLC. Comparing the chromatogram of an irradiated film with that of an unirradiated film (Figure 6) revealed that only two major peaks, at elution times of 10.95 and 13.04 min, were associated with new photoproducts. They were identified by model experiments as belonging to 2,3,5,6-tetraphenyl-1,4-dicarboxybenzene (6) and octaphenyl-4,4′-carboxybiphenyl (7).

The sequence of events leading from (2) to (6) was elucidated by DeBoer[2] (Scheme I). We have confirmed DeBoer's findings: a DTA scan of the crystals of 2 shows exothermic transitions at 174 and 188 °C, and a sample of 2 heated to 200 °C in the absence of air was quantitatively transformed into 4. The same transformation occurred, more slowly, in THF solution. In the presence of atmospheric oxygen, 4 is easily oxidized to the tetraphenylbenzene 6 and, to a lesser extent, to the octaphenylbiphenyl 7. In a melt of 4, however, the only major oxidation product is the biphenyl 7.

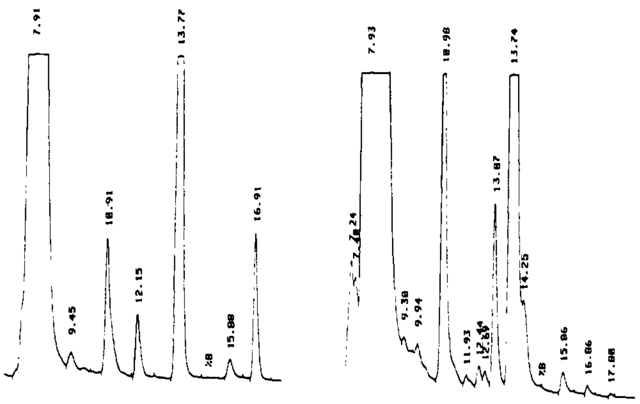
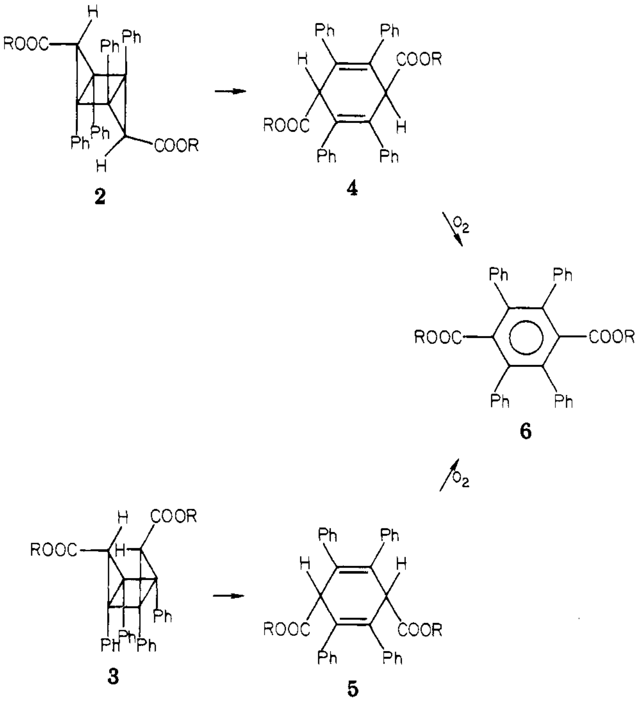
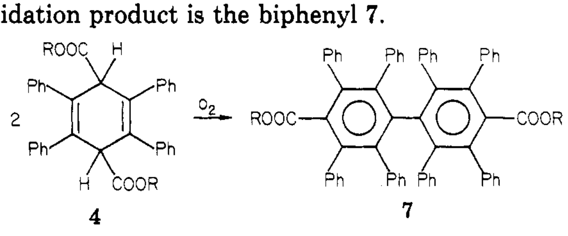


Figure 6. Chromatogram (HPLC on Lichrosorb RP18) of ester mixture after the hydrolytic workup of freshly coated unirradiated (left) and irradiated (right) films of PCP.

Scheme I





A control experiment in which an authentic sample of the dimer 2 was hydrolyzed and remethylated in the usual way produced about equal quantities of 6 and 7, but the dimer 2 itself did not survive the workup (see Figure 7). The presence of 6 and 7 in the final hydrolysis products of the irradiated films testifies therefore unambiguously to the formation of a tricyclic dimer in the cross-linking process.

The same final products are expected to result from both the anti- and the syn-dimers 2 and 3. Although we have no direct proof, we believe that the syn-dimer 3 is the principal product of the triplet-sensitized photoreaction in the solid matrix. We know from fluorescence experiments that excimers are involved in the photoprocess. At an excimer site the relative configuration of the two di-

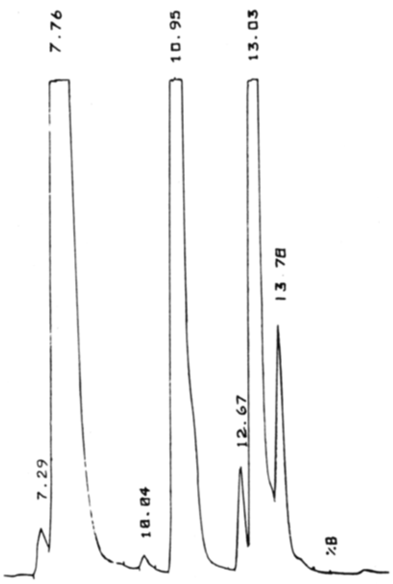


Figure 7. Chromatogram (HPLC on Licrosorb RP18) of the products of the hydrolysis and remethylation of dimer **2**. The peaks at elution times 10.95 and 13.03 min correspond to the tetraphenylbenzene **6** and the biphenyl **7**, respectively.

phenylcyclopropene chromophores must allow maximum overlap of the π orbitals, a geometry which leads spontaneously to a syn configuration in the cycloaddition product.

In the absence of a sensitizer, when radiation is absorbed directly by the CP chromophores, the mechanism of cross-link formation is different. A number of photoproducts appear in the workup of the irradiated films, but the tetraphenylbenzene **6** and the biphenyl **7** are not among them. At this stage we have not been able to identify any of the products of the singlet-state pathway.

Energy Migration. Energy migration appears to be a necessary condition for the high photosensitivity of the PCP polymer. The concentration of chromophores in the solid films is 2.24 mol L^{-1}, corresponding to an average chromophore separation of 9 Å. The spatial conditions for the transfer of singlet as well as triplet excitation are therefore fulfilled.

Singlet excitation transfer is indicated by several effects.

(i) The fluorescence of the films is quenched by the incorporation of singlet energy acceptors, and if the films are doped with fluorescent probes, probe fluorescence is observed on irradiation with light which is only absorbed by the CP chromophores. From the effect of quencher concentration the efficiency of energy transfer may be gauged.

Klöpffer[17] has used this method to demonstrate energy migration in poly(vinylcarbazole). He has defined a quenching factor Q by the ratio

$$Q = (\phi_f^0 - \phi_f)/\phi_f \qquad (4)$$

where ϕ_f^0 and ϕ_f are the fluorescence yields in the absence and in the presence of quencher. The quenching factor in the matrix is determined by the concentration of quencher sites (C_X) and by the average number (n) of transfers in the lifetime of the excitation.

$$Q = 0.66nC_X \qquad (5)$$

If a small concentration (C_E) of excimer sites is present, excimer emission is quenched by an extraneous guest quencher according to the expression

$$Q_E = 0.66nC_X/(1 + 0.66nC_E) \qquad (6)$$

We have used the fluorescent probe 4,4′-bis(benzoxazolyl)biphenyl[18] as quencher and determined the quenching factors from the induced fluorescence of the probe. The results are shown in Figure 8, where quenching factors are plotted logarithmically against quencher concentration. Using eq 5 one can infer from the position of the upper correlation line (curve 1) an apparent migration range of 75 transfers.

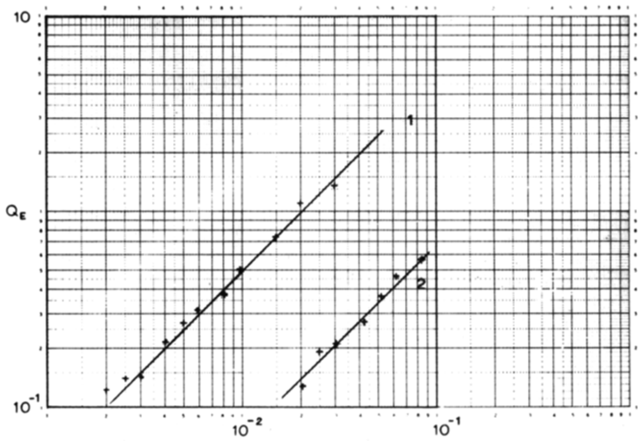


Figure 8. Logarithmic plot of the quenching factor Q as a function of quencher concentration: (1) induced fluorescence of the probe 4,4′-bis(benzoxazolyl)biphenyl; (2) quenching of CP fluorescence by hexachloroxylene.

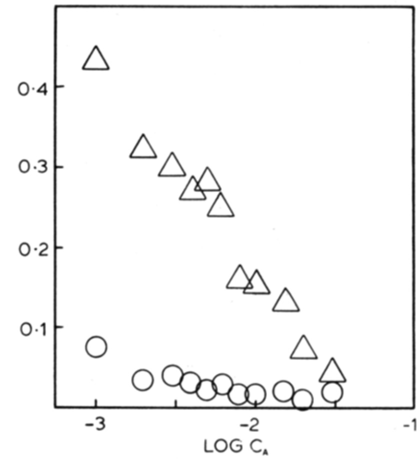


Figure 9. Polarization of the direct (△) and of the induced (○) emission of the fluorescent probe 4,4′-bis(benzoxazolyl)biphenyl in PCP. C_A is the mole fraction of the probe in the films.

(ii) Figure 9 shows the results obtained when linearly polarized radiation is used to excite the fluorescence of a guest molecule (probe) incorporated in the polymer film. If the film is exposed to polarized radiation which is directly absorbed by the probe, the resulting fluorescence shows a high degree of polarization (P) (see the points marked by triangles in Figure 9). However, the sensitized fluorescence obtained with radiation which is absorbed by the CP chromophores and subsequently transferred to the probe is found to be completely depolarized (points marked by circles in Figure 9). This indicates that in the sensitization process more than one transfer step must be involved. It is assumed that 5–6 transfer steps are required to erase the memory of a preferred polarization plane in the system.[21]

(iii) It is notoriously difficult to diagnose energy migration of moderate range, because of the possible competition from single-step dipole resonance (Förster) transfer. In that case, the range of energy migration is estimated with less ambiguity from experiments with "chemical" quenchers, which do not allow Förster transfer to occur. Following the work of Klöpffer,[17] we have used

$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro-$p$-xylene to quench the fluorescence of PCP films. The results of these experiments are summarized in curve 2 of Figure 8. With eq 6 and an excimer fraction of 0.02 they lead to an average number of about 12 transfers. Thus, most of the apparent migration implied by energy transfer to a fluorescent probe (curve 1 in Figure 8) is in fact caused by single-step Förster transfer.

(iv) The results obtained from quenching experiments with hexachloroxylene are in accord with the monomer lifetime of the CP chromophore in the solid films ($\tau \sim 200$ ps). If the average residence time of the excitation at a chromophore site is of the order of 10^{-11} s, as the few available data indicate,[19,20] the singlet excitation in PCP would survive some 10–20 transfers.

The range of triplet energy migration cannot be gauged from present data. However, work is in progress to determine it from the quenching of the cross-linking reaction by triplet energy acceptors.[22]

Summary and Conclusions

PCP is a highly photoreactive polymer. The quantum yield of cross-linking of the triplet-sensitized films approaches the theoretical maximum attainable in any single-step cross-linking process.[4] The high efficiency, achieved with only a small fraction of chromophores (~ 4%), implies extensive energy migration in the solid matrix. Singlet energy migration of modest range is indicated by quenching experiments and by the behavior of fluorescent probes. Triplet energy migration has a wider range.

The fluorescence of PCP films shows the presence of weakly bound excimers which disappear during irradiation and are therefore thought to be implicated in the cross-linking process. In the triplet-sensitized films only two photoproducts are observed. Both can be shown to originate in a tricyclic dimer of the type described by Breslow and DeBoer.[1,2] It is suggested that the syn isomer (boat form) is the principal product of the triplet photoreaction in the matrix.

It is of interest to compare the mechanism of cross-link formation in films of PCP with that in poly(vinyl cinnamate). In both, the cross-linking reaction is cycloaddition between two double bonds conjugated to an aromatic system and in both the fraction of reactive sites in the matrix is low (it is about 10% in poly(vinyl cinnamate)). However, the chromophores in PCP have the advantage of a much longer triplet lifetime. In PCP the triplet excitation migrates over a fairly wide range, while in poly(vinyl cinnamate) it does not.

The lifetimes of the excited states of cinnamoyl groups and related chromophores are short, because of the tendency of the ethylenic double bond to assume a perpendicular configuration.[23] In this configuration ground-state and excited-state energies approach each other, and the reduced energy gap favors a rapid deactivation of the excited states. In the CP chromophores this radiationless process is inhibtied by the rigid geometry of the cyclopropene ring. The success of PCP as a photopolymer can thus be attributed to the stability of the excited triplet state of the three-membered ring and to the consequent free mobility of the excitation in the polymer matrix.

Experimental Part

Gel Curves. Thick films of the photoreactive polymers were coated on quartz plates and were exposed under vacuum through the transparent support. The light source was a xenon arc (150 W) coupled to a Bausch and Lomb high-intensity monochromator. After exposure, the films were treated with dichloroethane, the insoluble gel residues were dried, and finally their thickness was measured with an interference microscope.

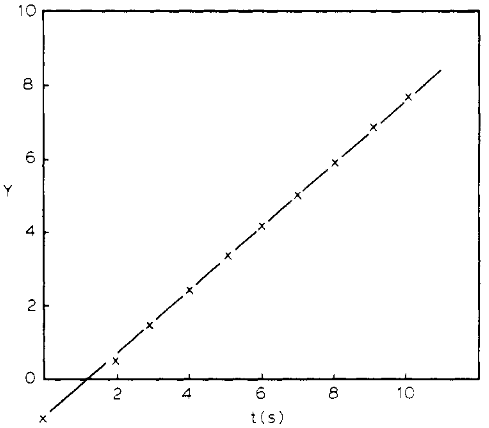


Figure 10. Determination of gel point exposure by the method of ref 7.

In Figure 1 the thickness of the insoluble gel is plotted as a function of the corresponding exposure time.[24] From these plots, the minimum exposure required for incipient gel formation can be read off directly. However, a more accurate procedure for determining E_G has been given in ref 8. To implement it, the dimensionless gel volume $H = 2.303\epsilon mh$ is calculated from the gel thickness h, and the dimensionless exposure $Y = E/E_G - 1$ is read off a theoretical correlation function $H = F(\gamma,\beta)$ given in ref 4, 5, or 24. If the correct function has been chosen, a plot of Y vs. t is linear and passes through the point $t = 0$, $Y = -1$. The slope of the plot is the reciprocal critical gel point exposure time t_G.

$$\mathrm{d}Y/\mathrm{d}t = 1/t_G \tag{7}$$

Figure 10 shows the correlation line $Y(t)$ for a film of sensitized PCP exposed to monochromatic radiation (380 nm), with a radiation flux[25,26] of 0.88×10^{-10} einstein cm^{-2} s^{-1}. The slope of the correlation line is $\mathrm{d}Y/\mathrm{d}t = 0.86$ s^{-1}, corresponding to a critical exposure time of $t_G = 1.16$ s and to a gel point exposure of $E_G = 1.02 \times 10^{-10}$ einstein cm^{-2}.

Molecular Weight. The weight-average molecular weight (M_w) required for the determination of the quantum yield via eq 1 is usually obtained by light scattering. However, for a complex copolymer like PCP the evaluation of light scattering data is rather uncertain and M_w was derived from the number-average molecular weight (M_n) and the dispersity of the molecular weight distribution (β).

$$M_w = M_n \exp(\beta^2) \tag{8}$$

The number-average molecular weight M_n was determined by osmometry in a Melabs CSM-1 (Wescan Instruments Inc.) osmometer, using a reconstituted cellulose membrane of Schleicher and Schuell, RC51, and 1,2-dichloroethane as solvent. The result was $M_n = 79\,500$. With a dispersity of molecular weight of $\beta = 1.13$ this corresponds to a weight-average molecular weight of $M_w = 287\,400$.

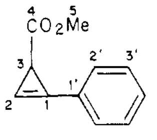
The molecular weight distribution was determined by gel permeation chromatography in THF solution. The columns used had average pore sizes of 10^6 and 10^4 Å and were calibrated with a set of monodisperse polystyrenes. The data calculated from the elution curve of the polymer are $M_n = 78\,760$, $M_w = 284\,700$, $M_w/M_n = 3.615$, and $\beta = 1.13$.

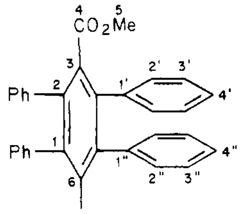
Dependence of Quantum Yield on Chromophore Conversion. The quantum yield of the photoreaction was determined from the change in the absorption spectrum of the films under irradiation. The films were cast from dilute solutions in dichloroethane–cyclohexanone (10:1) on the inside of quartz cells. The cells were sealed off under vacuum, placed in a Unicam SP800 spectrophotometer, and irradiated in situ. The quantum yield of the disappearance of the chromophore was calculated from eq 2. The results for sensitized and unsensitized films are shown in Figure 2.

Fluorescence Spectra. Emission spectra of solutions and films were recorded with a spectrofluorometer described earlier.[18] Polarized spectra were taken with the help of two Glan prisms at the entrance and exit slits of the cell compartment. Polari-

Table I

^{13}C and ^{1}H Chemical Shifts (ppm) of the Diphenylcyclopropene Chromophore and Its Photoproducts





	1	2	4	6	8
C1	107.6	46.0	133.0	138.3	138.6
C2					140.8
C3	21.5	49.9		N/O[c]	128.2
C4	175.3	167.7	171.4	N/O[c]	169.5
C5	51.7	51.3		51.5	51.5
C6					128.0
C1′	127.1	133.5	138.8	138.8	140.5
C2′	129.9	129.8	129.3	130.1	127.75/127.65
C3′	128.9	128.0	127.7	127.4	130.2/129.9
C4′	129.3	127.5	126.8	127.1	127.0/126.7
C1″					140.5
C2″					127.66/127.75
C3″					129.9/130.2
C4″					126.7/127.0
H3	2.84	3.73,[a] 3.81[b]	5.01,[a] 4.29[b]		
H5	3.70	3.34,[a] 3.35[b]	3.10,[a] 3.13[b]	3.11	3.22
H2′	7.69				
H3′, H4′	7.3, 7.5	7.27,[a] 7.29[b]	7.07,[a] 7.12[b]	7.07	7.1, 7.2

[a] $CDCl_3$. [b] CD_3CN. [c] N/O = not observed.

zations were calculated by the method of Azumi and McGlynn.[27] Fluorescence quantum yields were determined by the method of Parker and Rees.[28] The fluorescent probe used in the quenching experiments was 4,4′-bis(benzoxalyl)biphenyl, a fluorescent agent with unit quantum yield of fluorescence.[18] All spectra shown are presented without correction.

Fluorescence Lifetimes. Kinetic profiles of fluorescence emission were measured with a time-resolved fluorescence spectrometer described in an earlier paper.[12] The excitation source was a frequency-doubled, mode-locked dye laser (Spectra-Physics). The emitted light was analyzed by a Hilger and Watts D330 monochromator, and monitored by a single-photon-counting technique.[29] The data were processed on a Perkin-Elmer Interdata 7/32 computer.

Chemical Analysis. Only the photoproducts of the triplet-sensitized matrix reaction were investigated. The procedure was as follows:

Polymer films, sensitized with 2% by weight thioxanthone, were cast from dilute solution in dichloroethane on the inside of round-bottom Pyrex flasks (about 20 mg on the inner surface of a 100-mL flask). After careful drying, the films were exposed in a stream of nitrogen at 0 °C (ice water bath) to a medium-pressure mercury arc (Hanovia, 250 W). The radiation was filtered by a Corning filter no. 052 (glass no. 7380). The exposed and thereby cross-linked films were then hydrolyzed in situ with 1 M KOH in THF–methanol (20:1), using benzyltriethylammonium chloride as a phase-transfer agent. The reaction was conducted at room temperature and was completed after stirring for 3 h.

The hydrolysate was carefully neutralized (pH meter) with aqueous HCl and the neutral solution evaporated to dryness. The residue was suspended in water and the suspension extracted with ether. The ether was again washed with water, dried, and evaporated. In this way the free acids were recovered almost quantitatively. The mixture of acids was redissolved in dry ether (sodium wire) and methylated by the method of White, Baum, and Eitel,[30] using 1-methyl-3-*p*-tolyltriazene as methylating agent. After the reaction was finished, the ether solution was washed with 5 N HCl to remove *p*-toluidine. Traces of acid which had remained from this treatment were removed with Na_2CO_3. The ether solution was then repeatedly washed with water. A slight coloration was observed, which could be traced to the presence of condensation products of toluidine with thioxanthone (Schiff bases). The solution was dried with Na_2SO_4 and evaporated to dryness. The residue, a mixture of esters, was submitted to HPLC.

Analytic HPLC of the ester mixtures was carried out on a Hewlett-Packard chromatograph Type 1084B, using a Lichrosorb RP18 column, and a water–acetonitrile mixture as eluent. Figure 6 shows the trace obtained with an irradiated film of sensitized PCP worked up in the manner described. A nonirradiated film was subjected to the same treatment. Its HPLC trace is shown on the left-hand side of Figure 6.

The main peaks on the chromatogram were identified by comparison with authentic preparations: the broad peak at 7.91–7.96 min corresponds to the unreacted MeCP chromophore and thioxanthone, a small peak at 9.94 min is the cyclohexadiene **4**, the peak at 10.89–10.95 min is the tetraphenylbenzene **6**, the peak at 13.03–13.07 min is the octaphenylbiphenyl **7**, and the peak at 13.74–13.78 min belongs to a condensation product between toluidine and thioxanthone.

The four products **2**, **4**, **6**, and **7** were prepared in sufficient quantity to allow proper characterization.[2,3]

^{1}H and ^{13}C NMR measurements were made in $CDCl_3$ (or CD_3CN) solution, using JEOL FX100 or FX200 FT NMR instruments. In either case, digital resolution was 1.5 Hz/point and a sweep range of 240 ppm was used. ^{13}C chemical shifts were measured from the $CDCl_3$ signal (77.0 ppm) while ^{1}H spectra were referenced to Me_4Si. Assignments of carbon signals are based on comparison between calculated and observed shifts and in some cases on multiplicity. The NMR results are summarized in Table I.

References and Notes

(1) DeBoer, C. D.; Breslow, R. *Tetrahedron Lett.* **1967**, 1033.
(2) DeBoer, C. D.; Wadsworth, D. H.; Perkins, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 861.
(3) DeBoer, C. D. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 25.
(4) DeBoer, C. D. German Offen. 2027067 (Eastman Kodak Co.), Nov 4, 1971 (U.S. Appl., June 6, 1969).
(5) DeBoer, C. D.; Luckey, G. W. U.S. Patent 3677763 (Eastman Kodak Co.), July 18, 1972.
(6) Wadsworth, D. H.; Perkins, W. C. British Patent 1431904 (Eastman Kodak Co.), Apr 17, 1973.
(7) Parham, N. J. H.; Pitts, E.; Reiser, A. *Photogr. Sci. Eng.* **1977**, *21*, 14.
(8) Reiser, A.; Pitts, E. *J. Photogr. Sci.* **1981**, *29*, 187.

(9) Reiser, A.; Pitts, E. *Photogr. Sci. Eng.* **1976**, *20*, 225.
(10) Egerton, P. L.; Pitts, E.; Reiser, A. *Macromolecules* **1981**, *14*, 95.
(11) Reiser, A.; Egerton, P. L. *Photogr. Sci. Eng.* **1979**, *23*, 144.
(12) Giggino, K. P.; Roberts, A. J.; Phillips, D. *J. Phys. E.* **1980**, *13*, 476.
(13) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1969; Chapter 7.
(14) Martic, P. A.; Daly, R. C.; Williams, J. L. R.; Farid, S. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, 15, 295.
(15) Klöpffer, W. "Spektroskopie der Excimere und Exciplexe", Lecture Notes of Mainz University, 1978/1979.
(16) Padwa, A. In *Org. Photochem.* **1980**, *4*.
(17) Klöpffer, W. *J. Chem. Phys.* **1969**, *50*, 1689, 2337.
(18) Reiser, A.; Leyshon, L. J.; Saunders, D.; Mijovic, M. J.; Bright, A.; Bogie, J. *J. Am. Chem. Soc.* **1972**, *94*, 2414.
(19) Borkman, R. F.; Kearns, D. R. *J. Am. Chem. Soc.* **1966**, *88*, 3467.
(20) Lamola, A. A. In "Energy Transfer and Organic Photochemistry"; Lamola, A. A., Turro, N. J., Eds.; Interscience: New York, 1969; Chapter 2.
(21) Ferreira, J. A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 340.
(22) Farid, S. Y.; Daly, R. C. Eastman Kodak Research Laboratories, private communication, Mar 1982.
(23) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Methuen: London, 1963; Chapter 4.
(24) Reiser, A. *J. Chim. Phys.* **1980**, *77*, 469.
(25) Hatchard, G. C.; Parker, C. A. *Proc. R. Soc. London* **1956**, *235*, 518.
(26) Kurien, K. C. *J. Chem. Soc. B* **1971**, 2081.
(27) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* **1962**, *37*, 2413.
(28) Parker, C. A.; Rees, W. T. *Analyst (London)* **1960**, *85*, 587.
(29) Hackett, P. A.; Phillips, D. *J. Phys. Chem.* **1974**, *78*, 671.
(30) White, E. H.; Baum, A. A.; Eitel, D. E. "Organic Syntheses"; Wiley: New York, 1972; Vol. 4, p 797.

Exciplex Formation of *rac*- and *meso*-2,4-Di(*N*-carbazolyl)pentane with *m*-Dicyanobenzene. Model Systems for Fluorescence Quenching in Poly(*N*-vinylcarbazole)

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ABSTRACT: *N*-Isopropylcarbazole, *trans*-1,2-di(*N*-carbazolyl)cyclobutane, and the two diastereomers of 2,4-di(*N*-carbazolyl)pentane, model compounds for poly(*N*-vinylcarbazole), were quenched with *m*-dicyanobenzene. The fluorescence spectra of *N*-isopropylcarbazole and *trans*-1,2-di(*N*-carbazolyl)cyclobutane in the presence of *m*-dicyanobenzene show a new emission band with a maximum at 410 nm. This band was assigned to the emission of a normal exciplex. The fluorescence spectra of *meso*- and *rac*-2,4-di(*N*-carbazolyl)pentane, model compounds respectively for iso- and syndiotactic sequences in poly(*N*-vinylcarbazole), in the presence of *m*-dicyanobenzene both show a new emission band, with a maximum at 510 and 460 nm, respectively. These bands, more bathochromic than that of the normal exciplex, are assigned to the emission of a triple excited complex formed between the respective excimers and a *m*-dicyanobenzene acceptor molecule. The excimer formed by the meso compound (total spatial overlap of carbazole chromophores) has better donor properties than the excimer formed by the racemic compound (partial spatial overlap of the carbazole chromophores).

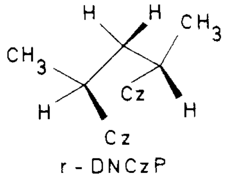
1. Introduction

Spectroscopic and kinetic studies of excited molecular aggregate systems in solution are among the most active fields of chemistry. Recently, there have been a number of reports concerning energy- and electron-transfer processes in micellar and polymer solutions, in biological cells, and in solid–liquid interfaces. For a detailed understanding, one should correlate the dynamics of these systems with the chromophore distribution and the configurational structure.

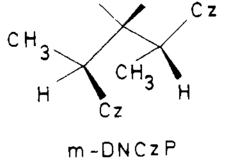
Studies on exciplexes with a structure (DDA)* composed of two donors and one acceptor and analogues $(D_nA_m)^*$ with higher aggregation number are necessary in addition to those of the normal exciplex (DA)*. Emission properties[1,2] and enhanced intersystem crossing[3] have been reported in a limited number of excited triple complexes (a complex, existing only in the excited state, consisting of three chromophores).

It has been pointed out that the fluorescence quenching of excited aromatic molecules and of their exciplexes obeys similar laws concerning a relation between quenching rate constant and free energy change due to electron transfer.[4] The polar electronic structure of the excited triple complex was directly confirmed by laser photolysis measurements. The absorption spectrum of the complex is reproduced by the superposition of bands of donor dimer cation and acceptor monomer anion.[5]

The occurrence of an excited triple complex was also suggested in quenching investigations of poly(*N*-vinylcarbazole) by dimethyl terephthalate.[6,7] In view of the structural inhomogeneity of poly(*N*-vinylcarbazole), adequate model systems for respective isotactic and syndiotactic sequences of this polymer were synthesized and their photophysical properties were reported.[8] *meso*-2,4-Di(*N*-carbazolyl)pentane (*meso*-DNCzP), the model for the isotactic sequence, gives the low-energy excimer, with total spatial overlap of the carbazole groups. *rac*-2,4-Di(*N*-carbazolyl)pentane (*rac*-DNCzP), the model for the syn-



r - DNCzP



m - DNCzP

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0024-9297/82/2215-1471$01.25/0