attributed to the greater main-chain flexibility of the polyacrylate series.

References and Notes

(1) Permanent address: Université de Rouen, Faculté des Sciences et des Techniques, 76130 Mont-Saint-Aignan, France.
(2) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 1405 (1970).
(3) I. Lukac, P. Hrdlovic, Z. Manasek, and D. Bellus, *J. Polym. Sci., Part A-1*, **9**, 69 (1971).
(4) K. P. Ghiggino, R. D. Wright, and D. Phillips, *Chem. Phys. Lett.*, **53**, 552 (1978).
(5) J. S. Aspler and J. E. Guillet, *Macromolecules*, **12**, 1082 (1979).
(6) Y. Nishijima, Y. Sasaki, M. Tsujisaki, and M. Yamamoto, *Rep. Prog. Polym. Phys. Jpn.*, **15**, 453 (1972).
(7) Y.-C. Wang and H. Morawetz, *Makromol. Chem., Suppl.*, **1**, 283 (1975).
(8) C. W. Frank and M. A. Gashgari, *Macromolecules*, **12**, 163 (1979).
(9) R. F. Ried and I. Soutar, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 231 (1978).
(10) D. A. Holden and J. E. Guillet, *Macromolecules*, **13**, 289 (1980).
(11) J. S. Aspler, C. E. Hoyle, and J. E. Guillet, *Macromolecules*, **11**, 925 (1978).
(12) A. Ueno and T. Osa, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 539 (1978).
(13) N. F. Pasch and S. E. Webber, *Macromolecules*, **11**, 727 (1978).
(14) R. B. Fox, T. R. Price, R. F. Cozzens, and W. H. Echols, *Macromolecules*, **7**, 937 (1974).
(15) Y. Amerik, Y. Y. Bairamov, and B. A. Krentsel, *Zh. Prikl. Spektrosk.*, **18**, 1023 (1973).
(16) M. Keyanpour-Rad, A. Ledwith, A. Hallam, A. M. North, M. Breton, C. Hoyle, and J. E. Guillet, *Macromolecules*, **11**, 1114 (1978).
(17) G. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(18) S. Kasman and A. Taurins, *Can. J. Chem.*, **34**, 1261 (1956).
(19) E. Selegny, L. Merle-Aubry, and N. Thoai, *Bull. Soc. Chim. Fr.*, 3166 (1967).
(20) W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 649 (1946).
(21) O. N. Witt and O. Braun, *Ber. Dtsch. Chem. Ges.*, **47**, 3216 (1914).
(22) M. Akram and R. D. Desai, *Proc. Indian Acad. Sci., Sect. A*, **11**, 149 (1940).
(23) K. Fries, *Ber. Dtsch. Chem. Ges.*, **54**, 711 (1921).
(24) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 864 (1934).
(25) K. Fries and K. Schimmelschmidt, *Ber. Dtsch. Chem. Ges.*, **58**, 2835 (1925).
(26) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966.
(27) D. F. Boltz, "Selected Topics in Modern Instrumental Analysis", Prentice-Hall, New York, 1952, p 150.
(28) T. Kilp, B. Houvenaghel-Defoort, W. Panning, and J. E. Guillet, *Rev. Sci. Instrum.*, **47**, 1496 (1976).
(29) T. Kilp and J. E. Guillet, *Macromolecules*, **10**, 90 (1977).
(30) J. L. Stratenus, Ph.D. Thesis, Leiden, 1966.
(31) D. Bellus, *Adv. Photochem.*, **8**, 109 (1971).
(32) Y. Ohto, H. Shizuka, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **47**, 1209 (1974).
(33) S.-K. L. Li and J. E. Guillet, *Macromolecules*, **10**, 840 (1977).
(34) B. Ranby and J. F. Rabek, "Photodegradation, Photooxidation and Photostabilization of Polymers", Wiley, New York, 1975.
(35) M. C. Shen and A. Eisenberg, *Rubber Chem. Technol.*, **43**, 95 (1970).
(36) A. M. North and I. Soutar, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1101 (1972).
(37) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1971.
(38) D. A. Holden, P. Y.-K. Wang, and J. E. Guillet, *Macromolecules*, **13**, 295 (1980).
(39) Y. Amerik and J. E. Guillet, *Macromolecules*, **4**, 375 (1971).
(40) H. C. Ng and J. E. Guillet, *Macromolecules*, **11**, 937 (1978).
(41) K. Sugita, T. Kilp, and J. E. Guillet, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1901 (1976).
(42) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.
(43) E. Dan, A. C. Somersall, and J. E. Guillet, *Macromolecules*, **6**, 228 (1973).
(44) P. J. Wagner, *Mol. Photochem.*, **3**, 169 (1971).
(45) N. Hadjichristidis and V. Desreux, *J. Macromol. Sci., Chem.*, **6**, 1227 (1972).
(46) K. G. Berdnikova, G. V. Tarasova, V. S. Shaska, N. A. Nikitiu, and G. V. Dyuzhev, *Vysokomol. Soedin.*, **6**, 2057 (1964).
(47) J. Brandrup and E. H. Immergut, Eds., "Handbook of Polymer Science", Wiley, New York, 1966. See ref 51 for a typical application.
(48) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter 14.
(49) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).
(50) V. E. Eskin and O. Z. Korotkina, *Vysokomol. Soedin.*, **2**, 272 (1960).
(51) G. Sitaramaiah and D. Jacobs, *Polymer*, **11**, 165 (1970).
(52) M. Kurata and W. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).
(53) T. L. Nemzek and J. E. Guillet, *Macromolecules*, **10**, 94 (1977).
(54) D. J. Angier, W. T. Chambers, and W. F. Watson, *J. Polym. Sci.*, **25**, 129 (1957).
(55) D. David, W. Demarteau, and G. Geuskens, *Polymer*, **10**, 21 (1969).
(56) G. Sanchez, Thesis, Université Louis-Pasteur de Strasbourg, 1975.

Laser Photolysis Studies of Excited-State Interactions of Poly(*N*-vinylcarbazole) and *N*-Isopropylcarbazole with Dimethyl Terephthalate

Uri Lachish, Robert W. Anderson, and David J. Williams*

Xerox Corporation, Webster Research Center, Webster, New York 14580.

Received December 26, 1979

ABSTRACT: The excited-state processes leading to exciplex formation and photoinduced electron transfer between excited poly(*N*-vinylcarbazole) (PVCz) and dimethyl terephthalate (DMT) and between its monomeric analogue *N*-isopropylcarbazole (NIPC) and DMT have been characterized by picosecond and nanosecond photolysis techniques. Comparison of absorption spectra of the transient species and their time evolution reveals the role of the specific polymeric environment on exciplex structure and dynamics. In toluene the absorption spectra in both the polymer and monomer systems indicate charge-transfer character in the exciplex state. However, the cation portion of the exciplex spectrum in the polymer is different from that in the monomer and indicates interaction of the carbazole cation with neighboring carbazole groups along the polymer chain. Exciplex decay in NIPC–DMT leads to enhancement of the NIPC triplet population while in the polymer system no triplet formation is observed. In dimethylformamide (DMF) dissociation to free ions is observed in both the polymer and monomer systems. Picosecond data indicate that molecular complexation is absent in PVCz–DMT prior to excitation and occurs by a diffusional process following excitation of the polymer.

The primary photophysical and photochemical processes in polymers have been the subject of intense interest in recent years. Structural features are often encountered in polymeric systems which alter the nature of excited-state processes and deactivation pathways. In poly(*N*-vinylcarbazole) (PVCz), the incorporation of the carbazole chromophore into the vinyl polymer chain leads to excited-state dynamics which are not observed in any of its monomer model compounds. The single-exponential fluorescence decay characteristic of carbazole monomers is not observed with PVCz at room temperature, but rather two red-shifted emission bands decaying with nonexponential and wavelength-dependent kinetics are observed. These observations were interpreted in terms of energy migration along the polymer chain and formation of two distinct excimer states in thermal interaction.[1]

Interactions between excited PVCz and a variety of small molecules were observed, leading to electron transfer[2,3] and exciplex formation.[4-6] The yield of electron transfer from photoexcited PVCz to *p*-dicyanobenzene (in a polar solvent) was found to be lower than that of the same process with monomeric *N*-ethylcarbazole as the donor.[2] The yield was found to be laser excitation intensity dependent in the polymer system but not in the monomer model system.[3] This dependence was attributed to excited-state annihilation within the polymer chain competing with electron transfer.

Quenching of PVCz* fluorescence by dimethyl terephthalate (DMT) and subsequent appearance of new red-shifted emission bands were observed by Yamamoto et al.[4] in nonpolar solutions and by Okamoto et al.[5] in films. These bands were interpreted in terms of exciplex formation between the excited carbazole chromophore and DMT. The fluorescence quenching in the PVCz–DMT system was compared to that in the model compound–ethylcarbazole (EtCz–DMT) system by Hoyle and Guillet.[7] Observing the exciplex emission decay by applying single-photon-counting techniques, they proposed a kinetic scheme whereby the exciplex formed between the excited carbazole chromophore and DMT further reacts with a nearby chromophore to yield a triple exciplex or exterplex of the form $[(\mathrm{Cz{-}Cz})^{+\cdot}\text{–}\mathrm{DMT}^{-\cdot}]^*$.

In order to evaluate the excited-state dynamics in the PVCz–DMT system we have applied picosecond and nanosecond laser photolysis techniques to observing the emission and absorption spectra of transient species and their time evolution. The results yield detailed information on the structure of the PVCz–DMT exciplex, on the dynamics of exciplex formation and decay, and of ionic dissociation and recombination processes. Similar measurements have been carried out with the monomer model compound *N*-isopropylcarbazole (NIPC–DMT) system and the specific effect of the polymeric environment on these processes is elucidated by comparing the results obtained with the two systems.

Experimental Section

Free radical polymerized PVCz was used for these experiments after purification by reprecipitation of a benzene solution of the polymer in methanol. Molecular weights determined by GPC gave values of $\bar{M}_n = 120\,000$ and $\bar{M}_w = 700\,000$. *N*-Isopropylcarbazole was purified by several recrystallizations from ethanol. Dimethyl terephthalate was purified by several recrystallizations from benzene. Toluene and dimethylformamide (DMF) were Burdick and Jackson "distilled-in-glass" spectroscopic solvents. Solutions were held in optical-grade quartz cells and were flushed with nitrogen prior to and during the measurements.

The pulsed N_2 laser photolysis system is similar to that described in ref 8. The energy density derived from the focused output of the exciting Molectron UV400 N_2 laser (8-ns fwhm, 337.1 nm) was about 55 mJ/cm^2 at the sample. The monitoring light source was a dc xenon 75-W lamp (Osram XB075); its brightness was increased 2 orders of magnitude by using a high-current pulser in parallel with the dc power supply. The exciting and monitoring lights were arranged in a collinear geometry, and the monitoring light transmitted through the sample was analyzed with a monochromator and photomultiplier connected to a fast oscilloscope.

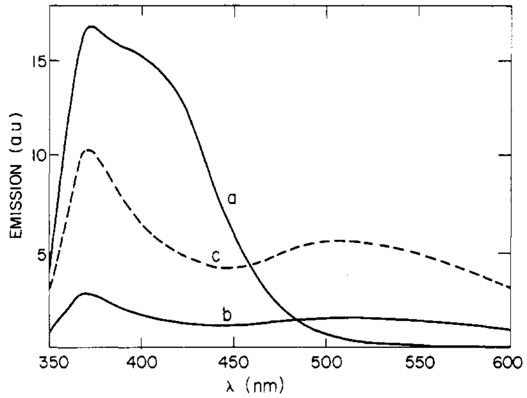

Figure 1. Fluorescence emission spectra of (a) 2.5 × 10^{-4} M PVCz in toluene, (b) 2.5 × 10^{-4} M PVCz + 0.07 M DMT in toluene (same sensitivity scale as a), and (c) 2.5 × 10^{-4} M PVCz + 0.07 M DMT in toluene (higher sensitivity scale than in b).

Since the present series of experiments involved measuring absorption transients with the same lifetime as that of the fluorescence emitted from the samples, it was essential to fine tune the system in such a way that the amount of fluorescence collected by the light detector was small compared to the amount of monitoring light, in order to avoid interference between them.

A mode-locked Nd^{3+}/glass laser system provided excitation and probe pulses for the picosecond photolysis experiments. Single laser pulses extracted from the train at 1064 nm had an energy of ~35 mJ after amplification and a width (fwhm) of 7 ± 2 ps. Second- and third-harmonic frequencies were generated in type-I and type-II KD*P crystals, respectively. In the picosecond photolysis system excitation is accomplished by focusing the laser third harmonic (355 nm) into an optically thin sample (1 mm). The probe pulse, a spectral continuum in the visible and near-infrared regions, is generated by focusing the 1064-nm pulse into a 2-cm cell of ethanol. Detection was accomplished with a Spex Model 1870 0.5-m spectrograph and a Princeton Applied Research optical multichannel analyzer. A detailed description of the apparatus and measurement technique is provided in ref 9.

Corrected fluorescence spectra were measured with a Perkin-Elmer Model MPF-44A spectrofluorimeter.

Results

The PVCz–DMT System. Figure 1 shows the fluorescence emission and emission quenching in the PVCz–DMT system. Figure 1a shows the corrected emission spectrum of 2.5 × 10^{-4} M PVCz in toluene excited at 337 nm. Figure 1b shows the emission spectrum of 2.5 × 10^{-4} M PVCz and 0.07 M DMT in toluene on the same sensitivity scale as Figure 1a, while Figure 1c shows the same spectrum on a more sensitivie scale (the excitation light is absorbed exclusively by the carbazole chromophore since DMT is transparent at this wavelength). It is seen that the PVCz ~420-nm emission band is completely quenched by DMT, while the 370-nm band is quenched to about 20% of its initial value and a new broad band appears at 510 nm. Similar results were reported in this system[4,6] and the new band was assigned to emission from an exciplex state formed between the excited carbazole chromophore and DMT.

Figure 2 shows the transient absorption spectrum in a toluene solution of 2.5 × 10^{-4} M PVCz and 0.14 M DMT obtained with the N_2 laser photolysis apparatus immediately following the decay of the exciting pulse (337.1 nm, 8 ns). The oscilloscope traces (inserts) show (a) the time dependence of the absorption signal at 530 nm and (b) the time dependence of the emission signal at 510 nm. Since the absorption and the emission signals decay with similar

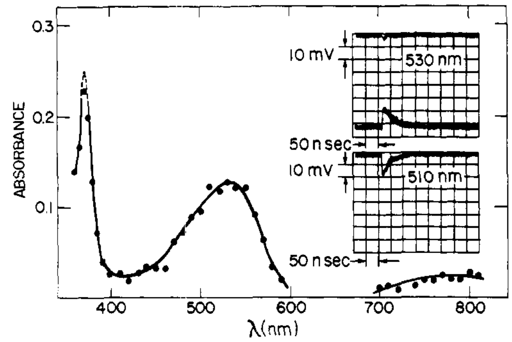

Figure 2. Transient absorption spectrum of 2.5 × 10^{-4} M PVCz + 0.14 M DMT in toluene immediately following the decay of the N_2 laser exciting pulse. Oscillograms of the 530-nm absorption and 510-nm emission decays are shown in the inserts.

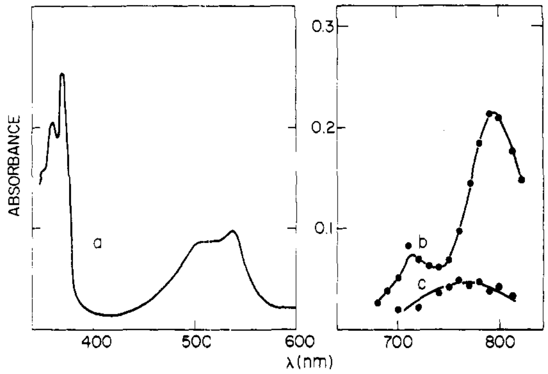

Figure 3. Absorption spectra of (a) the $DMT^{-}\cdot$ anion radical (data from ref 10), (b) the $NIPC^{+}\cdot$ cation radical (data from ref 3), and (c) the $PVCz^{+}\cdot$ cation radical (data from ref 3).

lifetimes ($\tau \sim$ 36 ns), it is reasonable to conclude that they originate from the same molecular excited state. Since the emission at 510 nm is assigned to the exciplex state formed between the excited PVCz donor and the DMT acceptor, the transient absorption spectrum (Figure 2) can most probably be assigned to the same state.

Figure 3a shows the absorption spectrum of the DMT anion radical ($DMT^{-}\cdot$) obtained by alkali metal reduction in THF (data obtained from ref 10). Figure 3 also shows the transient absorption spectra of $NIPC^{+}\cdot$ (Figure 3b) and $PVCz^{+}\cdot$ (Figure 3c) cation radicals obtained by photoinduced electron transfer to p-dicyanobenzene.[3] The exciplex spectrum shown in Figure 2 is seen to bear a close resemblance to the sum of the $DMT^{-}\cdot$ and $PVCz^{+}\cdot$ spectra, indicating the polar nature of the exciplex state.

Figure 4 shows the transient absorption spectrum of a DMF solution of 2.5 × 10^{-4} M PVCz and 0.14 M DMT obtained with the N_2 laser apparatus following the decay of the exciting pulse. The spectrum resembles that of the cation and anion radicals (Figure 3a,c) and that in toluene solution (Figure 2). However, in this polar solvent the lifetime of the absorbing species is 3 orders of magnitude longer than in toluene (nonpolar) solution. These results indicate that in polar solution the interaction between excited PVCz and DMT leads to photoinduced electron transfer and dissociation into free ions. Analysis of the absorption decay curve at 370 nm (the anion band, insert Figure 4) shows nearly exponential decay with a natural lifetime τ of 42 μs. Similar decay is observed at 790 nm (the cation band). Exciplex emission, if any, was too weak to be observed in the present experimental configuration.

In order to evaluate the ionic recombination mechanism in this system the transient absorption decay curve was remeasured and analyzed at 370 nm for 10^{-4} M PVCz and 0.14 M DMT in DMF solution (the lower PVCz concentration was selected for this measurement in order to achieve homogeneous excitation through the solution cell). In order to vary the concentration of ionic species the measurements were repeated with attenuated laser excitation intensities (the intensity was attenuated by glass filters up to 7% of its initial value). Each of them show nearly exponential decay with similar time constants. Since the initial excited-state concentration in the solution is roughly proportional to the excitation intensity, the meaning of these results is that the decay kinetics do not depend on the initial ionic concentration.

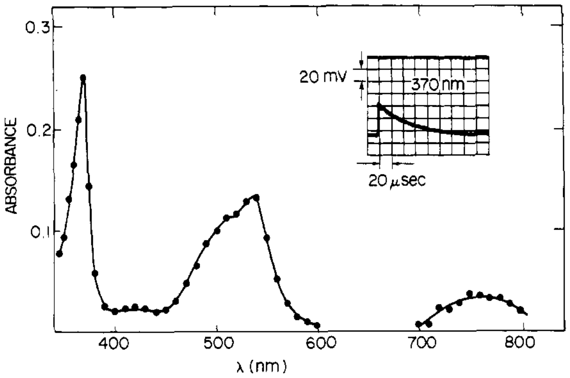

Figure 4. Transient absorption spectrum of 2.5 × 10^{-4} M PVCz + 0.14 M DMT in DMF immediately following the decay of the N_2 laser exciting pulse. An oscillogram of the 370-nm absorption decay is shown in the insert.

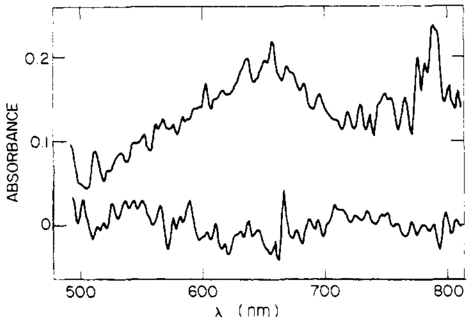

Figure 5. Transient absorption spectrum of 10^{-2} M PVCz in toluene observed with the picosecond photolysis apparatus at 10-ps delay from the excitation pulse.

In order to observe the formation of the exciplex state at the earliest possible times, picosecond laser photolysis measurements were performed. The transient absorption spectrum of a toluene solution of 10^{-2} M PVCz at 10-ps delay from the excitation pulse (7-ps fwhm, 354 nm) is shown in Figure 5. The same spectrum was obtained at longer delays up to 700 ps. The absorption bands at 650 and 790 nm are assigned to a state responsible for a red-shifted (with respect to NIPC) emitting species which has been termed the high-energy eximer state.[1] The formation of this state is indistinguishable from the convolution of the excitation and probe pulses and must occur on a subpicosecond time scale.[11]

Transient absorption spectra of a toluene solution of 10^{-2} M PVCz and 0.14 M DMT are shown in Figure 6. The spectra were obtained at (a) 10-, (b) 200-, and (c) 700-ps delays from the excitation pulse. The spectra exhibit a band at 530 nm which grows with time and a band at 650 nm decaying with time. The 700-ps spectrum is similar to that of $DMT^{-}\cdot$ (Figure 3a) and is therefore assigned to the exciplex state.

In order to monitor the dynamics of exciplex formation the absorption band at 530 nm was measured at a number of delay times following the excitation pulse. Comparison of Figures 5 and 6 indicates a considerable overlap of

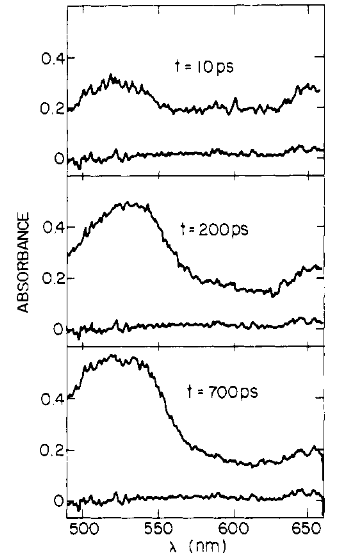

Figure 6. Transient absorption spectra of 10^{-2} M PVCz + 0.14 M DMT in toluene observed with the picosecond photolysis apparatus at 10-, 200-, and 700-ps delays from the excitation pulse.

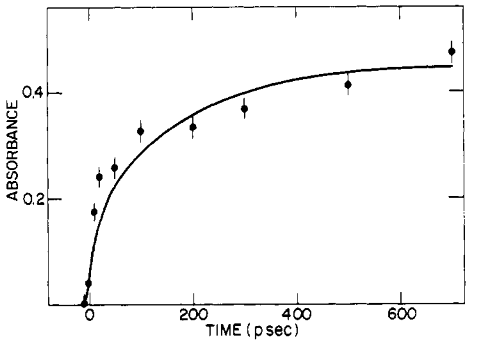

Figure 7. Corrected transient absorbance (see text) of the 530-nm band of 10^{-2} M PVCz + 0.14 M DMT in toluene as a function of delay from the picosecond excitation pulse.

$PVCz^*$ and $(PVCz^{+}\cdot{-}DMT^{-}\cdot)^*$ spectra at 530 nm. It was therefore necessary to correct for $PVCz^*$ absorbance by the following procedure. Let α denote the ratio of the optical density (OD) at 600 nm to that at 530 nm for $DMT^{-}\cdot$. Let β denote the same ratio for $PVCz^*$. From Figure 3a $\alpha = 0.24$ and from Figure 5 $\beta = 2.3$. The absorbance in the PVCz–DMT system can be expressed as

$$\mathrm{OD}(530\ \mathrm{nm}) = x + y \qquad (1)$$

$$\mathrm{OD}(600\ \mathrm{nm}) = \alpha x + \beta y \qquad (2)$$

where x and y are the $(PVCz^{+}\cdot{-}DMT^{-}\cdot)^*$ and $PVCz^*$ contributions to the absorbance, respectively. Substituting the values for α and β and solving eq 1 and 2 yield

$$x = 1.1[\mathrm{OD}(530)] - 0.47[\mathrm{OD}(600)] \qquad (3)$$

Thus the exciplex contribution to the 530-nm absorbance is expressed in terms of the overall absorbances of 530 and 600 nm. Figure 7 shows the buildup of the 530-nm-corrected exciplex absorption relative to the excitation pulse. The solid line was drawn according to the analysis given in the Discussion section.

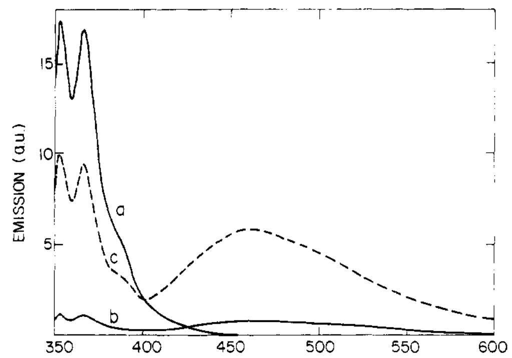

Figure 8. Fluorescence emission spectra of (a) 2.5 × 10^{-4} M NIPC in toluene, (b) 2.5 × 10^{-4} M NIPC + 0.07 M DMT in toluene (same sensitivity scale as a), and (c) 2.5 × 10^{-4} M NIPC + 0.07 M DMT in toluene (higher sensitivity scale than in b).

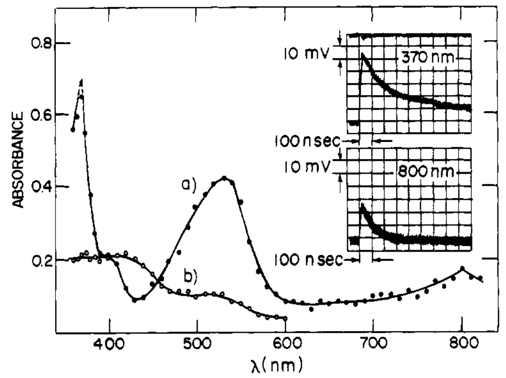

Figure 9. Transient absorption spectra of 2.5 × 10^{-4} M NIPC + 0.14 M DMT in toluene: (a) immediately following the decay of the N_2 laser excitation pulse; (b) at a 300-ns delay from the excitation pulse. Oscillograms of the 370- and 800-nm absorbance decays are shown in the inserts.

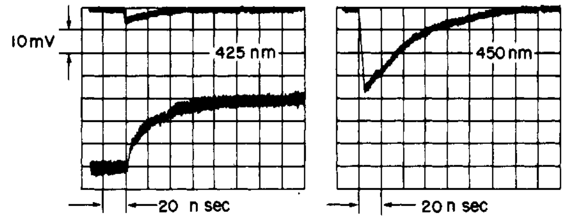

Figure 10. Oscillograms of (a) the 425-nm absorbance buildup and (b) the 450-nm emission decay following the N_2 laser excitation pusle in 2.5 × 10^{-4} M NIPC + 0.14 M DMT in toluene.

The NIPC–DMT System. Figure 8 shows the fluorescence emission and emission quenching in the NIPC–DMT system. Figure 8a shows the emission spectrum of 2.5 × 10^{-4} M NIPC in toluene excited at 337 nm. Figure 8b shows the emission spectrum of 2.5 × 10^{-4} M NIPC and 0.07 M DMT in toluene on the same sensitivity scale as Figure 8a, while Figure 8c shows the same spectrum on a more sensitive scale. It is seen that the typical emission spectrum of NIPC (355, 370 nm) is quenched by DMT and a new band appears with a maximum at 460 nm. As with the PVCz–DMT system this band has been assigned to emission from the exciplex formed between the excited NIPC donor and DMT acceptor.[7]

Figure 9 shows the transient absorption spectrum of a toluene solution of 2.5 × 10^{-4} M NIPC and 0.14 M DMT obtained with the N_2 laser photolysis apparatus (a) following the decay of the excitation pulse and (b) at a 300-ns delay. The inserts show oscilloscope traces of the absorption decay curves at 370 and 800 nm. The spectrum at the earlier time shows absorption peaks at 370, 540, and 790 nm. These peaks have decayed and disappeared after 300 ns while a new absorption peak which decays at a much slower rate is observed at 420 nm. The time dependence of the absorbance is illustrated in the oscilloscope traces. At 370 nm an initial fast decay is followed by a slow decay and at 800 nm only a fast decay is observed. The fast-decaying absorption spectrum is similar to the sum

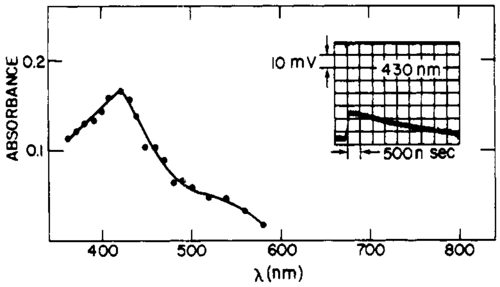

Figure 11. Transient absorption spectrum of 2.5×10^{-4} M NIPC in toluene immediately following the decay of the N_2 laser excitation pulse. An oscillogram of the 430-nm absorbance decay is shown in the insert.

of the NIPC$^{+}\cdot$ and DMT$^{-}\cdot$ spectra (Figure 3). The decay of the absorption peaks is similar to the exciplex emission decay (τ = 70 ns) so that the transient absorption spectrum can most probably be assigned to the exciplex.

Figure 10 shows oscilloscope traces of (a) the time evolution of the 425-nm absorbance on a fast time scale and (b) the decay of the emission at 450 nm on the same time scale (for the same solution as in Figure 9). It is seen that the buildup of the 425-nm absorption is similar to the emission decay, implying that this band belongs to a species which is mainly a product of the exciplex decay.

In order to identify the slowly decaying component of Figure 9b measurements were performed on NIPC solutions in the absence of DMT under the same experimental conditions. Figure 11 shows the transient absorption spectrum of a toluene solution of 2.5×10^{-4} M NIPC following excitation with the N_2 laser. An oscilloscope trace of the absorption decay at 430 nm is shown in the insert. The similarity to the triplet spectrum in ref 12 and the relatively long lifetime indicate that it is most probably due to the triplet state of NIPC. Since this spectrum is very similar to the slow-component absorption in the NIPC–DMT system (Figure 9b), the latter can also be identified as that of triplet NIPC. It should be noted that the triplet yield is higher in the NIPC–DMT system. These results suggest that in the NIPC–DMT system the triplet state is mainly a product of the exciplex decay.

Figure 12 shows the transient absorption spectrum of a DMF solution of 2.5×10^{-4} M NIPC and 0.14 M DMT (a) immediately following the decay of the N_2 laser excitation pulse and (b) at a delay of 100 μs. The initial absorbance resembles that of the sum of the DMT$^{-}\cdot$ and NIPC$^{+}\cdot$ spectra (Figure 3). The decay kinetics of these two species are different. The cation band (oscilloscope trace at 790 nm) is single exponential with a natural lifetime (τ = 10 μs), while the decay of the anion bands (oscilloscope trace at 370 nm) shows a similar initial decay followed by a second much slower process. After 100 μs (Figure 12b) the cation absorption completely disappears, while the anion absorption is still observed.

Discussion

The properties of exciplex systems have been extensively characterized in recent years. The exciplex state is usually described in terms of a charge-transfer complex between an acceptor and donor, one of which is electronically excited prior to complex formation.[13] The dynamics of exciplex decay may involve radiative and nonradiative deactivation, intersystem crossing to the triplet state, and ionic dissociation.[13-15] The results presented in this paper on the PVCz–DMT and NIPC–DMT exciplex systems are interpreted according to these general concepts of exciplex properties. In addition they illustrate the unique photophysical properties induced by the specific polymeric environment on the exciplex structure and dynamical processes.

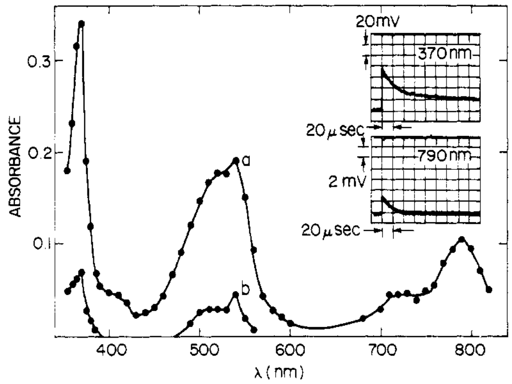

Figure 12. Transient absorption spectra of 2.5×10^{-4} M NIPC + 0.14 M DMT in DMF: (a) immediately following the decay of the N_2 laser excitation pulse; (b) at 100-μs delay from the excitation pulse. Oscillograms of the 370- and 790-nm absorbance decays are shown in the inserts.

Exciplex Structure in the Polymer vs. Monomer Systems. Exciplex formation between excited PVCz and DMT in toluene is manifested by quenching of the PVCz excimer fluorescence and appearance of a new broad-band emission at 510 nm (Figure 1). In the monomer system NIPC fluorescence is similarly quenched by DMT and a new broad-band emission appears at 460 nm (Figure 8). The transient absorption spectrum observed in each system with the laser photolysis apparatus (Figures 2 and 9) is equal to the sum of the corresponding PVCz$^{+}\cdot$ and DMT$^{-}\cdot$ or of the NIPC$^{+}\cdot$ and DMT$^{-}\cdot$ absorption spectra (Figure 3). These spectra were associated with the exciplex state by the similarity between the emission and absorption decay kinetics; they indicate that in these systems the exciplex is an excited charge transfer state.

However, there is a marked difference in the transient absorption and emission spectra between the two systems. The polymer exciplex emission is 50 nm red shifted compared to the monomer, and the PVCz$^{+}\cdot$ portion of the exciplex absorption is broad and much less intense than that of NIPC$^{+}\cdot$ (Figures 2, 3b,c, and 9). The difference was attributed[3] to interaction of the carbazole cation with nearby carbazole chromophores along the polymer chain, leading to charge delocalization. The emission red shift in the polymer system, indicating lowering of the exciplex energy levels, may be a result of this interaction. Similar structural features have been reported in the cation radicals of the cyclobutane dimer of *N*-vinylcarbazole[16] and the *N*-ethylcarbazole dimer cation.[2] Therefore it is reasonable to conclude that the relative carbazole ring conformation imposed by the polymer backbone is favorable for the delocalization of charge onto neighboring rings.

Hoyle and Guillet[7] recently proposed the existence of two emitting species in the PVCz–DMT system: an exciplex and an exterplex. The exterplex consists of two carbazole chromophores and one DMT [(Cz–Cz)$^{+}\cdot$–DMT$^{-}\cdot$]*. From time-correlated photon-counting experiments they concluded that the exterplex was formed by interaction between the bimolecular exciplex and a neighboring carbazole chromophore on a time scale of 20–50 ns. In such a case transition from initial cationic monomer-like absorption (i.e., that of NIPC$^{+}\cdot$) to cationic polymer absorption should have been observed in the PVCz–DMT exciplex system on this time scale. However, such a transition was not observed and the absorption was that of PVCz$^{+}\cdot$ at the earliest measurable time (8 ns), indicating that the cationic delocalization occurs on a much faster time scale.

The existence of triplet exciplexes consisting of two molecules of donor with one molecule of acceptor has been proposed to explain concentration-dependent red shifts in several instances.[17] A recent theoretical analysis[18] suggests that the sharing of positive charge in the (DDA)* structure leads to a more stable configuration than (DAD)*. The sharing of positive charge between rings is akin to the self-association stabilization of ion radical species with the neutral parent molecule[19] and can have important implications for the recombination mechanism.[20] This point is discussed below.

Exciplex Decay Mechanisms. Radiative deactivation by exciplex fluorescence (Figures 1 and 8) is observed for both the polymer and monomer systems and nonradiative decay is also a very probable deactivation pathway. However, the polymer system differs from its monomer analogue by the role of the triplet state in the decay mechanism of the exciplex state. In the NIPC–DMT toluene system the relatively long-lived triplet absorption is observed following the decay of the exciplex absorption bands (Figue 9), and since the triplet yield in this system is higher than in a NIPC (DMT free) system (Figure 11), the exciplex state must have an active role in triplet formation. Moreover, the fast oscilloscope traces (Figure 10) show gradual buildup of triplet absorption coinciding with the exciplex fluorescence decay, so in this system the triplet enhancement results mainly from exciplex decay.

In the polymer system triplet absorption is not observed. Neither exciplex decay (in donor–acceptor solutions) nor intersystem crossing from the singlet (also in acceptor-free solutions) produces an observable triplet spectrum. The reason for the absence of the triplet state is not clear, but several possibilities are apparent.[1] It is possible that the triplet is not formed at all, or if it is formed it may undergo rapid deactivation to the ground state by some efficient nonradiative process. It is also conceivable that the triplet spectrum may be broadened and lacks sufficient intensity to be observed under the present experimental conditions.

However, recent experiments on low molecular weight PVCz reveal that under similar excitation conditions the polymer (in a DMT-free solution) exhibits triplet-state absorption while the exciplex decay produces no observable triplets.[21] From this result we conclude that association of the cation with neighboring pendant groups in the polymer inhibits triplet formation and that loss of triplet through nonradiative deactivation is not a significant factor.

Exciplex Formation. Formation of the exciplex state by interaction between excited PVCz and DMT occurs on the picosecond time scale while its deactivation processes are observed to proceed in the nanosecond regime, so in analyzing the kinetic data on exciplex formation their effect can be neglected.

Exciplex formation in solution is generally regarded as being diffusion controlled. Recently, Chuang and Eisenthal[22] have shown that exciplex formation between anthracene and *N*,*N*-diethylaniline in solution is governed by a diffusional process which contains a time-dependent rate constant [$k(t)$]. The time dependence of the rate constants accounts for the establishment of local and bulk concentration gradients. Following their treatment[22] the solution of the formation rate equation with an instantaneous excitation pulse and uniform bulk absorption leads to

$$E(t) = E_\infty\left[1 - \exp\left(-\int_0^\infty k(t')\,\mathrm{d}t'\right)\right] \qquad (4)$$

where $E(t)$ is the exciplex concentration at time t, E is the concentration at long times (but before significant deactivation by radiative or nonradiative processes takes place), and $k(t')$ is the time-dependent rate constant which incorporates the diffusional parameters and time-dependent effects.

The analysis of the data in Figure 7 (the solid line) was conducted according to the treatment of ref 22. Namely, our data were fit to a modified version of eq 4 in which $k(t')$ takes the form of the time-dependent diffusion rate expression (eq 21 or ref 22) and with inclusion of the finite widths of the laser excitation pulse.

Several observations follow from this analysis. First, the inclusion of the transient nature of the diffusion process significantly improves the fit to the experimental data. However, it is not clear that this agreement is unique. In contrast a simple exponential build-up model provides a poor fit to the data by emphasizing either the early (0–50 ps) or late (50–700 ps) portions of the experiment. Finally, the observation of a fast buildup at very early times (0–20 ps) does not reflect an instantaneous event since the convolution of the 7-ps pulses exhibits an even steeper response in this time region. Thus we conclude that preexisting (ground state) complexes are not involved in this process.

Ionic Dissociation in a Polar Solvent. In a DMF polar solution the initial absorption spectra of the PVCz–DMT (Figure 4) and NIPC–DMT (Figure 12) systems are similar to those in toluene, namely, to those of the corresponding cations and anions. However, the ion lifetimes are 3 orders of magnitude longer and no emission is observed. These results indicate dissociation into free ions.

The effect of solvent polarity on the exciplex state was studied in detail for other exciplex systems.[13-15] It was found that the exciplex fluorescence was gradually red shifted and its yield was lowered by increasing the solvent polarity, and in highly polar solution it disappeared and complete ionic dissociation was observed. Thus the polar environment is stabilizing the ionic species and their back-recombination is slowed down.

There is a significant difference between the polymer and monomer systems in the recombination kinetics. In the PVCz–DMT system similar transient absorption decay kinetics are observed at the cation and anion bands. Each is nearly single exponential with the initial decay rate independent of the initial ionic concentration. These results indicate that the back-reaction proceeds by geminate-pair recombination rather than by a biomolecular reaction, since the rate of the latter process should have been proportional to the initial ion concentration.

In the NIPC–DMT system the anion and cation exhibit different decay kinetics. While the cation absorption decays with a single-component process, a fast decay followed by a slow one is observed in the anion bands. These results indicate that back electron transfer cannot be the simple geminate process observed in the polymer.

A possible explanation for these results is suggested by the well-known instability of the carbazole cation to oxidative coupling through the 3,3′ position of the carbazole ring.[23] If this reaction competes effectively with anion–cation recombination, the observed results would be expected (although, so far we have no direct confirmation for its occurrence in the present system). In view of the demonstrated association of cation with parent chromophore in the polymer chain it is significant that cation–anion recombination occurs in the polymer without a detectable level of side reactions. Restriction of motion with the chain due to steric constraints may not allow the chromophores to adopt the end-to-end conformation required for the oxidative coupling to occur.

Conclusions

The results presented in this study demonstrate the significant effect of the polymeric environment on the exciplex structure and excited-state dynamic processes. In particular spectral data suggest that charge delocalization between nearby chromophores in the polymer chain is an inherent feature of exciplex structure in the PVCz–DMT system. The intrachain ring interactions in the polymer system inhibit carbazole triplet formation resulting from exciplex deactivation and may also inhibit the oxidative coupling between polymeric carbazole cation radicals. We anticipate that incorporation of chromophores into a polymeric backbone may prove a useful method of controlling excited-state processes and directing them to preferred pathways.

Acknowledgment. We thank G. E. Johnson and A. Ledwith for helpful commments on the manuscript.

References and Notes

(1) W. Klopffer, *J. Chem. Phys.*, **50**, 2337 (1969); G. E. Johnson, *ibid.*, **62**, 4697 (1975).

(2) H. Masuhara, S. Owada, N. Mataga, A. Itaya, K. Okamoto, and S. Kusabayashi, *Chem. Phys. Lett.*, **59**, 188 (1978).

(3) U. Lachish, D. J. Williams, and R. W. Anderson, *Chem. Phys. Lett.*, **65**, 574 (1979).

(4) M. Yamamoto, K. Tanaka, T. Omiti, M. Ooka, and T. Nishijima, First Symposium on Charge Transfer Complexes, Nagoya, Japan, 1969, Preprints, p 105.

(5) K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 2613 (1973).

(6) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976); **50**, 22 (1977).

(7) C. E. Hoyle and J. E. Guillet, *Macromolecules*, **11**, 221 (1978); **12**, 956 (1979).

(8) C. R. Goldschmidt, M. Ottolenghi, and G. Stein, *Isr. J. Chem.*, 8, 29 (1970).

(9) R. W. Anderson, D. E. Damschen, G. W. Scott, and L. D. Tally, *J. Chem. Phys.*, **71**, 1134 (1979).

(10) T. Kowata and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **42**, 3352 (1969).

(11) R. W. Anderson, Uri Lachish, and D. J. Williams, to be submitted for publication.

(12) B. R. Henry and M. Kasha, *J. Chem. Phys.*, **47**, 3319 (1967).

(13) T. Forster in "The Exciplex", M. R. Gordon and W. R. Ware, Eds., Academic Press, New York, 1975, p 1.

(14) N. Orbach and M. Ottolenghi, ref 13, p 75; N. Mataga, *ibid.*, p 113.

(15) N. Mataga and M. Ottolenghi in "Molecular Association", Vol. 2, R. Foster, Ed., Academic Press, New York, 1979, p 1.

(16) S. Tagawa, S. Arai, M. Imamura, Y. Tabata, and K. Oshima, *Macromolecules*, **7**, 262 (1974).

(17) J. M. Pearson, S. R. Turner, and A. Ledwith, ref 15, p 79, and references therein; T. Mimura, M. Itoh, T. Ohta, and T. Okamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1665 (1977).

(18) R. A. Caldwell, D. Creed, and H. Ohta, *J. Am. Chem. Soc.*, **97**, 3246 (1975); D. Creed and R. A. Caldwell, *ibid.*, **96**, 7369 (1974); H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *ibid.*, **98**, 2002 (1976).

(19) A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **13**, 212 (1976).

(20) D. J. Freed and L. R. Faulkner, *J. Am. Chem. Soc.*, **94**, 4790 (1972).

(21) Uri Lachish and D. J. Williams, *Macromolecules*, **13**, 1322 (1980).

(22) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, **62**, 2213 (1975).

(23) J. F. Ambrose and R. F. Nelson, *J. Electrochem. Soc.*, **115**, 1159 (1968); P. Beresford, D. H. Iles, L. J. Kricka, and A. Ledwith, *J. Chem. Soc., Perkin Trans. 1*, 276 (1974).

Thermodynamics of Solutions of Poly(dimethylsiloxane). 1. Solutions of Poly(dimethylsiloxane) in Methyl Ethyl Ketone, Methyl Isobutyl Ketone, Ethyl *n*-Butyl Ketone, and Diisobutyl Ketone

Tomoo Shiomi, Zenichiro Izumi, Fumiyuki Hamada,* and Akio Nakajima

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received January 4, 1980*

ABSTRACT: Osmotic pressure, heats of mixing to infinite dilution, and volume changes on mixing were measured for mixtures of poly(dimethylsiloxane) with four solvents: methyl ethyl ketone, methyl isobutyl ketone, ethyl *n*-butyl ketone, and diisobutyl ketone. The expression for the combinatorial entropy of mixing, containing a correction for molecular bulkiness proposed by Prausnitz et al., was examined for these systems with comparatively small surface ratios, where the value of the correction term is large. The interaction parameters χ determined from osmotic pressure data were in agreement with theoretical values calculated according to Flory's new polymer solution theory; the exchange entropy parameter Q_{12} in the Flory theory, whose physical meaning is obscure, was not necessary. When the Flory–Huggins combinatorial entropy was used, a large value of Q_{12} was necessary to obtain agreement between the observed and calculated values of χ. The excess volume calculated from the Flory theory deviated considerably from the observed values in these systems.

Polymer solution theories based on the corresponding-states principle have successfully represented the thermodynamic properties of polymer solutions. These theories have enabled us to interpret the physical meaning of a lower critical solution temperature and to express volume changes on mixing. Patterson et al.[1,2] explained these phenomena on the basis of the Prigogine theory.[3,4] However, their theory, which employs a Lennard-Jones 6–12 potential, includes parameters difficult to determine and hence has a limitation in comparison with experiments for polymer solutions. The Flory theory[5,6] is expressed by such measurable parameters as thermal expansivities and thermal pressure coefficients. Therefore, the Flory theory has been applied to many polymer solutions.

Although the Flory theory can reproduce thermodynamic properties of polymer solutions, there remain some problems. One of them is the exchange entropy parameter Q_{12}.[7] This parameter is related only to the interaction

0024-9297/80/2213-1149$01.00/0 © 1980 American Chemical Society