extending the experiment to Θ-solvent conditions, where it should give information on the relative importance of intrachain and interchain entanglements on chain motions.

One of the main limitations of the experiment comes from the fact that, for chemical reasons, we are not able to synthesize labeled molecules of very large molecular weight. We then have to work at rather large polymer concentrations. This could be questionable for the polystyrene–benzene system, as the proximity of the glass transition temperature could introduce additional contributions not taken into account in the scaling approach. Additional experiments on polyisobutylene, for which T_g is very low, could allow a test of that point.

Our experiments demonstrate the originality of the forced Rayleigh scattering technique. In the case of entangled polymer solutions, it gives information on physical properties completely different from those deduced from ordinary quasi-elastic Rayleigh light scattering. The latter technique is sensitive to monomer concentration fluctuations, i.e., to cooperative motions of the chains, while FRS is sensitive to individual chain motions. It is a quite interesting tool in the study of entangled polymer chains since it allows one (i) to measure dynamical properties at mechanical equilibrium and (ii) to specifically follow one of the components in mixed systems.

References and Notes

(1) Daoud, M., et al. *Macromolecules* **1975**, *8*, 804.
(2) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979; Chapter III.
(3) de Gennes, P. G. *Macromolecules* **1976**, *9*, 594.
(4) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(5) Destor, G.; Rondelez, F. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 527.
(6) Munch, J. P., et al. *J. Phys. (Paris)* **1977**, *38*, 971.
(7) Pouyet, G., et al. *Macromolecules* **1980**, *13*, 176.
(8) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(9) Vidakovic, P.; Allain, C.; Rondelez, F. *J. Phys. (Paris), Lett.* **1981**, *42*, 323.
(10) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979; Chapter VIII.
(11) Hervet, H.; Léger, L.; Rondelez, F. *Phys. Rev. Lett.* **1979**, *42*, 1681.
(12) Hervet, H.; Urbach, W.; Rondelez, F. *J. Chem. Phys.* **1978**, *68*, 2725.
(13) *Tech. Chem. (N.Y.)* **1971**, *3*, Chapter II.
(14) "Handbook of Lasers"; CRC Press: Cleveland, Ohio, 1971; p 557.
(15) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(16) Klein, J. *Macromolecules* **1978**, *11*, 852.
(17) Daoud, M.; de Gennes, P. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(18) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.
(19) Bueche, F. *J. Chem. Phys.* **1968**, *48*, 1410.
(20) Kumagai, Y.; Watanabe, H.; Miyasaka, K.; Hata, T. *J. Chem. Eng. Jpn.* **1979**, *12*, 1.
(21) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A* **1979**, *365*, 53.
(22) Tanner, J. E. *Macromolecules* **1971**, *4*, 748.
(23) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*.
(24) Adam, M.; Delsanti, M. *J. Phys. (Paris), Lett.* **1979**, *40*, L-523.
(25) Onogi, S., et al. *J. Polym. Sci., Part C* **1966**, *15*, 381.
(26) Berry, G. C.; Nakayasu, H.; Fox, T. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1825.
(27) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 55.
(28) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(29) Klein, J. *Macromolecules* **1981**, *14*, 460.

Laser Photochemistry of Polymers Having 1,2-*trans*-Dicarbazolylcyclobutane Groups in Solution

Hiroshi Masuhara,* Hiroshi Shioyama, and Noboru Mataga

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Takashi Inoue, Noboru Kitamura, Toshio Tanabe, and Shigeo Tazuke

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan. *Received March 11, 1981*

ABSTRACT: Transient absorption spectra of polyurethanes, a polyacrylate, and a polymethacrylate having 1,2-*trans*-dicarbazolylcyclobutane groups were measured by a microcomputer-controlled N_2 gas laser photolysis system. The triplet–triplet absorption intensity of these polymers is weak compared to that of the monomer reference compound. Examining various possibilities, it is concluded that the intrapolymer S_1–S_1 annihilation is a main factor leading to this polymer effect. The excited polymers quenched by dimethyl terephthalate dissociate into ion radicals whose yields are related to the polymer structure. This ionic photodissociation of the polyurethane results in formation of a transient polyelectrolyte in organic solvents.

Introduction

Recently, primary photoprocesses of molecularly associated systems in solution have been studied in detail, revealing that their behavior is sometimes different from that of dilute homogeneous solutions. These results are worth studying since most practical systems with technical and biological importance involve the photoprocesses of molecular aggregate, membrane, microemulsion, micelle, and polymer systems. It is well-known that the photoprocesses in photosynthesis, vision, and biological clocks are coupled to their protein structural change. The photoinduced charge separation in solar cells, photoconductors, and photoimaging materials is the essential primary process for their operation.

In relation to the mechanisms of the above phenomena, we have investigated by laser photolysis the primary photoprocesses of polymers with pendant aromatic groups in solution.[1-5] Interesting dynamic behavior characteristic of the polymers has been observed, summarized as follows:[2,4,5] (1) Intense laser excitation produces several fluorescent chromophores in one polymer chain and their mutual interaction leads to efficient intrapolymer S_1–S_1 annihilation. (2) The addition of an electron acceptor converts more than one fluorescent chromophore into an

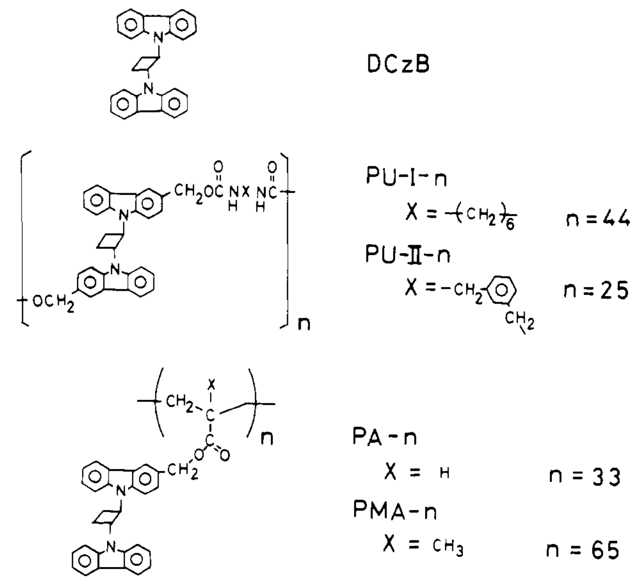

Figure 1. Molecular structures and abbreviations of the polymers. The notation *n* represents the mean degree of polymerization.

ion radical, resulting in the formation of a transient polyelectrolyte. (3) The yield of ionic photodissociation of polymers quenched by an electron donor or acceptor decreases as the mean degree of polymerization increases. (4) The absorption spectra of a polymer cation and their decay dynamics are different from those of its monomeric model compound.

The above results have been obtained in the case of poly(*N*-vinylcarbazole) (abbreviated hereafter as PVCz)[1-3,5] and polyesters having 1-pyrenyl groups.[4] Since these polymers show intrapolymer excimer emission, the dynamics obtained may be caused by the specificity of the polymer structure or by excimer formation. In order to exclude the latter factor, we have studied in the present work polyurethanes, a polyacrylate, and a polymethacrylate having 1,2-*trans*-dicarbazolylcyclobutane (DCzB) groups. These polymers have the same carbazole chromophore, but no excimer emission is observed.

Experimental Section

Molecular structures and abbreviations for the compounds used here are given in Figure 1. The preparation and purification methods are reported elsewhere.[6a] The molecular weights of the polyurethanes and other polymers were determined by VPO and GPC methods, respectively. Dimethyl terephthalate (DMTP) was the same as used previously.[5] *N*,*N*-Dimethylformamide (Dotaito, spectrograde) was purified by fractional distillation. All of the solutions were degassed by flushing with N_2 gas and were measured at room temperature.

Since the details of the absorption and emission spectra of the present new polymers will be published elsewhere,[6b] we summarize their characteristics which are indispensable for understanding the present laser photolysis results. The absorption band shape of the carbazole chromophore is almost the same as that of *N*-ethylcarbazole (ECz) and is independent of the polymer structure. The extinction coefficient of the DCzB unit is 7000 ± 700 at the longest wavelength band (344 ± 2 nm). The fluorescence spectra show vibrational structure which satisfies the mirror-symmetry relation, and the sandwich-type excimer and the so-called second excimer, which are observed for PVCz,[7] are not detected. These results indicate that there is no appreciable interaction between carbazole chromophores in both ground and fluorescent states.

The transient absorption spectra were measured by using a microcomputer-controlled N_2 gas laser photolysis system.[8] The excitation power focused on the sample cuvette is 0.7 mJ and the pulse width is 8 ns. The optical arrangement of the system was carefully set up so that a linear relation between transient absorbance and excitation intensity held. This was confirmed by examining an excitation intensity dependence of the triplet–triplet (T–T) absorption band of phenanthrene in methylcyclohexane.

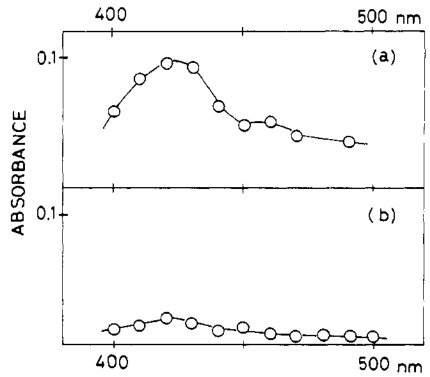

Figure 2. Transient absorption spectra of DCzB (a) and PU-I-44 (b) in *N*,*N*-dimethylformamide. The delay time is 500 ns.

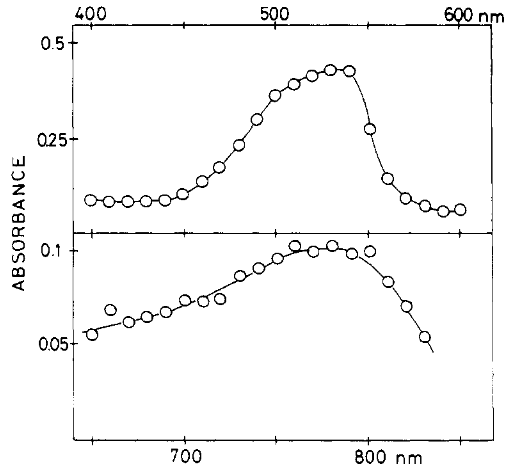

Figure 3. Transient absorption spectra of the DCzB–DMTP system in *N*,*N*-dimethylformamide. The delay time is 400 ns.

Results

Transient Absorption Spectra of Quencher-Free Systems. Laser photolysis was performed by adjusting the absorbance of the carbazole chromophore at 337 nm to about 1.0 at a 1-cm path length. The mean concentration of the carbazole unit was 3.4×10^{-4} M, indicating that there is no interaction between the polymers. As shown in Figure 2, the absorption spectra of DCzB in *N*,*N*-dimethylformamide, obtained at 500 ns after excitation, show a peak at 420 nm and a tailing to 500 nm. Since this band shape, its solvent dependence, and O_2 effect are quite similar to those of the T–T absorption band of ECz,[5] the present spectra are assigned to the triplet state of the carbazole chromophore. In the case of PU-I-44, the absorption intensity decreased to less than 20% of the level of the DCzB system, which was the same for all the polymers used here.

Transient Absorption Spectra of Systems Containing Quenchers. The absorbance of the carbazole chromophore at 337 nm was adjusted to 1.7 at a 1-cm path length, which corresponds to a mean chromophore concentration of 5.7×10^{-4} M. The concentration of DMTP was 0.26 M, which is just below saturation at room temperature. The transient absorption spectra of the DCzB–DMTP system in *N*,*N*-dimethylformamide are given in Figure 3. The band in the short-wavelength region is due to the DMTP anion,[5] while the weak broad band is ascribed to the DCzB cation.[9] This result indicates that ionic dissociation to the donor cation and the acceptor anion is

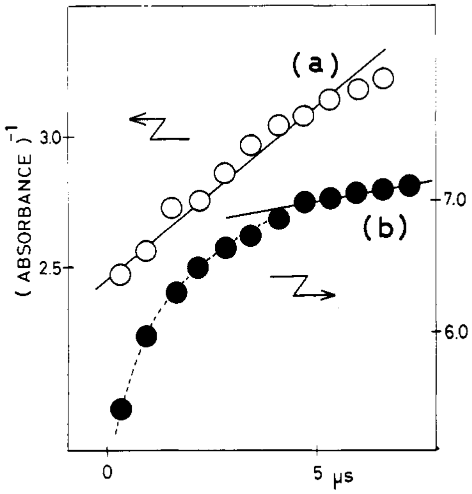

Figure 4. Second-order decay plot of DMTP anion: (a) the PU-I-44–DMTP system; (b) the PMA-65–DMTP system.

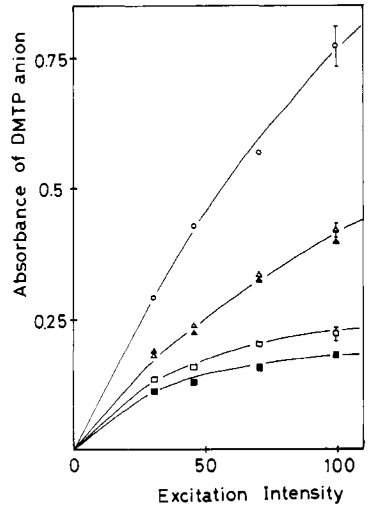

Figure 5. Excitation intensity effect upon absorbance of the dissociated DMTP anion. The systems are DCzB-DMTP (○), PU-I-44-DMTP (△), PU-II-25-DMTP (▲), PA-33-DMTP (□), and PMA-65-DMTP (■). The excitation intensity 100 corresponds to ~2 × 10^{16} photons cm^{-2}.

induced by interaction between the excited carbazole chromophore and DMTP. The same absorption spectra were observed for all the polymers quenched by DMTP; however, their intensity was weak compared to that of the DCzB-DMTP system.

Decay Dynamics of Ions Produced. Dissociated ion radicals of the relevant *N*-ethylcarbazole-DMTP system recombined with each other, showing second-order decay kinetics, while the decay of the cation was faster than that of the anion in the DCzB-DMTP system. This difference is considered to be due to the decomposition of the DCzB cation by a mechanism similar to the radiation-induced cycloconversion of tetraphenylcyclobutane.[10] The second-order decay process of DMTP anion is common to all the present systems except one. The PMA-65 system gives a fast component in addition to normal homogeneous recombination, which is shown in Figure 4.

Excitation Intensity Dependence of Formation of Ions. This was examined by plotting the DMTP anion absorbance at 530 nm, obtained by extrapolating the decay curve to zero, against the excitation intensity. The DCzB system gave an almost linear relationship, while the saturation tendency increased in the following order: PU-I-44 ~ PU-II-25 < PA-33 < PMA-65, as shown in Figure 5.

Table I
Excitation Intensity Effect upon Fluorescence Quenching Efficiency in *N,N*-Dimethylformamide

sample	Q_s,[a] %	Q_l,[b] %
DCzB	98	96
PU-I-44	98	92
PU-II-25	98	87
PA-33	97	88
PMA-65	98	86

[a] Q_s is the value obtained by the Aminco-Bowman spectrophotofluorometer. The excitation wavelength is 340 nm. [b] Q_l is the value obtained by exciting with the 337-nm pulse of the N_2 gas laser (2 × 10^{16} photons cm^{-2}). Concentration of DMTP quencher is 0.26 M.

Table II
Ionic Photodissociation of DCzB and Related Polymer Systems in *N,N*-Dimethylformamide

sample	ϕ_{ion}[a]	N_{ion}[b]
DCzB	0.71	0.2
PU-I-44	0.46	~6
PU-II-25	0.44	~3
PA-33	0.37	~2
PM-65	0.26	~3

[a] Quantum yield of ionic photodissociation obtained under a relative excitation intensity of 31. See text and Figure 5. [b] The number of ionized chromophores per polymer chain, obtained as [DMTP$^-$]/[polymer]. Since the absorption intensity of the DCzB cation is weak, the DMTP counteranion band was used. The relative excitation intensity is 100. See Figure 5.

Effect of Excitation Intensity on Fluorescence Quenching Efficiency. We examined the relationship between excitation intensity and fluorescence quenching efficiency, Q, defined as $(F_0 - F)/F_0$, where F and F_0 represent fluorescence intensity with and without DMTP, respectively. The efficiencies Q_s and Q_l, corresponding to the values obtained by exciting with steady light and laser pulse, respectively, are listed in Table I. It is worth noting that Q_s is equal to or larger than Q_l.

Quantum Yields of Ionic Photodissociation. Ionic photodissociation yields of the present systems were obtained by comparing the absorption intensity of the DMTP anion and the T-T transition of phenanthrene in methylcyclohexane. The equation is as follows:

$$\phi_{ion} = (\epsilon_{T-T}/\epsilon_{ion})(OD_{ion}/OD_{T-T})\phi_{isc}$$

Here ϕ_{ion} and ϕ_{isc} are the quantum yields of ionic dissociation and intersystem crossing of the reference phenanthrene, respectively. Molecular extinction coefficients ϵ_{T-T} and ϵ_{ion} are 24000 ± 2000 M^{-1} cm^{-1} at 480 nm[11] and 17000 M^{-1} cm^{-1} at 530 nm.[12] OD is the absorbance at the corresponding wavelength, and ϕ_{isc} is 0.7 ± 0.12.[11] In this equation it is assumed that the distribution of the excited singlet state is common to all systems. The results are listed in Table II, where excitation intensity is adjusted to 31% of that of the normal photolysis condition (see Figure 5). The yield decreases in the following order: DCzB > PU-I-44 ~ PU-II-25 > PA-33 > PMA-65. The number of ionized chromophores per polymer chain is calculated and given in this table. It is worth noting that 6 DCzB units of PU-I-44 are converted into cation radicals by the N_2 laser excitation. This indicates that a kind of transient polyelectrolyte with a lifetime of tens of microseconds is formed in neutral organic solvents.

Discussion

Polymer Effect on the T-T Absorption Intensity. The absorption spectrum and the intensity of the triplet state of the DCzB system is almost the same as that of

N-ethylcarbazole. Therefore the decrease of intensity in polymer systems is considered as inherent to the polymer. In the following discussion we examine some possible mechanisms.

1. Chemical impurities bound to the polymer chain may quench the excited state of the carbazole chromophore. Inspection of the preparative methods of these polymers convinces us that the possibility of such contamination is marginal.[6a] This is also supported by the fact that different types of polymers give the same effect.

2. A change in the T–T absorption band shape may lead to an apparent decrease in the triplet yield. Broadening and shifting of the T–T band is expected when chromophores attached to a polymer associate with each other. It is concluded from an examination of various aromatic liquids and crystals that the spectral change from dilute solutions to aggregates is small and does not explain the distinct polymer effect observed in this study.

3. An efficient S_1–S_1 annihilation leads to a decrease in the excited singlet state was observed in the case of the PVCz system excited with the second harmonic of a Q-switched ruby laser.[5] The present polymer systems may involve a similar process which results in the reduced formation of the triplet state.

4. The T–T annihilation process may also lower the concentration of the triplet state. However, it is difficult to assume that this deactivation process operates without S_1–S_1 annihilation, since the latter is considered to be due to Förster's long-range dipole–dipole coupling interaction. Furthermore, we cannot observe any rapid decay of the T–T absorption band within our time resolution.

We consider that the present polymer effect upon the T–T absorption intensity is due to the third mechanism. The concentration of the excited singlet carbazole can be estimated by using the T–T absorbance, the extinction coefficient of this transition, and the intersystem crossing yield. It was assumed that the latter two values of DCzB are the same as those of carbazole.[14] The calculated concentration indicates that about half of the DCzB units are effectively excited during a pulse irradiation, which means that several excited chromophores are produced in one polymer molecule. The resulting excited state is expected to migrate along the chain due to the Förster-type long-range energy transfer. The critical transfer distance of this process is calculated to be 21.34 Å for *N*-methylcarbazole,[15] which is larger than the mean distance between the carbazole chromophores of the present polymers. Owing to efficient energy migration, the fluorescent states interact with each other, leading to the S_1–S_1 annihilation.

This S_1–S_1 process may compete with electron transfer quenching if one adds DMTP to the polymer solutions. The quenching efficiency should depend upon excitation intensity, of which the S_1–S_1 process is a function. As shown in Table I, the Q_s and Q_l values are identical within experimental error in the case of the DCzB–DMTP system, while $Q_s > Q_l$ is observed in the polymer system. It was confirmed that this inequality is consistent with the S_1–S_1 annihilation process.[5] Therefore we have come to the conclusion that the polymer effect on the T–T absorption intensity is caused by intrapolymer S_1–S_1 annihilation.

Polymer Effect on Ionic Photodissociation. We have been studying ionic photodissociation of typical electron donor–electron acceptor systems in solution and have proposed a simple but general mechanism.[16] The electron transfer quenching leads to formation of a transient ionic complex whose electronic structure is extremely polar, and solvent reorientation around it is not complete. In this complex, the dissociation to the solvent-shared ion pair and radiationless transition to the neutral ground state compete with each other. The ionic photodissociation yield is given by

$$\phi_{\text{ion}} = k_d/(k_d + k_n)$$

where k_d and k_n are the rate constants of the dissociation and deactivation processes, respectively. It was considered that k_n is related to the electronic structure of the transient ionic complex and k_d depends on solvent properties.

This concept of ionic photodissociation is applied to the present results on polymer–DMTP systems. Whereas k_n is considered to be insensitive to these polymer structures, the k_d value may be reduced by the low micropolarity and high microviscosity around the transient ionic complex compared to the monomer reference system.[17] In the case of the PU-I-44 and PU-II-25 systems, the mean distance of the DCzB unit is rather large and the reorientational motion of the solvent molecules may occur easily. However, since the DCzB units of the PA-33 and PMA-65 systems are rather crowded, solvent reorientation may be hindered. Therefore k_d will decrease in the following order: DCzB > PU-I-44 ~ PU-II-25 > PA-33 > PMA-65, which is in accordance with the results listed in Table II.

In addition to the above competing processes of dissociation and deactivation in the transient ionic complex, we must consider the fate of the solvent-shared ion pair. Under the conditions of high microviscosity and low micropolarity, the contribution of geminate recombination should be considered along with the rapid solvation to free ions. This recombination is another main factor decreasing the dissociation yield. Actually, we have observed a rapid decay of DMTP anion in the PMA-65-DMTP system.

Comparisons with Results on PVCz Systems. The results we obtained from PVCz systems in solution were similar to the present ones.[1-3,5] However, the contribution of two kinds of excimer state in the PVCz systems did not permit the simple and direct explanation given in this paper. The unknown intersystem crossing yield from both excimer states indicated the possibility that the reduced triplet yield of the PVCz systems is due not only to the intrapolymer S_1–S_1 annihilation but also to the low value of intersystem crossing from excimer states. It was considered that the quenching of excimer states leads to the triple complex formation of $D_2^+A^-$ and an increase in the k_n value. Therefore both k_d and k_n of the PVCz systems are affected by polymer structure, and their explanation was complicated. However, since no excimer emission is observed in the present polymer systems, it is concluded unambiguously that the observed polymer effects have nothing to do with excimer states of polymers but consist of general effects arising from chromophore aggregation.

Laser-Induced Formation of a Transient Polyelectrolyte. In Table II, the number of ionized DCzB units per polymer chain is given. It is rather large in the case of PU-I-44, where the conversion efficiency from neutral to ionized DCzB units of the latter compound is about 13%. This indicates that a polyelectrolyte with a lifetime of tens of microseconds is produced by intense pulse excitation. This is the second example of this particular behavior which was first reported for PVCz.[2,5] In a previous paper,[5] we showed that the laser-induced formation of a polyelectrolyte is observed in the case of polymers satisfying the following conditions: (1) the absorption cross section of the chromophore attached to the polymer chain at the excitation wavelength is large; (2) energy migration between chromophores is low; (3) the solvation to free ions is very rapid; and (4) any radiationless transitions other than ionic dissociation occur with a small rate constant. Conditions 1 and 4 are functions of the chromophores used, while conditions 2 and 3 are related to the polymer structure. The carbazole chromophore satisfies the former conditions to some extent, and the present polyurethane has a suitable structure for the latter conditions. Therefore, the conversion efficiency of PU-I-44 is higher than that of PVCz-394 under almost the same experimental conditions.[2]

Acknowledgment. The cost of the present investigation was partly defrayed by the Matsunaga Science Foundation and a Grant-in-Aid from the Ministry of Education, Culture, and Science of Japan.

References and Notes

(1) Masuhara, H.; Ohwada, S.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *Chem. Phys. Lett.* **1978**, *59*, 188.

(2) Masuhara, H.; Ohwada, S.; Yamamoto, K.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *Chem. Phys. Lett.* **1980**, *70*, 276.

(3) Masuhara, H.; Ohwada, S.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *Kobunshi Ronbunshu* **1980**, *37*, 275.

(4) Masuhara, H.; Ohwada, S.; Mataga, N.; Sato, K.; Tazuke, S. *Photochem. Photobiol.* **1980**, *32*, 9.

(5) Masuhara, H.; Ohwada, S.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *J. Phys. Chem.* **1980**, *84*, 2363.

(6) (a) Tazuke, S.; Inoue, T.; Tanabe, T.; Hirota, S.; Saito, S. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 11. (b) Kitamura, N.; Inoue, T.; Tazuke, S. *Polym. Prepr. Jpn.* **1980**, *30*, 1348.

(7) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697. Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082.

(8) Yasoshima, S.; Masuhara, H.; Mataga, N.; Suzaki, H.; Uchida, T.; Minami, S. *J. Spectrosc. Soc. Jpn.* **1981**, *30*, 93.

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

(10) Takamuku, S.; Kigawa, H.; Miki, S.; Sakurai, H. *Chem. Lett.* **1979**, 797.

(11) Bowers, P. G.; Porter, G. *Proc. R. Soc. London, Ser. A* **1967**, *299*, 348.

(12) Private communication from M. Yamamoto (Kyoto University) (1976).

(13) Ohno, T.; Kato, S. *Chem. Lett.* **1976**, 263. Higuchi, M.; Nakayama, T.; Itoh, N. *J. Phys. Soc. Jpn.* **1976**, *40*, 250. Morris, J. M.; Yoshihara, K. *Mol. Phys.*, **1978**, *36*, 993.

(14) Brinen, J. S. In "Molecular Luminescence"; Lim, E. C., Ed.; W. A. Benjamin: New York, 1969; p 333. Griffin, R. N. *Photochem. Photobiol.* **1968**, *7*, 175.

(15) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973; p 207.

(16) Masuhara, H.; Hino, T.; Mataga, N. *J. Phys. Chem.* **1975**, *79*, 994. Hino, T.; Akazawa, H.; Masuhara, H.; Mataga, N. *Ibid.* **1976**, *80*, 33. Masuhara, H.; Saito, T.; Maeda, Y.; Mataga, N. *J. Mol. Struct.* **1978**, *47*, 243. Hinatu, J.; Yoshida, F.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1978**, *59*, 80.; Masuhara, H.; Mataga, N. *Acc. Chem. Res.*, in press.

(17) Tazuke, S.; Matsuyama, Y. *Macromolecules* **1975**, *8*, 280. Tazuke, S.; Sato, K.; Bamba, F. *Ibid.* **1977**, *10*, 1224. Huan, H. L.; Tazuke, S.; Sato, K. *Polym. Prepr. Jpn.* **1980**, *29*, 1329. Iwaya, Y.; Tazuke, S. *Ibid.* **1979**, *28*, 1334.

Functionalized Polyionenes. 2. Absorption and Fluorescence Properties of a Polyionene and Relevant Model Compounds Bearing (9-Anthryl)methyl Groups

Yasuzo Suzuki*

Research Institute for Polymers and Textiles, 1-1-4 Higashi, Yatabe-cho, Tukuba-gun, Ibaragi 305, Japan

Shigeo Tazuke

Research Laboratory of Utilization, Tokyo Institute of Technology, 4259, Nagastuta, Midori-ku, Yokohama 227, Japan. *Received June 3, 1981*

ABSTRACT: Aiming at understanding the correlation between polymer conformation and polymer functionality in water-soluble polymers, we have measured the absorption and fluorescence spectra of a polyionene bearing pendant anthryl groups, poly[oxycarbonylmethylene-1,6-hexamethylenebis(dimethyliminio)methylenecarbonyloxy-2-[(9-anthryl)methyl]propylene dichloride] (PIA-6), and relevant low molecular weight model compounds, hexamethylenebis[[[(9-anthrylpropoxy)carbonyl]methyl]dimethylammonium chloride] (DIA) and 2-[(9-anthryl)methyl]-1,3-propanediol bis(triethylammonio)acetate dichloride (MIA). The absorption spectrum of PIA-6 (${}^1L_a$ band of the pendant anthryl groups) in water was broader than that of DIA or MIA while the absorption spectra in methanol were nearly the same for all samples, suggesting association between anthryl groups of PIA-6 brought about by hydrophobic interaction. Such ground-state association between pendant anthryl groups was also found in the fluorescence excitation spectra. Fluorescence emission spectra of PIA-6 and DIA in water showed broad excimer emission around 500 nm while excimer emission from MIA was negligible. The excimer emission intensity relative to the monomeric emission of PIA-6 and the model compounds was measured in various media, and these results are discussed from the viewpoint of a polymer conformation–photodimerizability correlation in the polyelectrolyte system.

Introduction

In previous articles on photodimerization reaction of polyionenes bearing pendant anthryl groups,[1,2] we have shown that (1) the neutral salt effects on photodimerizability of the polyionenes are different from those of the relevant monomeric or oligomeric ionenes, (2) the reactivity of the polyionenes is sensitive to changes in the environments rather than to their chemical structure, indicating that the reactivity is determined by a delicate balance between Coulombic and hydrophobic interaction, and (3) the photoreactivity is not decided only by the local concentration of anthryl groups. In these studies, a polyelectrolyte conformation–functionality correlation for the polyionenes was discussed on the basis of the photodimerization reaction of pendant anthryl groups and the viscosity behavior as indices of functionality and polymer chain conformation, respectively.

In this article, we deal with the correlation between polymer conformation and interchromophore interaction as detected by spectroscopic studies of a polyionene and the relevant low molecular ionenes. In particular, the excimer emission is informative as to the nature of the polymer-bound anthryl groups as already shown for polyesters.[3,4] The results on excimer studies of the ionenes

0024-9297/81/2214-1742$01.25/0