(15) Nemzek, T. L.; Guillet, J. E. *Macromolecules* **1977**, *10*, 94.
(16) Fuoss, R. M. *J. Polym. Sci.* **1948**, *3*, 603.
(17) Strauss, U. P.; Smith, E. H. *J. Am. Chem. Soc.* **1953**, *75*, 6186.
(18) Liberti, P. A.; Stivala, S. S. *J. Polym. Sci., Part B* **1966**, *4*, 137.
(19) Kay, P. J.; Treloar, F. E. *Makromol. Chem.* **1974**, *175*, 3207.
(20) Burckhalter, J. H.; Fuson, R. C. *J. Am. Chem. Soc.* **1948**, *70*, 4184.
(21) Mulvaney, J. E.; Dillon, J. G.; Laverty, J. L. *J. Polym. Sci., Part A-1* **1968**, *6*, 184.
(22) Merle-Aubry, L.; Merle, Y. *Eur. Polym. J.* **1980**, *16*, 227.
(23) De Baer, J.; Backer, H. J. "Organic Syntheses"; Rabjohn, N., Ed.; Wiley: New York, 1963; Vol. 4, p 250.
(24) Kilp, T.; Houvenaghel-Defoort, B.; Panning, W.; Guillet, J. *Rev. Sci. Instrum.* **1976**, *47*, 1496.
(25) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.
(26) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.
(27) Jaffé, H. H.; Orchin, M. "Theory and Application of Ultraviolet Spectroscopy"; Wiley: New York, 1970.
(28) Brandrup, J.; Immergut, E. M. "Polymer Handbook"; Wiley: New York, 1975.
(29) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1966**, *5*, 753.
(30) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5898.
(31) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

Laser Photolysis Studies of Photoinduced Aggregation in Polymers Containing Spiropyran Units

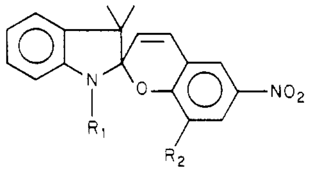
Yehoshua Kalisky and David J. Williams*

Xerox Webster Research Center, Webster, New York 14580. *Received April 14, 1983*

ABSTRACT: The photoinduced processes which lead to isomerization and complexation in polymers and copolymers containing pendant indolinobenzospiropyran groups are investigated by nanosecond transient absorption spectroscopy techniques. The monomer 1-(β-(methacryloxy)ethyl)-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-[2*H*-1]benzopyran] (SP) was copolymerized with methyl methacrylate (MMA) to form copolymers (MMA_m-*co*-SP_n) and homopolymerized PSP. In solution, the copolymer undergoes a photoinduced ring-opening reaction to form B, the fully isomerized transform via a short-lived nonplanar ring-opened intermediate (X) on the subnanosecond time scale. A second transient (AB) is formed by a bimolecular reaction between the lowest triplet state of SP ($^3A^*$) with a ground-state ring (A) on the same chain. Efficient AB formation is observed even in the copolymer which is most dilute in SP ($MMA_{99.9}$-*co*-$SP_{0.1}$). A further red shift occurring at later times is taken to be evidence for higher aggregate formation $(AB)_n$ or $(A_mB)_n$. The sterically hindered environment of the homopolymer leads to deactivation of X to the ground state rather than isomerization or complexation is observed. Polar environments produce a similar effect. A detailed mechanism for the observed behavior is proposed.

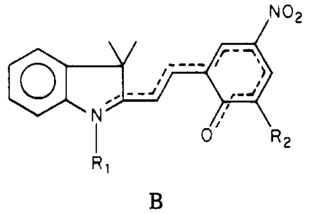
Introduction

In recent years there has been considerable interest in photoresponsive polymers with spirobenzopyran side groups.[1-3] Conformational changes induced in the polymer by photoisomerization of the side groups have been compared to those processes occurring in membranes where photoinduced conformational changes elicit changes in the state of assembly of membranes which control nerve responses and enzymatic activity. There has also been considerable recent activity to understand the process of photoinduced color formation in spirobenzopyran systems such as IA which exhibit spontaneous aggregation of the photoinduced species and lead to "quasi-crystal" formation.[4] When quasi-crystals are formed in an external electric field, they exhibit a polar structure and second-order nonlinear optical effects.[5] Considerable insight into the structure of these aggregates has been gained through spectroscopic and nonlinear optical studies.[6]



IA, R_1 = $(CH_2)_2OCO(CH_3)C{=}CH_2$, R_2 = H
IIA, R_1 = CH_3; R_2 = $CH_2OCO(CH_3)C{=}CH_2$

Irie and co-workers[2] have recently reported solvent-dependent photoinduced viscosity changes in copolymers derived from methyl methacrylate and IIA and attributed the effect of solvation of the ring-opened merocyanine form (B) by the methacrylate units of the same polymer chain.



B

Time-resolved absorption spectra following pulsed laser excitation were obtained to help elucidate the nature of the process.

We have recently reported a picosecond and nanosecond time-resolved absorption[7] study on IA in polar and nonpolar solvents. In that study the following mechanism was proposed to account for the primary photoprocesses leading to photocoloration in the picosecond to microsecond time frame:

$$\begin{tikzcd}
 & {}^3A^* \arrow[r, "{[A]}", "k_{AB}"'] \arrow[dl, "k_T"'] & {[AB]} \\
A \arrow[r, "h\nu"] & {}^1A^*\ (X^* \text{ or } {}^3A^{*\ddagger}) \arrow[u, "k_{isc}"'] \arrow[d, "k_x"'] \arrow[dr, "k_B^*"] & \\
 & X \arrow[r, "k_B"'] \arrow[ul, "k_n"] & B
\end{tikzcd}$$

where A is the parent molecule, X is the nonplanar cis-cisoid ring-opened form, B is the planar trans isomer, and AB is a dimer. At long times AB forms higher aggregates

---

* Present address: Research Laboratories, Eastman Kodak Co., Rochester, NY 14650.

0024-9297/84/2217-0292$01.50/0 © 1984 American Chemical Society

of B that may slowly complex with A. The primary photoprocesses occurring within the first few picoseconds are unclear. Since $^1A^*$ exhibits no detectable fluorescence, rapid intersystem crossing to a nearby $n\pi^*$ triplet, which internally converts to a vibrationally excited $\pi\pi^*$ triplet ($^3A^{*\ddagger}$) or a vibrationally excited ring-opened form (X^*), is thought to occur and may provide a direct isomerization route to B. The rate constants have the following values or limits in nonpolar solvents:[7]

$$k_{isc} \sim k_x < 8 \times 10^{12}\ s^{-1}$$

$$k_B > k_n \sim 4 \times 10^9\ s^{-1}$$

$$k_B{}^* < 10^8\ s^{-1}$$

$$k_{AB}[A] > k_T \sim 10^5\ s^{-1} \quad \text{for } [A] = 10^{-3}\ M$$

The question arises whether there is a relationship between the photoinduced processes leading to spontaneous aggregation in molecules of type I and II and the photoinduced conformational changes in polymers containing these chromophores. Krongauz and Goldburt[8] have prepared homopolymers of II and copolymers of II with methyl methacrylate (MMA_m-*co*-SP_n). They showed that highly crystalline materials could be obtained from the homopolymer with various solvent treatments. Interestingly, the spiropyran to merocyanine conversion proceeded in the dark as the polymer crystallized, indicating the considerable thermodynamic stability to be gained from association of the polar dye groups. In this instance the dye aggregates were spectrally distinct, exhibiting a substantial blue shift, with respect to the aggregates formed in the quasi-crystals.

In this article we report investigation of photoinduced aggregation in a polymer PSP derived from I and copolymers MMA_m-*co*-SP_n in solution. Time-resolved transient absorption measurements are used to investigate the initial photoprocesses and the role of the photoinduced intermediates in the aggregation process.

Experimental Section

Transient absorption spectra were obtained with a pulsed N_2 laser and detection system. The laser was a Lumonics TE861S excimer laser operating on an N_2/He mixture at 337.1 nm with a maximum pulse energy density at the sample of 170 mJ/cm^2. The detection system was similar to that reported previously.[9,10] All measurements were performed at ambient temperatures, and N_2 was bubbled through the solutions prior to and during measurement unless otherwise specified.

The spiropyran SP was prepared according to the method of Zajtseva et al.[11] The final product was recrystallized from 1:10 benzene–hexane. Positive identification was made through IR and NMR analysis. The colorless crystalline material exhibited a melting point that was heating-rate dependent and had a maximum of 105 °C. The solvents, toluene and acetonitrile, were Burdick and Jackson High Purity and used without further purification. The solutions for measurement were held in optical-grade quartz cells.

The polymer PSP was prepared by initiation of a 15% solution of SP in methyltetrahydrofuran (MTHF) with 1% 2,2′-azobis(isobutyronitrile) at temperatures from 40 to 80 °C under vacuum. The polymer was precipitated by methanol, purified by reprecipitation, and dried under vacuum at room temperature. The copolymers $MMA_{98.3}$-*co*-$SP_{1.7}$ and $MMA_{99.9}$-*co*-$SP_{0.1}$ were prepared by using similar methods. The copolymer compositions were determined by using the molar extinction coefficient of SP in toluene (8×10^3 cm^{-1} M^{-1}) at 350 nm.

Molecular weights were not measured, but polymers prepared by similar methods were reported[8] to exhibit an $M_w \sim 3 \times 10^4$.

Results

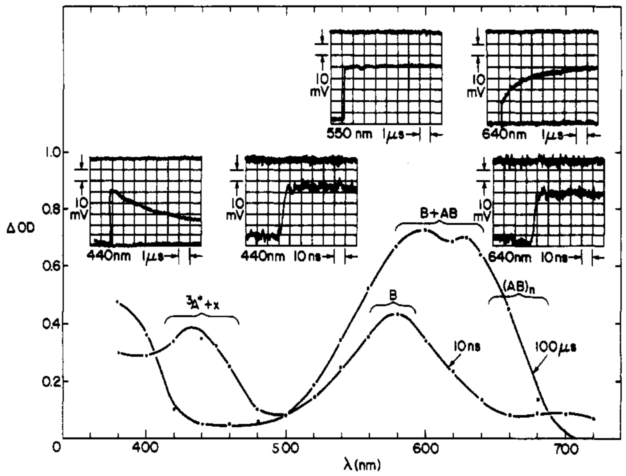
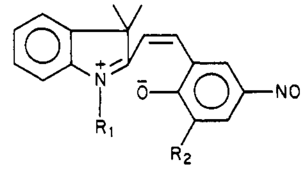


Figure 1. Transient absorption spectra at 10 ns and 100 μs following laser excitation at 337.1 nm for SP in toluene (1×10^{-4} M). Insets are the oscilloscope traces at various wavelengths.

A. Copolymers (MMA_m-*co*-SP_n). Transient absorption spectra for SP in toluene (1×10^{-4} M) at two times following pulsed laser excitation are shown in Figure 1. Also shown are oscilloscope traces of transmission vs. time following excitation at several wavelengths and time intervals. The species absorbing in the various spectral regions have been assigned previously[7,12,13] and are indicated in the figure. In the 400–500-nm region the $\pi\pi^*$ triplet ($^3A^*$) and X, the indicated ring-opened species retaining the geometry of SP, exhibit optical absorption albeit in different time intervals.



X

In toluene X is considerably shorter lived ($<10^{-9}$ s) than $^3A^*$ ($\sim 10^{-5}$ s), and its absorbance is red-shifted from but strongly overlapping with $^3A^*$. The species B, the isomerized form, absorbs at 550 nm, is formed within 300 ps, and is stable over the time scale of the measurements (10 ps to 1 ms). A complex that is thought to be composed of B and A is formed from a bimolecular reaction of $^3A^*$ with A. A gradual and slower shift to the red is attributed to the formation of aggregates $(AB)_n$ or possibly $(A_mB)_n$ (n, m = 2, 3).

Transient absorption spectra for $MMA_{98.3}$-*co*-$SP_{1.7}$ in toluene (4×10^{-5} M in SP) are shown in Figure 2. The time intervals are the same as those in Figure 1. A remarkable similarity can be noted between the spectral and temporal features in the two figures. On the basis of this similarity we attribute the absorbance in the 400–500-nm region to $^3A^*$ and the initial absorbance at 580 nm to B. The slow buildup in absorbance at 640 nm is similar to that observed for SP but somewhat lower in intensity relative to B. We believe that this is associated with formation of AB complexes within the same polymer chain. Further evidence for this is given below. A discernible rapid component to the decay of the 400-nm signal can be seen which is not present in SP. Similarly a buildup in signal at 550 nm in the same time interval which is not present in SP can also be seen. A possible explanation for this effect may lie in the increased lifetime expected for X in a polar sterically hindered environment. The extended lifetime of X was observed in acetonitrile, and the methacrylate units could have a similar effect in stabilizing X. The decay of X could therefore be superimposed on $^3A^*$ at early

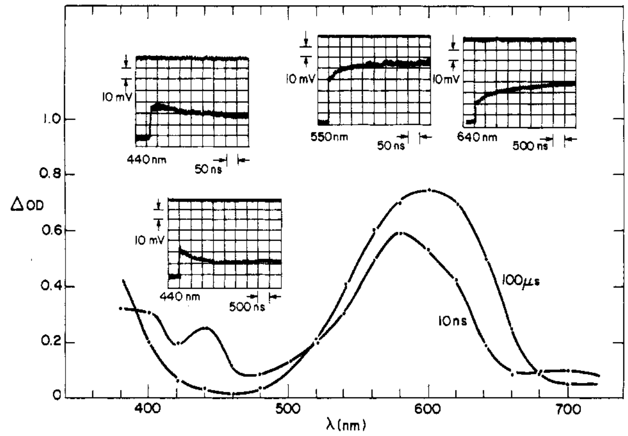


Figure 2. Transient absorption spectra for $MMA_{98.3}$-*co*-$SP_{1.7}$ in toluene (4×10^{-5} M in SP) at 10 ns and 100 μs following the pulsing laser excitation at 337.1 nm. Insets are the oscilloscope traces at various wavelengths.

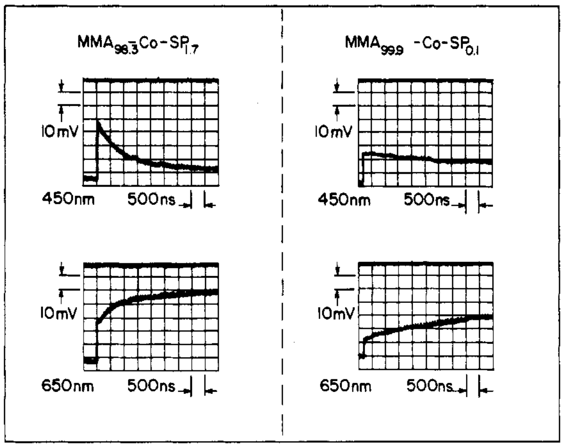


Figure 3. Oscilloscope traces of the transients at 450 and 650 nm of $MMA_{98.3}$-*co*-$SP_{1.7}$ and $MMA_{99.9}$-*co*-$SP_{0.1}$ in toluene.

times. If X isomerizes to B, some small amount of additional absorbance at 550 nm over the same time frame could result.

Transient transmission signals at 450 and 650 nm for $MMA_{98.3}$-*co*-$SP_{1.7}$ and $MMA_{99.9}$-*co*-$SP_{0.1}$ are shown in Figure 3. In the figure, transmission decreases with increasing vertical deflection. The horizontal line at the bottom of the traces is the transmission of the sample with no excitation pulse. The concentration of SP in the solution of $MMA_{98.3}$-*co*-$SP_{1.7}$ and $MMA_{99.9}$-*co*-$SP_{0.1}$ was 1.7 × 10^{-4} M, respectively. The latter solution, however, was 4 times more concentrated in polymer. The shapes of the decay curves did not change when concentrations were varied. It is apparent that the triplet decay and buildup at 650 nm attributed to AB formation are considerably faster in $MMA_{98.3}$-*co*-$SP_{1.7}$. Since the polymer is a factor of 4 less concentrated, one can conclude that the complexation process is intrachain in origin. This is a distinctly different situation than exhibited when ring opening occurs accompanying crystallization of PSP.[8]

Figure 4 is a semilog plot of OD_{440} vs. time for the two polymers. The decay curves are nonexponential, but the limiting slopes exhibit exponential decay. Rate constants for the two copolymers are 3.4 × 10^5 and 1.5 × 10^5 s^{-1} for the higher and lower SP content polymer, respectively. At the lower concentration the triplet lifetime in the absence of the bimolecular reaction may dominate its decay. Semilog plots of $[OD^{\infty} - OD]_{\lambda}$, where OD^{∞} is the value of OD at long times, at several wavelengths λ are shown in Figure 5. The rate constants derived from the 640-nm data are 4.6 × 10^5 and 0.8 × 10^5 s^{-1} for the higher and lower SP content polymer, respectively. The rate constant at 670 nm for $MMA_{98.3}$-*co*-$SP_{1.7}$ is 1.5 × 10^5 s^{-1}, almost a factor of 3 lower than at 640 nm. We have noted previously[7,12] the decrease in rate constant on the red shoulder of this absorption band in SP and attributed it to higher aggregate formation $(AB)_n$ or $(A_mB)_n$, $m = 2, 3$. This may indicate multiple SP units per chain in the aggregate or formation of interchain aggregates. At this time we cannot distinguish between these possibilities.

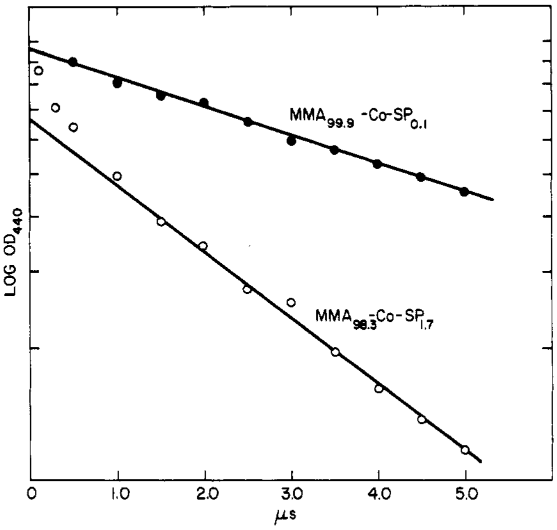


Figure 4. Semilog plot of log OD_{440} vs. time for the two copolymer solutions in toluene.

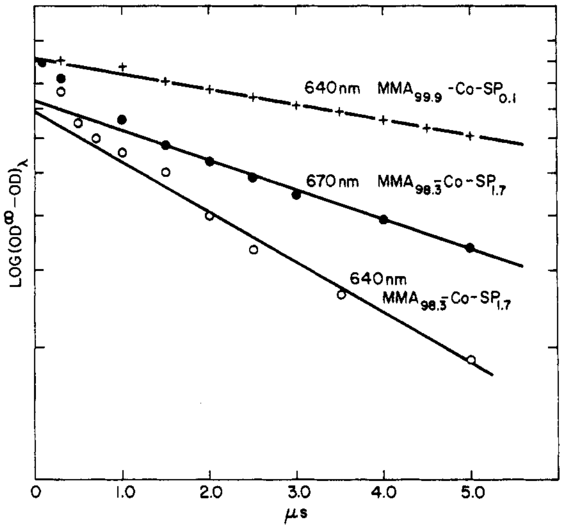


Figure 5. Semilog plot of log $[OD^{\infty} - OD]_{\lambda}$ (λ = 640, 670 nm) vs. time for $MMA_{98.3}$-*co*-$SP_{1.7}$ and $MMA_{99.9}$-*co*-$SP_{0.1}$ in toluene.

B. Homopolymer PSP. Transient absorption spectra for PSP in toluene (1 × 10^{-4} M) at various delays following excitation are shown in Figure 6. Oscilloscope traces of transmission vs. time at various wavelengths are also shown. The behavior exhibited by PSP is considerably different from that of the copolymer. An intense, short-lived transient (50 ns) gives rise to absorption in the 400–500-nm region and beyond about 650 nm. This species quickly decays and is not accompanied by an increase in absorption in any other observable spectral region. The short-lived species exhibits a maximum in its absorption in the vicinity of 470 nm. Krysanov et al.[13] have observed a band in this region by picosecond excitation of B at 528 nm. The band decays in less than 600 ps, and the bleached B signal exhibits 80% recovery in the same time domain.

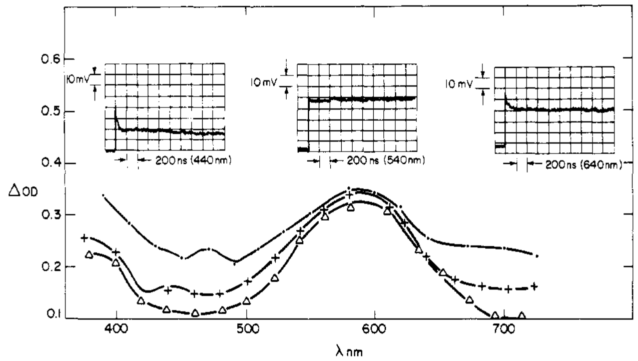


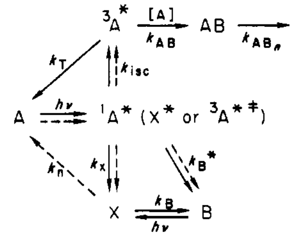
Figure 6. Transient absorption spectra at 10 ns, 200 ns, and 100 μs following laser excitation at 337.1 nm. Insets are the oscilloscope traces at various wavelengths.

Although their interpretation of the band is unclear, we attribute it to species X, which we have proposed previously as being the precursor of the 530-nm band which is formed in less than 300 ps when A is excited at 353 nm. In the polymer PSP, X is apparently considerably longer lived and decays to the ground state rather than undergoing isomerization to B. The origin of B must therefore be a vibrationally excited species formed from the initial singlet state. The nature of the species will be discussed further below. Both the steric influence and polarity of the polymeric environment could contribute to the extension of the lifetime of X.

In the vicinity of 440 nm the short-lived species decays and a longer lived signal remains which by analogy with previous results[7] we attribute to the triplet $^3A^*$. In contrast to the results for the copolymers and SP in toluene, no growth in signal in the 550–680-nm region accompanies the decay of $^3A^*$. Apparently the steric restrictions of the PSP environment preclude the geometry required to form the complex AB. The triplet state therefore is deactivated by decay to the ground state, with a lifetime longer than that of the monomer or copolymer.

Discussion

We propose the $^3A^{*\ddagger}$ photochemical model to account for the photoinduced processes occurring in MMA$_m$-*co*-SP$_n$ and PSP. The model is an adaptation of that previously proposed for SP.[7]



The dashed arrows depict the routes followed by PSP and the solid lines those followed by the copolymers and SP. Following excitation to the singlet state, rapid intersystem crossing to $^3A^*$, the $\pi\pi^*$ triplet, or X, the vibrationally relaxed ring-opened nonplanar cis–cisoid isomer, occurs. The intermediacy of $^3A^{*\ddagger}$, the $n\pi^*$ triplet or a vibrationally excited $\pi\pi^*$ triplet, or X^*, a vibrationally excited form of X, has been proposed, but no spectral evidence other than the proximity of $n\pi^*$ to $^1A^*$ supports this part of the mechanism. The rate constants k_{isc} and k_x are thought to be 10^{11} s^{-1}. The species X absorbs light in the 400–500-nm region and converts to B for SP and copolymer MMA$_m$-*co*-SP$_n$ in solvents such as toluene in the 300–600-ps time scale. In polar and sterically hindered environments such as PSP in toluene or SP in acetonitrile, X is considerably longer lived and undergoes radiationless deactivation to the ground state.

Transient absorption data in the $^3A^*$ (440 nm) and AB (650 nm) region indicate photoinduced association involving the SP substituents. This is in contrast to the behavior observed by Irie et al.,[2] where attachment of the (methacryloxy)methyl substituent occurs through the R_1 position. Their data do not appear to indicate the formation of AB. The complex AB and higher aggregates are therefore very dependent on steric factors.

There is considerable difference of opinion in the literature[4-8,14,15] regarding the assignment of the nature of the various transient species and photoproducts observed in the visible region of the spectrum for SP and the various polymers and copolymers containing the spirobenzopyran group. This is certainly due to the complexity of the processes involved and the number of possible intermediate states which have been proposed. Several areas of disagreement and our reasons for making the assignments as we have are discussed below.

We associate the species X with the short-lived (<50 ns) species observed in the 400–500-nm region with a maximum in the 460–470-nm region. Its lifetime is solvent dependent and possibly dependent on the steric environment. It appears to deactivate exclusively through C–O bond formation in polar solvents but isomerizes in the copolymers to the opened form B. Krysanov et al.[13] have observed a species with an absorption maximum at 460 nm following excitation of B in ethanol at 528 nm. Since they have assigned the 430-nm peak formed upon excitation at 353 nm to X, they assume the 460-nm peak must be due to another species, possibly the $S_n \leftarrow S_1$ of B. They also observe that the 460-nm peak decays in 600 ps and the signal attributed to B recovers in this time frame. We have independently observed that B forms on a similar time scale when A is excited at 353 nm. Since the time scales involved are so similar, we assume that the $X \rightleftharpoons B$ portion of the proposed mechanism is supported by all of the data. We cannot reject the possibility, however, that the 460-nm peak is due to an excited state of the trans–trans isomer and closely overlaps the peak we have attributed to X. We are confident, however, that contributions from X and $^3A^*$ are time resolved and that the evidence supports the assignment of the 430-nm peak to $^3A^*$.

A second possible source of confusion arises from the observation of absorption spectra for PSP and SP in 2-methyltetrahydrofuran in the dark.[8] A series of peaks with very low intensity relative to the absorption bands for A are observed at ~480, 560, 600, and 650 nm, with the intensity decreasing with increasing wavelength. A finite amount of thermal interconversion between A and the ring-opened form has been noted in the past and accounts for these peaks. We believe that these peaks are due to the thermal generation of the same species that are produced by photoexcitation with the exception that the $^3A^*$ is missing in the dark. Differences in solvent and the fact that the 460-nm peak rides on the tail of the $S_1 \leftarrow S_0$ absorption of A could account for slight differences in the position of the absorption band. The fact that a dynamic equilibrium exists requires the presence of an isomer where the probability of ring closure is favorable. We therefore suggest that the data of Figure 5 in ref 8 are consistent with the following equilibrium processes and spectral assignments.

$$A \rightleftharpoons X\ (480\ \text{nm}) \rightleftharpoons B\ (560\ \text{nm}) \rightleftharpoons AB\ (600\ \text{nm}) \rightleftharpoons (AB)_n \text{ or } (A_mB)_n$$

We note that the concentration of various species observed in the transient absorption spectrum is likely to be different from that observed under equilibrium conditions. Although no transient absorption peak is observed at 600 nm for PSP, this does not preclude a contribution to its steady-state absorption spectrum.

The positions of the various equilibria will be dependent on the thermodynamic characteristics of the environment in which the chromophores are found. The complexed and aggregated species are more stable in nonpolar sterically unhindered environments. In sterically hindered environments entropy factors would favor the uncomplexed species X and B. Similarly the polar species X and B would be favored in polar environments. Although these assignments differ from those provided in ref 8, we believe they are consistent with the observations and models we have proposed for SP, PSP, and MMA$_m$-*co*-SP$_n$.

Conclusions

We have conducted a time-resolved transient optical absorption study of the processes occurring in copolymer MMA$_m$-*co*-SP$_n$ and a polymer PSP in toluene. The results were compared with published data on SP and for the polymers, and a model was proposed to account for the observed behavior.

The observed photoprocesses in the copolymers closely mimic those observed for SP under similar conditions. The key process for photoinduced conformational changes in the polymer is the intrachain complexation of the triplet state with a ground-state chromophore to form intrachain complexes AB. The copolymer composition dependence of the decay of the triplet state and formation of AB is the key to this interpretation. Evidence for higher order aggregation involving additional AB units or A units also exists. Since evidence exists[4] that the final state of aggregation involves $(A_nB)_m$ complexes, incorporation of additional A units may be the preferred route.

Steric crowding of A units in the polymer PSP apparently retards the isomerization of X, the initial ring-opened form, and prevents complexation to form AB. The species B is formed from a higher energy precursor to X, perhaps X*, a vibrationally excited X, or a more highly excited triplet than $^3A^*$, the relaxed $\pi\pi^*$ triplet.

Because of the divergence of opinion in the literature regarding assignment of the various colored forms of SP, a comparison was made with current data from recently reported studies.

Acknowledgment. We wish to thank Professor Valeri Krongauz for preparation of the polymers and helpful discussions during the experiments.

Registry No. MMA$_m$-*co*-SP$_n$, 51816-58-1; PSP, 57981-89-2.

References and Notes

(1) G. Smets, J. Breaken, and M. Irie, *Pure Appl. Chem.*, **50**, 845 (1978).
(2) M. Irie, A. Menju, and K. Hayashi, *Macromolecules*, **12**, 1176 (1979).
(3) A. Menju, K. Hayashi, and M. Irie, *Macromolecules*, **14**, 755 (1981).
(4) V. A. Krongauz, *Isr. J. Chem.*, **18**, 304 (1979).
(5) G. R. Meredith, V. A. Krongauz, and D. J. Williams, *Chem. Phys. Lett.*, **87**, 289 (1982).
(6) G. R. Meredith, D. J. Williams, S. N. Fishman, E. S. Goldburt, and V. A. Krongauz *J. Phys. Chem.*, **87**, 1697 (1983).
(7) Y. Kalisky, T. E. Orlowski, and D. J. Williams, *J. Phys. Chem.*, **87**, 5333 (1983).
(8) V. A. Krongauz and E. S. Goldburt, *Macromolecules*, **15**, 1382 (1982).
(9) C. R. Goldschmidt, M. Ottolenghi, and G. Stein, *Isr. J. Chem.*, **8**, 29 (1970).
(10) U. Lachish, R. W. Anderson, and D. J. Williams, *Macromolecules*, **13**, 1143 (1980).
(11) E. L. Zajtseva, A. L. Prokhoda, L. H. Kurkovskoya, R. R. Shifrina, N. S. Kardash, D. R. Drapkina, and V. A. Krongauz, *Khim. Geterotsikl. Soedin.*, **10**, 1362 (1973).
(12) Y. Kalisky and D. J. Williams, *Chem. Phys. Lett.*, **91**, 77 (1982).
(13) S. A. Krysanov and M. V. Alfimov, *Chem. Phys. Lett.*, **91**, 77 (1982).
(14) V. A. Krongauz, J. Kivi, and M. Graetzel, *J. Photochem.*, **13**, 89 (1980).
(15) A. A. Parshutkin and V. A. Krongauz, *Mol. Photochem.*, **6**, 437 (1974).

Fluorescence Probes in Polymer Chemistry. Application of 5-(Dimethylamino)-1-naphthalenesulfonamides to the Study of Solvation of Styrene–Divinylbenzene Copolymers

Kenneth J. Shea,* Yoshio Okahata, and T. Kirk Dougherty

Department of Chemistry, University of California, Irvine, California 92717.
Received May 9, 1983

ABSTRACT: A method for studying solvation of styrene–divinylbenzene copolymers is described. Styrene–divinylbenzene copolymers doped with derivatives of 5-(dimethylamino)-1-naphthalenesulfonamides were prepared. The fluorescence emission spectra of the copolymers were recorded in a variety of solvents. Comparisons of these data with the fluorescence emission of the probe molecule in pure solvent were used to provide information regarding copolymer solvation.

Chemical reactions of functionality embedded in highly cross-linked polymers take place at the solvent–polymer interface. These reactions involve an interplay between polymer-bound functionality, homogeneous reagents, and solvents that vary in their ability to solvate pendent polymer chains.[1] Reactivity of functionality embedded in less highly cross-linked polymers is further influenced by the solvent's ability to swell the gel, thereby permitting access to the interior of the gel particle.

The role of solvent in these reactions is critical. It must provide a suitable medium for the reaction transition state and also solvate, or swell, a polymer. Often these requirements are mutually exclusive.

Our program in functionalized macromolecules utilizes a template synthesis method to selectively introduce sites of organic functional groups at or near the surface of highly cross-linked macroreticular styrene–divinylbenzene copolymers.[2] The template synthesis method requires lib-

0024-9297/84/2217-0296$01.50/0