Macromolecules 1988, *21*, 51-55

Light-Induced Spectral Changes in Rose Bengal End-Capped Polystyrene

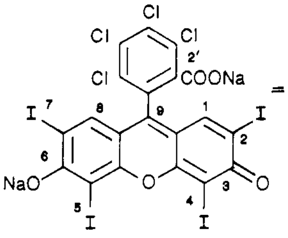
S. N. Gupta, S. M. Linden, A. Wrzyszczynski, and D. C. Neckers*

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403. *Received December 2, 1986*

ABSTRACT: Light-induced changes in the absorption spectra of Rose Bengal end-capped polystyrenes in nonpolar solvents have been observed. The spectra of the Rose Bengal polymers obtained after irradiation are clearly indicative of the photochemical conversion of Rose Bengal monomer to Rose Bengal aggregate in the nonpolar solvent. The results suggest that a photochemically induced polymer backbone conformational change driven by intramolecular dye–dye aggregation is giving rise to the observation.

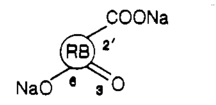
Background

Rose Bengal (tetrachlorotetraiodofluorescein) is a xanthene dye. Like other phthalein and xanthene indicators, it has two different visible absorption spectra depending on the ionization state of the C-6 functionality.[1,2] In its C-2′, C-6 dianionic form and in the C-2′ ester, C-6 monoanionic form, the absorption spectrum of Rose Bengal is characterized by two peaks with maxima at approximately 565 and 525 nm, respectively. The ratio of these two peaks is about 3:1 in polar solvents but decreases in nonpolar solvents, Table I. On the other hand if the C-6 function is bound covalently, the spectrum is composed of two much broader peaks centered around 490 and 410 nm, respectively (Figure 1). The λ_{max}s of the C-6 covalently bound systems are of much lower molar absorptivity than are the λ_{max}s of the dianionic or the C-6 monoanionic system. We were particularly interested in the effect of solvent polarity on the coefficient of the two peaks $A_{\lambda_1}/A_{\lambda_2}$ because we knew from other studies that this ratio was diagnostic for the formation of H-type dye aggregates as a function of concentration in the solvent in question.[3]



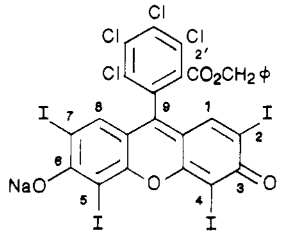
Rose Bengal, disodium salt

=



Rose Bengal abbreviated

=



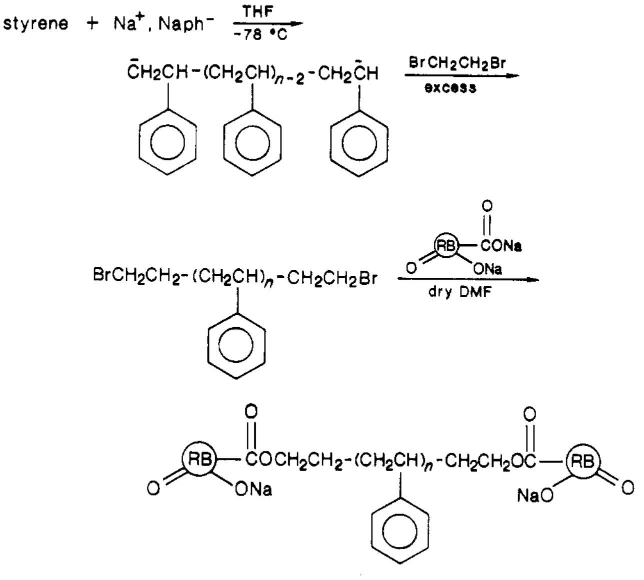
Rose Bengal, C-2′ benzyl ester, C-6 sodium salt

Most monomeric derivatives of Rose Bengal are essentially insoluble in toluene and benzene. Low molecular weight polystyrenes end capped with Rose Bengals, however, provide the capability of studying the spectral properties of the polar dye even with inorganic gegenions at C-6 and even in the most nonpolar solvents. We chose to synthesize end-capped polystyrene systems for that purpose, with a specific interest in determining the parameters which affect the spectral characteristics of the xanthene dye under conditions which are most unfavorable to such a bulky, ionic substance. The unusual results which follow focus on such systems.

Table I
Ratio of $A_{\lambda_1}/A_{\lambda_2}$ for Rose Bengal, C-2′ Benzyl Ester, Mono Sodium Salt in Different Solvents

solvent	concn	λ_1	λ_2	ϵ_1/ϵ_2
THF	1.54×10^{-6}	564	525	2.25
MeOH	9.95×10^{-6}	563	522	3.00
DMF	1.47×10^{-5}	570	527	3.48
DMSO	9.81×10^{-6}	572	529	3.49

Scheme I



I

Results and Discussion

Polystyrene was prepared by anionic polymerization initiated with sodium naphthalide under argon in THF. The living polymer was terminated with an excess of 1,2-dibromoethane. Displacement of bromide from the linear polystyrene chain ends with Rose Bengal disodium salt in DMF gave Rose Bengal end-capped polystyrene (I) (Scheme I). Molecular weights were measured viscometrically and verified by GPC (Table II).

The absorption spectra of the polymers, I, in methylene chloride and in methanol are similar to those observed in these solvents with Rose Bengal ester derivatives.[4] Thus the ratio of two peaks at 562 and 534 nm, ϵ_1/ϵ_2, decreases as the polarity of the solvent decreases (Figure 2). This change can be explained both because polar dyes tend to aggregate in nonpolar solvents and because the C-6 ion pair is less solvent separated in totally nonpolar media. We shall show shortly that the change must be the result of dye/dye aggregation.

When each of the polymers, I, is irradiated at 560 nm in either toluene or benzene in the presence of air the 534-nm peak increases in absorbance and the ratio of ϵ_1/ϵ_2

0024-9297/88/2221-0051$01.50/0

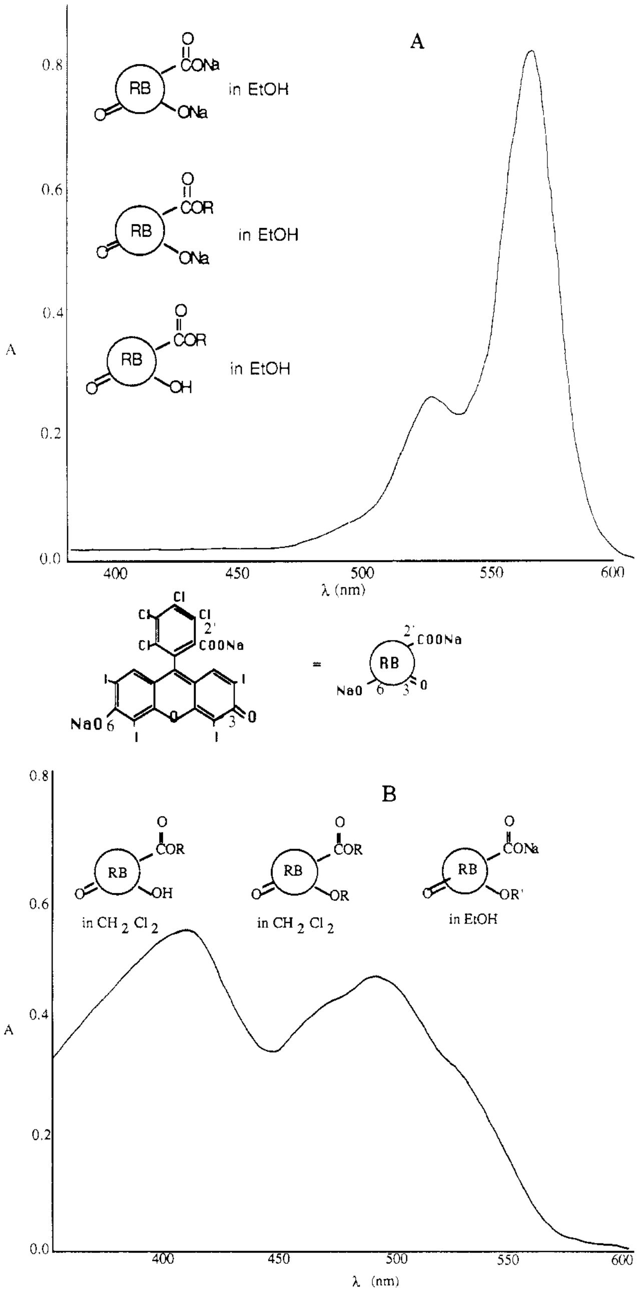
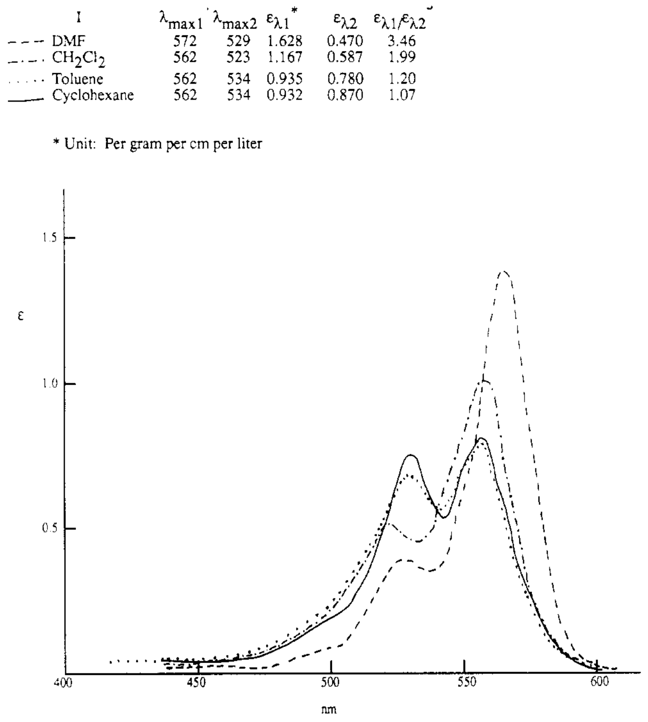


Figure 1. Two distinctly different visible absorption spectra of Rose Bengal derivatives: (A) the dianionic form; (B) the molecular form.

decreases from 1.30 to 0.9 accordingly. Thus, as one can see from Table III and Figure 3, ϵ_1 at 562 nm remains the same during the irradiation period of 165 min, while ϵ_2 at 534 nm increases by ≈34%. When the irradiation is carried out under argon, ϵ_1 decreases by ≈13% while the ϵ_2 increases by ≈23%, after 1 h as shown in Table IV and Figure 4. An isosbestic point (527 nm) exists in the case of irradiation both in air or under argon. On the basis of exhaustive studies of aggregation phenomena of xanthene dyes in both protic organic solvents and in water,[3] this observation is clearly indicative of the formation of stacked Rose Bengal/Rose Bengal dimers in solution. Thus it seems that the photochemical reaction is inducing the formation of stacked dimers from the Rose Bengal termini of the end-capped polystyrenes in nonpolar solvents. Bleaching is indicated by a concomitant decrease in both peaks. In the presence of air bleaching begins after 165 min. In the absence of air, bleaching begins at the same time as the photochemical rearrangement. These data



I	λ_{max1}	λ_{max2}	$\varepsilon_{\lambda1}$*	$\varepsilon_{\lambda2}$	$\varepsilon_{\lambda1}/\varepsilon_{\lambda2}$
- - - DMF	572	529	1.628	0.470	3.46
_._. CH_2Cl_2	562	523	1.167	0.587	1.99
..... Toluene	562	534	0.935	0.780	1.20
___ Cyclohexane	562	534	0.932	0.870	1.07

* Unit: Per gram per cm per liter

Figure 2. Absorption spectra of I in different solvents.

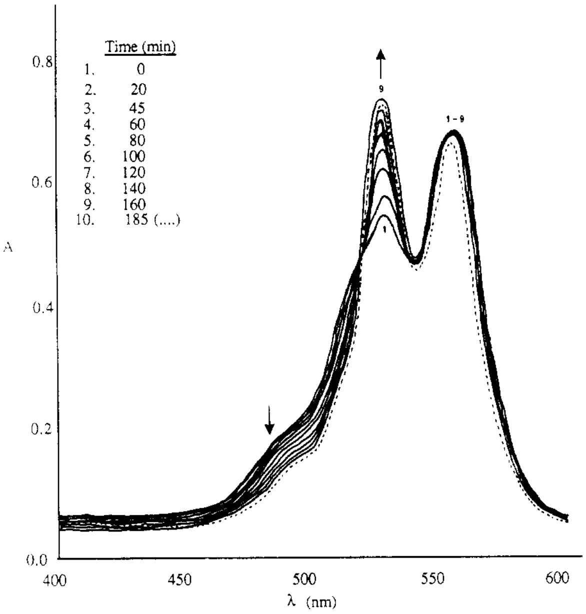
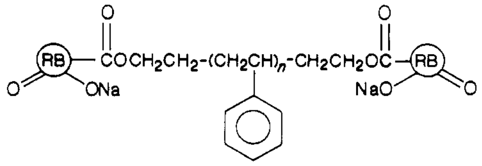


Figure 3. Spectral change of I upon irradiation.

Table II
Molecular Weights of the Polymer Samples I



polymer	n^a	MW^b	polymer	n^a	MW^b
1	33		4	270	-
2	67	3.6×10^4	5	670	1.84×10^5
3	130		6	19	1.0×10^{4c}

[a] Calculated by DP = n = 2 × mole of monomer/mole of initiator. [b] Calculated by the Mark–Houwink–Sakurada relation $[\eta] = KM^{\alpha}$, at 25 °C for polystyrene $K = 1.7 \times 10^{-4}$, $\alpha = 0.69$.[4] [c] Calculated from ε's of sample 2: $\epsilon_1 = 5.0 \times 10^3$ per RB; $\epsilon_2 = 4.0 \times 10^3$ per Rose Bengal.

Table III
Effect of Irradiation on the ϵ_1/ϵ_2 Ratio of I[a]

time, min	A_1	A_2	ϵ_1/ϵ_2[b]
0	0.685	0.557	1.23
20	0.685	0.590	1.16
45	0.685	0.635	1.08
60	0.685	0.662	1.04
80	0.685	0.690	0.99
100	0.685	0.714	0.96
120	0.685	0.726	0.94
140	0.685	0.737	0.93
165	0.680	0.746	0.92
185	0.672	0.744	0.90[c]

[a] Solution 4, Table V was used in this study; concentration 1.37 × 10^{-4} M in Rose Bengal. [b] ϵ_2 increases 34% during a 165-min irradiation. [c] A referee has suggested that end-to-end cyclization might be observed from a change in viscosity before and after irradiation. We have measured the viscosity of these solutions carefully, before and after irradiation. Within experimental error there is no difference in the viscosity of the solution before and after the reaction.

Table IV
Effect of Irradiation on ϵ_1/ϵ_2 Ratio[a] of I under Argon

time, min	A_1	A_2	ϵ_1/ϵ_2[b]
0	0.553	0.423	1.31
5	0.548	0.444	1.23
15	0.535	0.475	1.13
30	0.517	0.509	1.02
60	0.479	0.519	0.92
120	0.410	0.472	0.87

[a] Concentration 1.37 × 10^{-4} M in Rose Bengal. [b] ϵ_1 decreases 13.4% during a 60-min irradiation; ϵ_2 increases 22.7% during a 60-min irradiation.

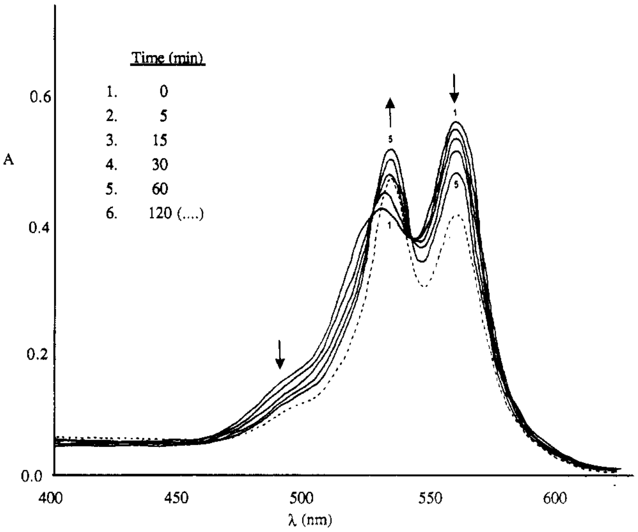


Figure 4. Spectral change of I upon irradiation (under argon).

Table V
Effect of Concentration on ϵ_1, ϵ_2, and the ϵ_1/ϵ_2 Ratio of I under Argon[c]

soln	concn × 10^5, M	ϵ_1(562 nm)[a] × 10^{-3}	ϵ_2(534 nm)[a] × 10^{-3}	ϵ_1/ϵ_2[a]	ϵ_1/ϵ_2[b]
1	68.68	9.37	7.74	1.21	0.91
2	27.48	9.46	7.67	1.24	0.89
3	13.74	9.65	7.67	1.25	0.88
4	6.87	9.46	7.47	1.27	0.92
5	6.04	9.28	7.27	1.28	0.90
6[d]	2.75	9.10	7.00	1.30	0.90
7	1.099	9.10	6.73	1.30	0.86
8	0.659	9.38	7.87	1.12	
9	0.330	9.56	8.08	1.18	

[a] Freshly prepared solution. [b] Ambient room light, for 9 days. [c] Concentration range studied = 6.87 × 10^{-4} to 3.30 × 10^{-6} M; unit of ϵ = M^{-1} cm^{-1}. [d] Polymer sample 6 with MW = 1.0 × 10^4 was used in this study.

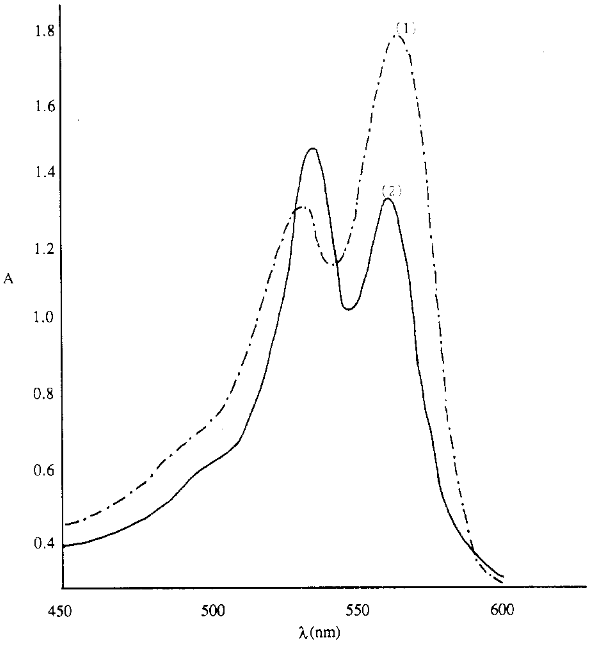
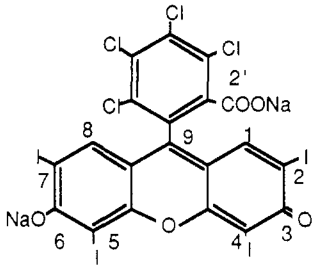


Figure 5. Spectral of irradiated I after dissolution in CH_2Cl_2 and toluene.

coincide with a general trend observed for the Rose Bengal and the other xanthenes. Namely, the rate of the photobleaching process is faster under anaerobic conditions.[5] The concentration of the solution has no effect on the ratio ϵ_1/ϵ_2 produced in the photochemical process (Table V). Thus *intermolecular* dye/dye aggregation can be ruled out as the reason for the observed spectral change. In the concentration range 10^{-4}–10^{-6}, intermolecular aggregation is not significant in dark samples either. No spectral change in the unirradiated sample occurred after 3 days when the solution was kept in the dark. Thus the reaction involves a photochemical reaction and is not the result of a thermal change in solution.

When the toluene was removed from the irradiated sample of I and the residue redissolved in toluene, the ratio ϵ_1/ϵ_2 remained the same, 0.90, as it had been immediately after irradiation. When the irradiated polymer was dissolved in methylene chloride instead, however, the ratio ϵ_1/ϵ_2 reverted to 1.90, the same value obtained when the spectrum of the unirradiated sample is taken in methylene chloride. One can argue that the factor or factors causing the increase of ϵ_2 are unaffected by toluene but were reversed by methylene chloride, a more polar solvent. However, this cannot be the case since the ratio is returned to 0.90 again when irradiated polymer I residue—after removing methylene chloride—was redissolved in toluene for the third time (Figure 5). This recycling of the ϵ_1/ϵ_2 ratio which alternates between 0.90 and 1.90 by changing solvents from toluene to methylene chloride could be continued several times over as long as one takes the precaution to get rid of all methylene chloride completely before adding the toluene. The same observation holds for the unirradiated sample except that the value alternates between 1.30 and 1.90. Thus the phenomenon causing the change is not reversed by methylene chloride.

Since the light-induced ϵ_2 increase was not accompanied by appearance of an absorption of 410 nm, formation of the nonionized or molecular form of Rose Bengal is not a likely factor and does not account for the observed spectral changes.[1] In the molecular form the C-6 ion pair



is so tightly bound that the full xanthene chromophore is unable to develop. Thus the spectrum of the molecular form of the dye is completely different from that of the C-6 dissociated ion pair. The former compound is orange with peaks at 410 and 490 nm, Figure 1B. The latter system is red and has the typical Rose Bengal absorptions, Figure 1A. That the effect is not due to tighter ion pairing after irradiation in toluene is also substantiated by the spectral data for Rose Bengal C-2′ ester, C-6 onium salts in different solvents. The large organic countercation in these cases also assists in solubilizing the dye in nonpolar solvents. When these systems were studied, the extent of ionization at C-6 was shown to not only be affected by the structure of the countercation and solvent but also by the concentration in solution. These systems show that a larger spectral change occurs as a result of tighter ion pairing than is being observed in the end-capped polystyrene case.[6] For example, the spectrum of Rose Bengal C-2′ benzyl ester, C-6 2,4,6-triphenylpyrilium changes from $\epsilon_1/\epsilon_2 = 3.14$ in EtOH to 2.53 in methylene chloride. This decrease is accompanied by the appearance of peaks at 410 and 494 nm which are due to the C-6 tight ion pair. This is not the phenomenon observed in the case of any of the samples of the polymers, I.

The unique increase in ϵ_2 observed when I is irradiated in toluene is not observed when I is irradiated in either a thin film or in more polar solvents such as methylene chloride or a toluene solution containing as little as 5% of MeOH. Both ϵ_1 and ϵ_2 decrease simultaneously in these solvents, indicating that the only photochemical reaction is dye bleaching. Dye bleaching is accompanied in model systems by complete disappearance of both the peaks at 565 and 534 nm and appearance of absorption at shorter wavelengths.

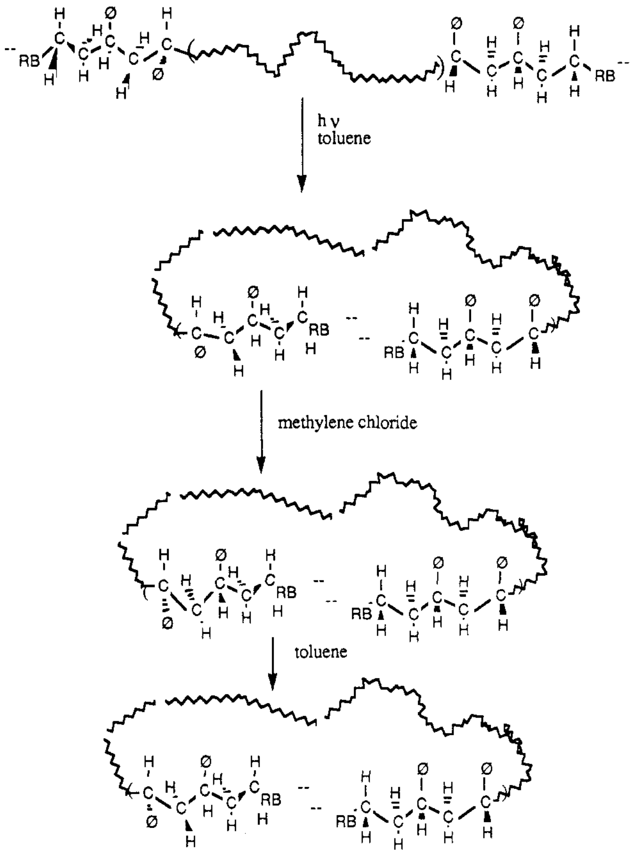
We know of no other way to explain the results than to suggest that when irradiated at 560 nm in toluene solution, I underdoes an irreversible conformational change which produces the aggregate or the dimer spectrum of the Rose Bengal. The data indicate the possibility that the photochemical process forces different conformations after irradiation which bring the ends of the polymer chains together giving rise to different spectral patterns before and after irradiation. The conformational changes produce stable materials which retain their structural integrity after several cycles between a nonpolar hydrocarbon and more polar chlorocarbon solvent. We suggest a conformational change in the backbone of the polymer is leading to the formation of the stacked dye/dye aggregates in the case of these polystyrene samples with Rose Bengal end caps. We suggest that what is occurring is shown in Scheme II.

We are now working on model compounds to determine whether the two dye moieties are forced together in nonpolar solvents by Coulombic effects or if a chemical process such as electron transfer from one dye to another provides the driving force for the conformational reorganization.

Experimental Section

Toluene, THF, and DMF were purified[7] and stored under nitrogen. Rose Bengal disodium salt (Dye Tel) was used as received. Electronic absorption spectra were recorded on a Varian Cary 219 UV/VIS instrument. Irradiation was carried out with a Bausch and Lomb grating monochromator set at 560 nm and equipped with a SP-200W mercury lamp (Osram). Molecular weights were determined by viscometry using the known values of K and α for polystyrene.[8] The intrinsic viscosities were measured at 25 °C with a Cannon-Ubbelohde viscometer immersed in a constant temperature bath equipped with both heating and cooling systems. High-pressure gel permeation on a chromatogram (GPC) were run on a Waters Associates instrument equipped with both refractive index and UV detectors and a set of μ-styrogel columns (10^4 and 500 Å). Methylene chloride was used as the eluent and a series of 11 polystyrene standards whose molecular weights ranged from 600 to 90 000 were used as reference.

Scheme II
Photochemical Transformations in Rose Bengal End-Capped Polystyrenes



Preparation of Rose Bengal End-Capped Polystyrene I. Recrystallized naphthalene (2.56 g, 20 mmol) was dissolved under argon in 100 mL of freshly distilled dry THF. To this solution sodium (0.46 g, 20 mmol) was added in small pieces and the mixture was stirred until all of the sodium was dissolved to give a deep green solution. The concentration of this solution after it was filtered through sintered glass under argon was determined by titration with a standard acid. For polymerization an appropriate amount of this initiator was transferred into a 100-mL three-neck flask fitted with a gas inlet and outlet system and a septum through which extra THF was injected to make the solution volume about 50 mL. A dry, inhibitor-free styrene (6 mL) was injected into the flask after it was cooled to about −78 °C in a dry ice–isopropyl alcohol bath. The solution turned red immediately and the polymerization was continued for 1 h. The living polymer chains were then quenched with an excess of dry, distilled 1,2-dibromoethane until the deep red solution became colorless. The polymer was subsequently precipitated with methanol and purified by repeated precipitation from benzene solution with methanol.

Rose Bengal was attached to the polymer chains by adding Rose Bengal disodium salt (4 g, 4 mmol) into a dry DMF solution (50 mL) containing 2 g of the polystyrene prepared above. The mixture was stirred and heated for 24 h under nitrogen in the dark at 70 °C. The red polymer was precipitated from the cooled solution with methanol and purified by repeated precipitation with methanol from a benzene solution. The purified Rose Bengal red polymer was then dried in vacuo at 45 °C overnight.

Acknowledgment. This work was supported by the National Science Foundation (DMR 8404001). We are grateful for their support. We also acknowledge the experimental assistance of S. R. Wu.

References and Notes

(1) Neckers, D. C.; Paczkowski, J.; Lamberts, J. J. M.; Paczkowska, B. *Free Radicals Biol. Med.* **1985**, *1*, 345.

(2) Neckers, D. C.; Linden, S. M.; van Loon, A.; Xu, D. *J. Photochem.* **1987**, *38*, 357.

(3) Neckers, D. C.; Xu, D. *J. Photochem.*; Valdes-Aquiler, O.; Neckers, D. C.

(4) Lamberts, J. J. M.; Neckers, D. C. *Z. Naturforsch., B* **1984**, *39B*, 474.

(5) Linden, S. M.; Neckers, D. C., presented at the 18th Central Regional Meeting of the American Chemical Society, June, 1986. Linden, S. M.; Neckers, D. C. *Photochem. Photobiol.*, in press.

(6) Koizumi, M. *Mol. Photochem.* **1972**, *4*, 57.

(7) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 429–436.

(8) Brandcup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1975; p IV-17, Tables of Viscosity–Molecular Weight Relations.

Morphology Changes and Volume Deformation of Individual Phases of Polymer Blends: Fluorescence Studies of Polymer Colloids. 9

Mitchell A. Winnik,* Onder Pekcan, and Liusheng Chen[†]

Department of Chemistry, and Erindale College, University of Toronto,
Toronto, Canada M5S 1A1

Melvin D. Croucher

Xerox Research Centre of Canada, Mississauga, Ontario, Canada L5K 2L1.
Received February 17, 1987

ABSTRACT: Fluorescence decay measurements were carried out on micron-sized nonaqueous dispersions of poly(methyl methacrylate) (PMMA) particles sterically stabilized with polyisobutylene (PIB) and labeled in the PMMA phase with naphthalene (N) groups. The decays were nonexponential and mean decay times $\langle\tau\rangle$ were intermediate between those of similar N groups in pure PMMA (53 ns) or PIB (43 ns) samples. These mean lifetimes $\langle\tau\rangle$ decrease with increasing local N concentration. When samples of the dispersions in isooctane or hexadecane are annealed above 60 °C, their room temperature $\langle\tau\rangle$ values increase, and when powder samples are so annealed, $\langle\tau\rangle$ decreases. These results point to the presence of an extensive PMMA–PIB interphase, with solvent swelling, and annealing leading to changes in the extent of interphase formation. Both environmental factors and the extent of naphthalene self-quenching [$N^* + N \rightarrow 2N$] affect the value of $\langle\tau\rangle$.

Many polymer systems of commercial importance are composed of separate phases of different compositions. These come about through blending or phase separation in graft or block copolymers. Although the mechanical properties of such materials depend intimately on the nature and size of the phases and their interface characteristics, measurements of these properties or other bulk responses of the system provide only indirect insights into the origins of these properties. It would be advantageous to have experiments sensitive to phenomena occurring only within certain phases of the material. Labeling techniques permit such experiments. With judicious use of isotopic or heavy atom labeling, one could examine individual phases by NMR or by neutron or X-ray scattering.[1]

In this report we describe experiments directed toward developing such a method based upon fluorescence spectroscopy. We examine a material with a morphology best described as an interpenetrating network of a rubbery polymer (polyisobutylene, PIB) in a glassy matrix [poly(methyl methacrylate), PMMA], with the PMMA chains labeled with naphthalene (N) groups. This material is prepared as a sterically stabilized nonaqueous dispersion in isooctane,[2] with particle size ranging from 1 to 3 μm. Chemical and spectroscopic analysis indicates a mole ratio of IB/MMA to be 13/100, which corresponds to a particle composition of 9% PIB dry volume.[3]

The particle morphology was originally inferred from fluorescence quenching experiments,[4] with further supporting evidence from X-ray scattering studies of particles doped with tetraphenyl lead.[5] The particles contain a thin surface shell of PIB which serves as the steric barrier against flocculation. The remainder of the PIB penetrates throughout the particle enveloping PMMA domains. This morphology is created because chemical bond formation (grafting) occurs between the PIB and PMMA during particle preparation. Thus, while PIB and PMMA are incompatible polymers and phase separate, they are still held together by the covalent bonding between them. Furthermore, we anticipate the existence of an extensive interphase between the two discrete homopolymer phases. In a different system dispersed in cyclohexane, we have documented[6] that the presence of 7–8% of a low T_g stabilizer transforms 50% of the glassy particle into an interphase containing both polymers as well as solvent. A pictorial representation of this morphology is shown in Figure 1.

Operationally, the PMMA phase in the particle is labeled by incorporating a comonomer containing a naph-

---

* To whom correspondence should be addressed.

[†] Permanent address: Institute of Chemistry, Academia Sinica, Beijing, China.

0024-9297/88/2221-0055$01.50/0