296 *Macromolecules* **1984,** *17,* 296–300

ferent 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

eration of masked functional groups in a chemical step subsequent to polymerization. The local environment of the template assemblies exerts an important influence on their chemical reactivity. It is important, therefore, to gain an appreciation of the influence of solvents on these polymers, specifically as it relates to changes in the local environment of functionality embedded in the polymer.[3]

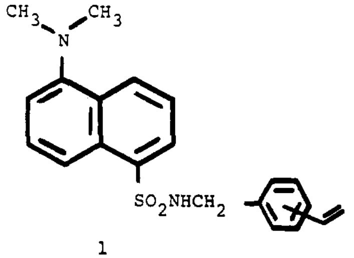
Macroreticular poly(divinylbenzene) has been characterized as having several domains, one consisting of a highly cross-linked nucleus that is assumed to be impervious to solvent and reagents, and a second, less highly cross-linked domain of pendent polymer chains.[4] This perception of macroreticular poly(divinylbenzene) leads to the expectation of certain similarities between the "working region" (that which is accessible to external reagents) of the solid and less highly cross-linked styrene–divinylbenzene copolymers. This assumption also implies that certain regions of the macromolecule will be insensitive to external reagents and solvents. We undertook the present study to test these assumptions and to obtain more detailed information regarding polymer solvent effects on the microenvironment of functionality embedded in macroreticular poly(divinylbenzene).

Of the numerous diagnostic probes for solvent effects on polymers,[5] we selected fluorescence spectroscopy as the most suitable for our particular needs.[6] This decision was based upon the sensitivity of the technique and abundant precedent for its use as an environmental probe in biopolymers.[7]

In the present study we report the application of a fluorescence probe to the problem of polymer solvation.[8] We note that there are important differences in solvation between macroporous poly(divinylbenzene) and less highly cross-linked styrene–divinylbenzene copolymers. Furthermore, it is also shown that these probes can provide a useful diagnostic for swelling in gels.

Results and Discussion

The fluorescent probe chosen for study is 5-(dimethylamino)-1-(((*p*(*m*)-vinylbenzyl)amino)sulfonyl)naphthalene (1), prepared from 5-(dimethylamino)-1-naphthalenesulfonyl chloride and *p*(*m*)-vinylbenzylamine. The excited-state chemistry of (dimethylamino)naphthalenesulfonamide derivatives has been well characterized. The fluorescence maximum of these derivatives exhibits a large solvatochromic shift and is relatively insensitive to oxygen.[9]



1

Table I

solvent	π^{*a}	α^a	β^a	$\tilde{\nu}^{fl}{}_{max}{}^b$	$\tilde{\nu}^{fl}{}_{calcd}{}^c$
hexane	−0.08	0	0	22.03	22.06
EtOEt	0.27	0	0.47	21.14	21.0
dioxane	0.55	0	0.37	20.62	20.44
THF	0.58	0	0.55	20.41	20.27
EtOAc	0.55	0	0.45	20.33	20.39
acetone	0.71	0.09	0.49	19.84	19.94
DMF	0.88	0	0.69	19.61	19.52
EtOH	0.54	0.83	0.77	19.53	19.54
CH_3CN	0.85	0.21	0.31	19.34	19.66
CH_3OH	0.60	0.93	0.62	19.27	19.42
Me_2SO	1.00	0	0.76	19.23	19.21
H_2O	1.09	1.17	0.18	18.59	18.40

[a] For definition of solvent parameters, see text and ref 14. [b] $\tilde{\nu}^{fl}{}_{max}$ are experimental values of the fluorescence maximum in the indicated solvents for the probe monomer 1 (1×10^{-5} M). [c] $\tilde{\nu}^{fl}{}_{calcd}$ are calculated fluorescence maxima determined from the dual linear regression equation $\tilde{\nu}^{fl}{}_{calcd} = 21.88 - 2.22\pi^* - 0.82\alpha - 0.60\beta$.

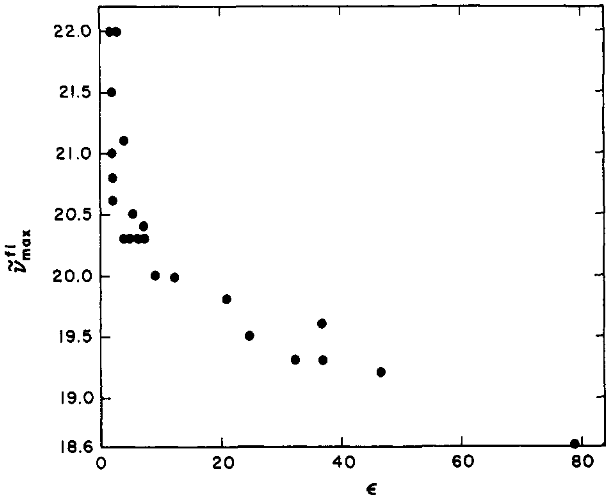


Figure 1. Plot of fluorescence emission maximum, $\tilde{\nu}^{fl}{}_{max}$ ($\times 10^3$ cm^{-1}), of monomer probe 1 vs. solvent dielectric constant.

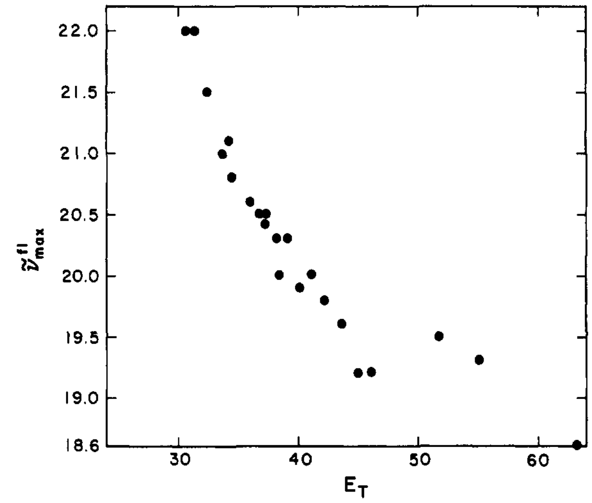


Figure 2. Plot of fluorescence emission maximum, $\tilde{\nu}^{fl}{}_{max}$ ($\times 10^3$ cm^{-1}), of monomer probe 1 vs. solvent E_T values.

To establish the influence of the medium on the fluorescence properties of the monomeric probe 1, its spectrum was recorded as a homogeneous solution in a variety of solvents (1×10^{-5} M). The absorption maximum remained invariant (λ_{max} 360 ± 1 nm) over a wide range of solvents. The emission maximum exhibited an expected red shift with increasing solvent polarity.[10] The data are summarized in Table I. Plots of $\tilde{\nu}^{fl}{}_{max}$ ($\times 10^3$ cm^{-1}) vs. a variety of commonly used indices of solvent properties are given in Figures 1–5. These include dielectric constant and several empirical solvent polarity scales, including Dimroth and Reichard's E_T scale,[11] Hildebrand's solubility parameter (δ),[12] Kosower's Z values,[13] and Taft's multiple solvatochromic parameters.[14] In the first four instances (Figures 1–4), dielectric constant, the E_T scale, Z values, and δ, the plots exhibit double-linear dependence with steeper slopes in nonpolar solvents. Although the origin of the nonlinear behavior remains somewhat controversial,[15] the break occurs in a solvent region roughly dividing

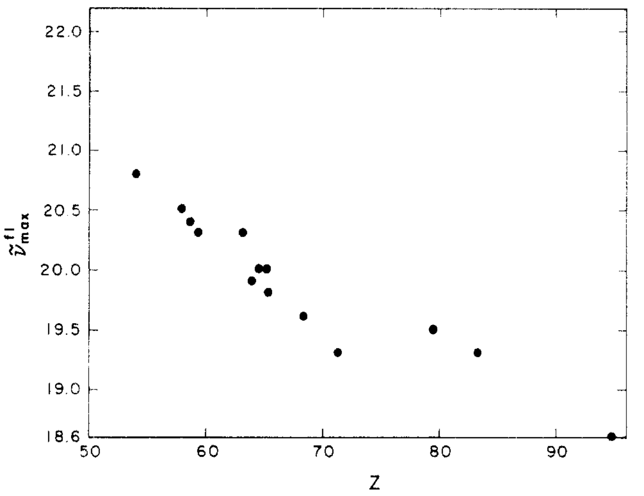


Figure 3. Plot of fluorescence emission maximum, $\tilde{\nu}^{fl}_{max}$ ($\times 10^3$ cm^{-1}), of monomer probe 1 vs. solvent Z values.

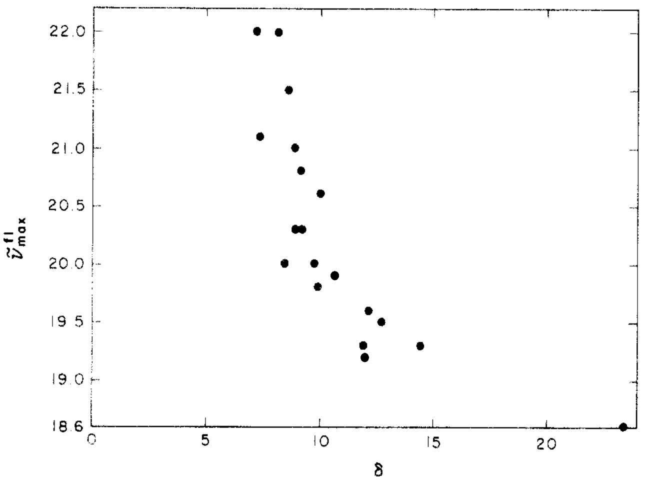


Figure 4. Plot of fluorescence emission maximum, $\tilde{\nu}^{fl}_{max}$ ($\times 10^3$ cm^{-1}), of monomer probe 1 vs. Hildebrand's solubility parameter (δ).

polar protic solvents from polar aprotic solvents. Consideration of the chemical nature of the fluorescent probe suggests that the nonlinear behavior can be attributed to the onset of contributions from specific solvent–solute interaction—i.e., hydrogen bonding. The importance of hydrogen bonding has been pointed out recently by Taft and Kamlet in their analyses of solvent effects on fluorescence behavior.[16] When the contributions from specific solute–solvent interactions are taken into consideration, linear correlations of spectroscopic data can be obtained.

We have chosen the multiparameter solvation energy relationship developed by Taft and Kamlet for correlation of the emission spectra of 1 with solvent. This treatment resolves solvent effects into a combination of three indices of solvent properties, solvent polarity/polarizability (π^*), hydrogen bond donor acidity (α), and hydrogen bond acceptor basicity (β). Dual linear regression analysis of the emission maximum of 1 with 12 select organic solvents gives a best fit equation (eq 1) for the emission of 1 (Table

$$\tilde{\nu}^{fl}_{calcd} = 21.88 - 2.22\pi^* - 0.82\alpha - 0.60\beta \qquad (R^2 = 0.97) \tag{1}$$

I). A plot of $\tilde{\nu}^{fl}_{calcd}$ calculated with the equation vs. the observed emission maximum is given in Figure 5. The average deviation (±2.7 nm) approaches the experimental precision of the measurement (±2 nm) (Table I). The correlation line forms the basis of comparison of the same fluorescent probe attached to the styrene–divinylbenzene copolymers.

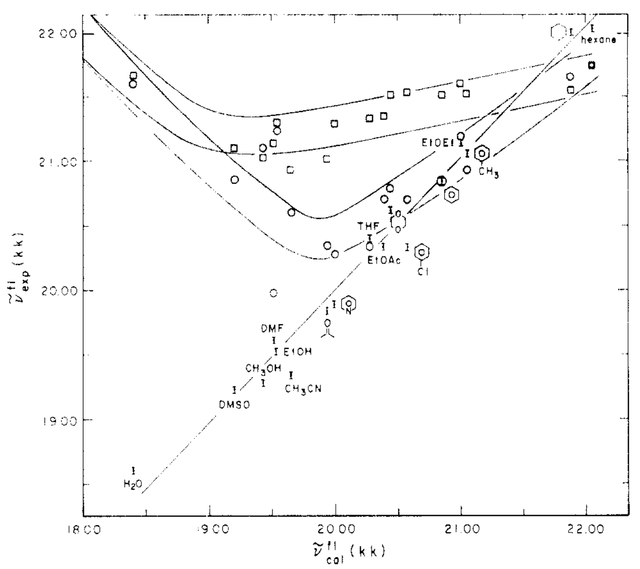


Figure 5. (•) Plot of $\tilde{\nu}^{fl}_{max}$ vs. $\tilde{\nu}^{fl}_{calcd}$ (see text). Superimposed over this line are plots of $\tilde{\nu}^{5}_{exp}$ (○) (fluorescence emission of 5-SDVB) and $\tilde{\nu}^{50}_{exptl}$ (□) (fluorescence emission of 50-SDVB) in the specified solvent. Data for this plot are found in Tables I and II. The shaded areas encompass the majority of data points for 50-SDVB (□) and 5-SDVB (○) and emphasize the difference in the probe environment as a function of solvent for the two types of copolymers.

Three styrene–divinylbenzene copolymers were prepared by bulk polymerization. Each of the macromolecules contained the fluorescent probe (1) at a concentration of 1×10^{-5} m/g. The divinylbenzene:styrene ratio was varied from 5% (5-SDVB) to 15% (15-SDVB) to 50% (50-SDVB). Bulk polymerizations were carried out by using acetonitrile as the inert diluent ($f_m = 0.5$).[17] By the cyclohexane regain criteria of Millar,[18] 50-SDVB is classified as a macroreticular copolymer.

When styrene–divinylbenzene copolymers containing fluorescent probe 1 are examined spectrophotometrically in a number of solvents, striking differences from the monomeric species 1 are noted. The position of each emission maximum in the indicated solvent is reported in Table II. The spectral data were conveniently recorded from suspensions of polymer particles (75–250 μm) in the indicated solvent. The particles were allowed to absorb solvent until no further change was noted. This usually required no more than $^1/_2$ h. A number of samples were equilibrated for 2 days with no observable differences in the emission maximum.

The final emission maximum was identical regardless of whether dry polymer was added directly to solvent or "good" solvents, such as toluene, were successively replaced by poorer solvents, i.e., CH$_3$OH.[17]

A plot of the emission maximum of several copolymers ($\tilde{\nu}^{fl}_{max}$ vs. $\tilde{\nu}^{fl}_{calcd}$) superimposed over the monomer correlation line is given in Figure 5.

Surprisingly, the macroreticular polymer (50-SDVB) exhibits very little change in the emission maximum as the solvent is varied from hexane to water (top shaded area in Figure 5). Although the polymer is wetted by virtually all the solvents (with the exception of H$_2$O), the average probe environment appears to be most strongly influenced by the polymeric matrix poly(divinylbenzene). A solvent mixture of hexane–toluene appears to match most closely the average probe environment of 50-SDVB. We have not been able to observe double emission maxima for these

Table II
Fluorescence Emission Maximum of Covalently Bound 1 to Styrene–Divinylbenzene Copolymers

solvent	polymer		
	$\tilde{\nu}^{5}_{\text{exptl}}$[a]	$\tilde{\nu}^{15}_{\text{exptl}}$[b]	$\tilde{\nu}^{50}_{\text{exptl}}$[c]
hexane	21.74	21.74	21.74
cyclohexane	21.64	21.64	21.55
EtOEt	21.19	21.28	21.60
dioxane	20.79	21.28	21.51
THF	20.33	20.70	21.32
EtOAc	20.70	20.92	21.37
acetone	20.33	20.28	21.05
DMF	19.96	20.41	21.14
EtOH	21.23	20.92	21.28
CH_3CN	20.58	20.45	20.92
CH_3OH	21.40	20.83	21.01
Me_2SO	20.83	20.70	21.10
H_2O	21.60	21.65	21.65
CCl_4	21.50	21.70	21.70
$CHCl_3$	20.20	20.70	21.30
CH_2Cl_2	20.40	20.60	21.00
benzene	20.83	21.10	21.51
toluene	20.92	21.32	21.51
anisole	20.58	21.28	21.37
pyridine	20.28	20.70	21.28
chlorobenzene	20.70	20.96	21.51

[a] Fluorescence emission maxima of covalently bound probe 1 on 5-SDVB. [b] Fluorescence emission maximum of covalently bound probe 1 on 15-SDVB. [c] Fluorescence emission maximum of covalently bound probe 1 on 50-SDVB.

systems, which would indicate two domains in the polymer. We cannot as yet, however, define the limits for detecting two emission maxima since the peaks are quite broad. Experiments at higher resolution are planned that will explore the potential for probing multiple domains in suspensions of polymer solids as well as the possible extension of this technique to include homogeneous polymer solutions.

Chemical investigations of functionalized 50-SDVB reveal that under the proper conditions a very high fraction (>90%) of functionality is accessible to chemical reagents.[2b] This implies that the total volume of "nuclei" that remains impervious to reagents is small (<10%), a finding consistent with the fluorescence results. It is also clear, however, that although the sites of functionality are accessible to reagents, their environment is not *significantly* modified by solvents.

Less highly cross-linked polymers exhibit dramatic differences from 50-SDVB. For example, the emission maximum of the 5% divinylbenzene copolymer (5-SDVB) parallels the monomer probe correlation line in good swelling solvents such as benzene, diethyl ether, dioxane, ethyl acetate, chlorobenzene, and chloroform (bottom shaded area in Figure 5).

A sharp departure in the correlation is noted in a region that includes polar protic solvents (EtOH) and polar aprotic solvents (acetone, CH_3CN, and Me_2SO). This of course defines a class of solvents that do not swell these lightly cross-linked gels. In poor swelling solvents, the average local probe environment is that of styrene–divinylbenzene. Apparently in "good" polymer solvents, the microenvironment of the probe begins to resemble the pure solvent rather than the polymer matrix. *Thus, the response of the probe to changes in the local environment parallels gel swelling.*

The copolymer containing 15% divinylbenzene (15-SDVB) (not included in Figure 5 for purposes of clarity) exhibits behavior intermediate between 50-SDVB and 5-SDVB (Table II).

These results demonstrate that the fluorescent probe technique provides a very convenient and rapid method for evaluating the microenvironment of polymeric materials and also provides direct qualitative assessment of a solvent's ability to swell a macromolecular gel. We are presently involved in an effort to quantify the solvation of macromolecules using the fluorescence probe technique.

Experimental Section

Materials. *p*(*m*)-Vinylbenzylamine. A 150-mL Carius tube, cooled to −78 °C, was charged with *p*(*m*)-vinylbenzyl chloride (32 g, 0.21 mol, Dow Chemical) and liquid NH_3 (60 mL). After warming to room temperature over 1 h an exothermic reaction ensued. The reaction mixture was shaken at room temperature for 12 h. Excess NH_3 was allowed to evaporate, and the resulting yellow liquid was dissolved in ether, washed (H_2O), dried ($MgSO_4$), and evaporated to give crude amine (28 g). Distillation [40 °C, (0.1 mm Hg)] yielded 5.9 g (20%) of vinylbenzylamine: IR (neat) 3380, 3280, 3040, 3000, 2920, 2860, 1660, 1560, 990, 900, 795, 710 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.05 (AB, 4 H, ArH), 6.7–6.2 (m, 1 H), 5.6–4.9 (m, 2 H), 3.70 (s, 2 H), 1.50 (s, 2 H).

5-(Dimethylamino)-1-(((*p*(*m*)-vinylbenzyl)amino)sulfonyl)naphthalene (1). A solution of vinylbenzylamine (0.6 g, 4.5 mmol) in pyridine (5 mL) and benzene (10 mL) was treated with a benzene solution (10 mL) of dansyl chloride (1.0 g, 3.7 mmol) at room temperature. After stirring for 6 h the reaction mixture was poured into H_2O, and the organic layer was washed with 1 N HCl (3 × 10 mL), H_2O, 10% $NaHCO_3$, and H_2O and then dried ($MgSO_4$). Concentration followed by chromatography on silica gel with $CHCl_3$ as eluent (R_f 0.2) yielded a green fluorescent fraction of pure sulfonamide 1 (1.1 g, 79%): ^1H NMR (250 MHz, $CDCl_3$) δ 9.51 (m, 1 H), 8.34 (m, 2 H), 8.3–8.2 (m, 2 H), 7.5–7.4 (m, 2 H), 7.2–6.9 (m, 5 H), 6.65–6.38 (m, 1 H, $CHCH_2$), 5.7–5.1 (m, 3 H, $CHCH_2$, NH), 4.08 (m, 2 H), 2.87 (s, 6 H). Inspection of the multiplet at δ 6.65 indicates a meta/para ratio of 1:3.2.

Fluorescent Polymers. Bulk polymerizations were carried out in medium-walled glass tubes which were degassed under high vacuum by five freeze–thaw cycles. Freshly distilled technical grade divinylbenzene (Matheson) was used; typical GC analysis of the distillate reveals 42% *m*-divinylbenzene, 15.9% *p*-divinylbenzene, 28.9% *m*-ethylvinylbenzene, and 12.6% *p*-ethylvinylbenzene. The composition of the polymerization mixture for the three copolymers is as follows: 5-SDVB, DVB (1 g), S (9 g), 1 (0.2 g), CH_3CN (10 mL), AIBN (0.08 g); 15-SDVB, DVB (3 g), S (7 g), 1 (0.2 g), CH_3CN (10 mL), AIBN (0.08 g); 50-SDVB, DVB (10 g), 1 (0.2 g), CH_3CN (10 mL), AIBN (0.08 g). Polymerization tubes were heated at 80 °C for 20 h and then at 120 °C for 20 h. The resulting polymers are ground, sized by sieving, washed in a Soxhlet extractor for 60 h (toluene), and dried under high vacuum.

Fluorescence Measurements. Aliquots of a solution of 1 were evaporated and the residue was disolved and diluted to 1×10^{-5} M. The fluorescence emission spectrum was recorded on a Hitachi Perkin-Elmer MPF-2A spectrophotometer using an excitation wavelength of 360 mm.

Dried polymer was soaked in the appropriate solvent in a 2-mm (i.d.) Pyrex capillary tube for 24 h. The tubes were placed directly in the fluorescence spectrometer (excitation wavelength 360 mm).

Acknowledgment. We thank the National Institutes of Health for generous support of this work and Professor Robert Taft for helpful discussions. Acknowledgment is also made to the Hughes Aircraft Co. for a fellowship to T.K.D.

Registry No. 1, 88454-12-0; (divinylbenzene)·(styrene) (copolymer), 9003-70-7; vinylbenzylamine, 52352-11-1; dansyl chloride, 605-65-2.

References and Notes

(1) (a) Rebenfeld, L.; Makarewicz, P. J.; Weigmann, H.-D.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem.* **1976**, *C15*, 279. (b) Millich, F.; Carraher, C. E., Jr. "Interfacial Synthesis", Marcel Dekker: New York, 1977; Vol. 1. (c) Guyot, A.; Bartholin, M. *Prog. Polym. Sci.* **1982**, *8*, 277.

(2) (a) Shea, K. J.; Thompson, F. A.; Pandey, S. D.; Beauchamp, P. S. *J. Am. Chem. Soc.* **1980**, *102*, 3149. (b) Shea, K. J.; Thompson, E. A. *J. Org. Chem.* **1978**, *43*, 4253. (c) Shea, K. J.; Dougherty, T. K., unpublished results.

(3) For general treatments of polymer solvation see: (a) Billmeyer, F. W., Jr. "Textbook of Polymer Science", 2nd ed.; Wiley-Interscience: New York, 1971; p 23. (b) Kwei, T. K. In "Macromolecules: An Introduction to Polymer Science"; Bovey, F. A., Winslow, F. H., Eds.; Academic Press: New York, 1979.

(4) (a) Heitz, W. *Fortschr. Hochpolym.-Forsch.* **1977**, *23*, 1. (b) Funke, W. *Chimica* **1968**, *22*, 111.

(5) (a) Tager, A. A.; Tselepotkina, M. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1978**, *47*, 87. (b) Lee, L., Ed. "Characterization of Metal and Polymer Surfaces"; Academic Press: New York, 1977; Vol. I and II.

(6) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978. (b) Gribault, G., Ed. "Fluorescence: Theory, Instrumentation and Practice"; Marcel Dekker: New York, 1967.

(7) (a) Beavan, S. W.; Hargreaves, J. S.; Phillips, D. *Adv. Photochem.* **1979**, *11*, 207. (b) Chapay, L. L.; DuPre, D. B. *Methods Exp. Phys.* **1980**, *16A*, 404. (c) Edelman, G. M.; McClure, W. O. *Acc. Chem. Res.* **1968**, *1*, 65.

(8) For additional studies of the application of fluorescence spectroscopy to polymer solvation, see: (a) Mikes, F.; Strop, P.; Tuzar, Z.; Labsky, J.; Kalal, J. *Macromolecules* **1981**, *14*, 175. (b) Strop, P.; Mikes, F.; Kalal, J. *J. Phys. Chem.* **1976**, *80*, 694, 702. (c) Chen, H.-L.; Morawetz, H. *Macromolecules* **1982**, *15*, 1445.

(9) Himel, C. M.; Mayer, R. T.; Cook, L. L. *J. Polym. Sci., Part A-1* **1970**, *8*, 2219.

(10) Li, Y.-H.; Chan, L.-M.; Tyer, L.; Moody, R. T.; Himel, C. M.; Hercules, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3118.

(11) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1.

(12) Hildebrand, J. H.; Scott, R. L. "Regular Solutions"; Prentice-Hall: Englewood Cliffs, NJ, 1962; pp 89-103.

(13) Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968; p 293.

(14) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

(15) (a) Reeves, R. L.; Maggio, M. S.; Costa, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 5917. (b) Coosemans, L.; De Schryver, F. C.; van Dormael, A. *Chem. Phys. Lett.*, *1979*, *65*, 95.

(16) (a) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* **1981**, *77*, 69. (b) For a recent comprehensive review of solvent effects, see: Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: New York, 1979.

(17) Lloyd, W. G.; Alfrey, T., Jr. *J. Polym. Sci.* **1962**, *62*, 301.

(18) (a) Millar, J. R.; Smith, D. G.; Kressman, T. R. E. *J. Chem. Soc.* **1965**, 304. (b) Sederel, W. L.; De Jong, G. J. *J. Appl. Polym. Sci.* **1973**, *17*, 2835.

(19) (a) Millar, J. R. *J. Chem. Soc.* **1960**, 1311. (b) Millar, J. R.; Smith, D. G.; Marr, W. E.; Kressman, T. R. E. Ibid. **1963**, *218*, 2779.

Morphology of Random Alternating Block Copolymers of Bisphenol A Polycarbonate and Poly(dimethylsiloxane)

Arthur C. Lind

McDonnell Douglas Research Laboratories, St. Louis, Missouri 63166.
Received April 27, 1983

ABSTRACT: The results of a hydrogen nuclear magnetic resonance study of random alternating block copolymers of bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS) support a proposed domain morphology in which the longest blocks reside at the center and the shortest blocks reside at the surface, with a gradation of block lengths between. The free-induction decay signals from these solid block copolymers contain rapidly decaying Gaussian and slowly decaying Lorentzian components. As the copolymer temperature was increased from 180 to 460 K, the amplitude of the Gaussian component gradually decreased to zero as the BPAC passed through its glass transition. This temperature dependence is attributed to a distribution of BPAC glass transition temperatures caused by a distribution of BPAC block lengths. The data were used to accurately determine the number-average BPAC block lengths and calculate the distributions of BPAC block lengths. The distributions were geometric for copolymers with number-average BPAC block lengths of about 15 but were narrower for copolymers with number-average BPAC block lengths of about 4. The BPAC domain morphology was proposed to explain the ability of BPAC blocks of different lengths to independently undergo motion associated with their individual glass transition temperatures.

Introduction

Block copolymers frequently exhibit phase separation in which blocks of like type associate into domains whose dimensions are on the order of 10 nm. The morphology of monodisperse diblock (AB) and triblock (ABA) copolymers can consist of highly ordered spheres, cylinders, or lamellae, and criteria for phase separation and predictions of domain size and shape have been developed in terms of molecular and thermodynamic variables.[1-5] Random alternating block copolymers (ABAB···ABA) in which both the A and B blocks are polydisperse exhibit a morphology that is generally less ordered, and rigorous calculations for predicting the morphology have not been attempted. Adding to the complexity, the morphology of most block copolymers is strongly dependent upon the solvent from which the sample is cast (i.e., whether the solvent favors A, B, or neither)[6,7] and subsequent heat treatment.[7,8]

When the domain sizes are sufficiently large, their shapes can be easily determined and their sizes can be measured using electron microscopy.[9,10] For smaller sizes, this determination becomes increasingly difficult and other measurement techniques are employed, such as small-angle X-ray scattering,[7,8,10-12] small-angle neutron scattering,[13,14] differential scanning calorimetry (DSC),[15-17] electron paramagnetic resonance,[18] and nuclear magnetic resonance (NMR).[15,19-22] The latter technique was used in this study.

The bisphenol A polycarbonate (BPAC)/poly(dimethylsiloxane) (DMS) block copolymers used in this study are random alternating block copolymers (ABAB···ABA) having polydisperse blocks.[23] Copolymers having a range of number-average block lengths and compositions were studied. The morphology of these copolymers is thought to vary with composition in the following way. At low BPAC concentrations, the BPAC blocks associate into rigid domains scattered throughout a continuous mobile

0024-9297/84/2217-0300$01.50/0