Solvent and Temperature Effects on Polymer-Coated Glass Fibers. Fluorescence of the Dansyl Moiety

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E-type glass fibers were coated with poly(γ-aminopropyltriethoxysilane), treating them with a 1% (v/v) monomer aqueous solution. The fibers were labeled with a dansyl–sulfonamide conjugate by reaction of acetonitrile solutions of dansyl chloride with the amine groups immobilized on the glass fiber surface. Interactions of the labeled coating polymer with solvents of different polarities were estimated by measurements of the fluorescence band shifts of the label. It was found that for aprotic solvents, the solvent dipolar coupling relaxation mechanism is dominated by thermodynamic interactions of the solvent with the polymer matrix, while for protic solvents this mechanism is dominated by specific interactions between solvent molecules and the excited state of the chromophore. Different experimental excited-state dipole moments were obtained for nonpolar and polar solvents ($\mu_{NP}^* = 7.2 \pm 1.6$ D, $\mu_P^* = 11.9 \pm 1.5$ D). Using the AM1 method, excited-state dipole moments for the first and second singlets were calculated and it was concluded that $\mu_{NP}^* \approx \langle \mu_1^{*2} \rangle^{1/2}$ and $\mu_P^* \approx \langle \mu_2^{*2} \rangle^{1/2}$. Accordingly, neither the glass support nor the coating polar influence the excited-state properties of dansyl. The temperature dependence of dansyl emission allows the determination of the relaxation temperature of the coating polymer, which was estimated as 175 K for the coating used.

INTRODUCTION

E-type glass fibers are usually employed as reinforcing fillers in polymer matrix composites. For improving the interfacial adhesion, glass fibers are surface treated with coupling agents such as γ-aminopropyltriethoxysilane (APES). In the first step, this silane condenses with the glass surface and, in the second, with other monomers, yielding a reactive polyorganosiloxane polymer-coated surface [1]. Although the structure of this polyorganosiloxane coating has been widely studied, it is not exactly known yet [2–4]. Glass fiber surfaces treated in such a way become functionalized with amine groups that may react with the polymer matrix during the curing stage of the composite; as a result, the resistance against adverse water effects and the mechanical properties of the composite are greatly enhanced [5].

The accessibility through the glass/coupling region and coupling region/polymer matrix interfaces, as well as the structural flexibility of the coupling regions, are, among others, important features which determine the interfacial properties of the composite [6]. Although several adhesion mechanisms have been proposed [7], how the polymer matrix diffuses through the polyorganosiloxane phase remains unknown. In principle, such a diffusion process should be governed by the thermodynamic compatibility between the polymer matrix and the coating and by the wetting kinetics, which in turns depends, among other factors, on the open character of the coating

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structure or its structural flexibility. A suitable way to estimate the flexibility of the coupling region under in-service conditions consists of the determination of the relaxation temperatures of the cross-linked polymer in the coupling region. Unfortunately, the mass fraction of polymer at the surface is small (less than 1%) and thermal methods are not adequate.

The electronic excited state of a solvatochromic fluorescent molecule such as the dansyl moiety is stabilized by solvent relaxation processes [8]. Its fluorescence spectrum provides information on the dielectric coupling between the excited chromophore and the solvent and, therefore, on the local polarity of the fluorophore environment [9]. On the other hand, dielectric coupling depends on the mutual mobility of the solvent and fluorophore in the solvation shell; as a consequence, the temperature dependence of the fluorescence emission should reflect changes in the mobility of the solvation cage [8].

Dansyl chloride (DNS) reacts with amine groups, yielding sulfonamide derivatives with (i) a very high quantum yield of fluorescence, (ii) an emission in the visible region, and (iii) a Stokes shift large enough so as to avoid autoabsorption effects. DNS is commonly used in biochemistry [10], characterization of polar sites in polymeric systems [11,12], and chemically modified silicic surfaces [13–15].

In this work, it is proposed to label an environmentally sensitive probe, such as DNS (5-N,N-dimethylaminophthalene-1-sulfonyl chloride), to the surface of glass fibers. The solvatochromic effects induced by low molecular weight solvents in contact with the glass fibers are used as a tool for studying the accessibility of small molecules through the coupling region/solvent interface. In addition, the temperature dependence of the fluorescence response of the label allows the determination of the thermal transitions of the polymer network. Combining experimental results and quantum mechanical calculations, the dipole moments of the ground state and S_1 and S_2 excited states are calculated. Solvent effects are explained in terms of the alternative estabilization of S_1 or S_2, depending on the nature of the solvent.

EXPERIMENTAL

Materials

E-type glass fibers from Vetrotex were used. γ-Aminopropyltriethoxisilane (APES) and 5-dimethyl-amino-1-naphthalenesulfonyl chloride (DNS) were purchased from Dynamic Nobel and Lancaster Synthesis, respectively, and used without further purification. Tolu-

ene was distilled over sodium just before use. The other solvents were high-quality products of fluorimetric grade.

Sample Pretreatments

Glass fibers were calcinated at 450°C for 1 h to remove all organic matter. Then they were subjected to an activation treatment with a 10% HCl aqueous solution for 3 h and repeatedly washed with distilled water until Cl$^-$ was removed. Fiber samples were dried at 110°C for 1 h and kept in a desiccator until silanization occurred.

Silanization

Silanization of activated fibers was performed using a 1% (v/v) APES aqueous solution during 10 min. Polymerization of silanized fibers was performed at 110°C for 1 h in an oven, and afterward they were subjected to Soxhlet extraction with dried toluene for 16 h and vacuum-dried for 8 h. Silanized samples were stored in a desiccator until use.

Dansylation

Well-dried silanized glass fibers were put in contact for 10 min at room temperature with a DNS solution (10^{-4} M) in acetonitrile (AcN). Then the fibers were Soxhlet extracted with dried toluene for 16 h and vacuum-dried for at least 8 h.

Fluorescence Measurements

Silanized glass fibers labeled with a dansyl group were immersed in the 15 solvents listed in Table I for 12 min. After that period, steady-state fluorescence spectra were recorded on a Perkin–Elmer LS-50B fluorimeter, using the standard front-face excitation accessory. The excitation wavelength was set at 340 nm and emission spectra were recorded from 360 to 600 nm. For each sample/solvent pair, excitation spectra were also recorded at $\lambda_{em} = 460$ nm. In both emission and excitation spectra, the slits and scan speed were set at 3 nm and 120 nm/min, respectively.

Low-temperature measurements were performed with the sample inside the oven of a Perkin–Elmer DSC-7 calorimeter using a light guide coupling with the fluorimeter. Details of the experimental arrangement are described elsewhere [16]. Fluorescence spectra were recorded between −155 and 100°C in steps of 5°C, waiting for 5 min between each measurement for proper thermalization.

Table I. Wavenumber at the Fluorescence Band Maximum and Solvent Parameters of Interest

Solvent (code)	δ	ε	μ (D)	Z (kcal mol^{-1})	E_T (kcal mol^{-1})	v_a (cm^{-1})	v_e (cm^{-1})	π^*	α	β
Cyclohexane (1)	8.20	2.02	0.0	60.1	31.2	29,586	21,668	0.08	0	0
1,4-Dioxane (2)	10.13	2.2	0.45	64.55	36.0	29,283	21,528	0.55	0	0.37
Toluene (3)	8.91	2.4	0.39		33.9	29,499	21,715			
Propylamine (4)	10.7	5.08	1.33			29,325	22,148			
Ethyl acetate (5)	9.1	6.0	1.88	64.0	38.1	29,369	21,692	0.55	0.0	0.45
THF (6)	9.9	7.6	1.75	58.8	37.4	29,542	21,834	0.58	0	0.55
CH$_2$Cl$_2$ (7)	9.88	8.9	1.55	64.2	41.1	—	—	0.82	0.3	0.00
n-Butanol (8)	11.60	17.5	1.75	77.7	50.2	29,630	21,810			
n-Propanol (9)	12.18	20.3	1.7	78.3	51.9	29,586	21,786	0.52	0.8	—
Acetone (10)	10.0	20.7	2.69	65.7	42.2	29,325	21,254	0.71	0.1	0.49
MeOH (11)	14.5	32.6	1.66	83.6	55.5	29,851	21,459	0.60	0.9	0.62
AcN (12)	12.11	35.9	3.44	71.3	46.0	29,498	22,026	0.85	0.2	0.31
DMF (13)	12.2	38.3	3.86	68.5	43.8	29,283	22,124	0.88	0.0	0.69
Me$_2$SO (14)	12.0	46.4	4.3	70.2	45.0	29,585	22,198	1.00	0	0.76
H$_2$O (15)	23.53	78.3	1.84	91.1	63.1	29,369	21,459	1.09	1.2	0.18
Dried fibers						28,818	21,882			

RESULTS AND DISCUSSION

Solvent Dependence of the Emission Spectra

The general solvatochromic effect of dansyl can be explained in terms of a dielectric relaxation mechanism [8]. The excited state of the dansyl group (π^*) has a higher dipole moment than the ground state; this leads to a reorientation of the solvent dipoles around it, lowering the energy of the emitting state. The higher the dielectric coupling between the excited chromophore and the solvent molecules, the higher the "stabilizing" effect and thus the longer the Stokes shift. This Stokes shift is defined as $\Delta v = v_a - v_e$, where v_a is the wavenumber of the absorption maximum (or the excitation spectrum band) and v_e is the wavenumber of the emission maximum.

Some examples of the changes in the emission spectra due to solvent effects are shown in Fig. 1, in which the emission spectra for different solvents are presented. It can be clearly appreciated how the wavelength of the emission maximum, λ_{em}, shifts depending on the solvent characteristics.

Solvatochromic shifts were analyzed in three ways: (i) variation of the Stokes shift as a function of some commonly used indices of solvent properties—Hildebrand's solubility parameter δ, Kosower's Z value, Dimroth and Reichard's E_T scale, the dielectric constant ε, and the dipole moment μ; (ii) the difference between the maximum emission wavelength, λ_{max}, from a model compound (free fluorophore) and that from the attached fluorophore in different solvents; and (iii) variation of the
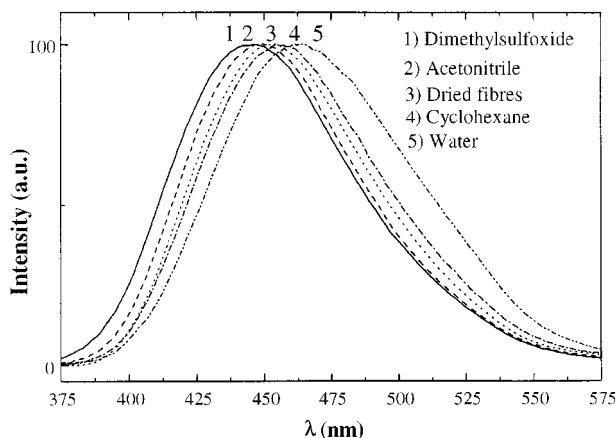

Fig. 1. Steady-state fluorescence spectra for dansyl-labeled glass fibers under the effects of some solvents.

Stokes shift with the orientational polarizability function (Δf) [8,17].

Table I summarizes the fluorescence results and solvent properties, δ, ε, μ, Z, and E_T, in addition to other parameters that will be defined further. Figures 2, 3, 4, 5, and 6 present the spectral shifts, Δv, vs the values of ε, μ, Z, E_T, and δ, respectively, for each solvent. These parameters are useful for correlating general solvent properties with the photophysical behavior of the dansyl chromophore.

Dielectric Constant. Figure 2 shows that there exists a clear linear correlation between the solvent dielectric constant and the electronic transition energy for the protic solvents 4, 8, 9, and 11. As expected, when the solvent polarity increases, the excited state of the fluorophore is
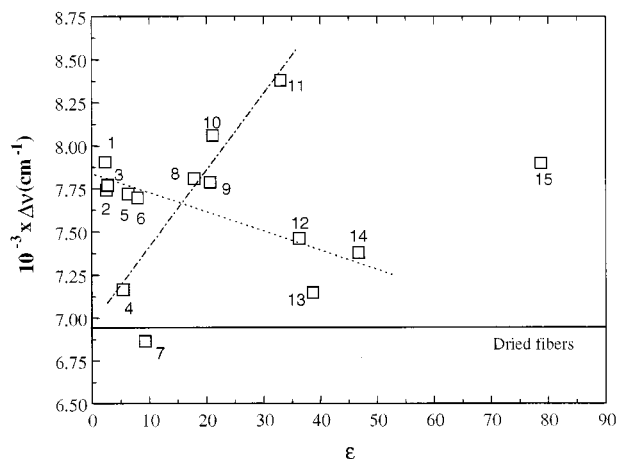
Fig. 2. Stokes shift ($\Delta v = v_a - v_e$) of the dansylamide conjugate emission as a function of the dielectric constant, ε, of several solvents.
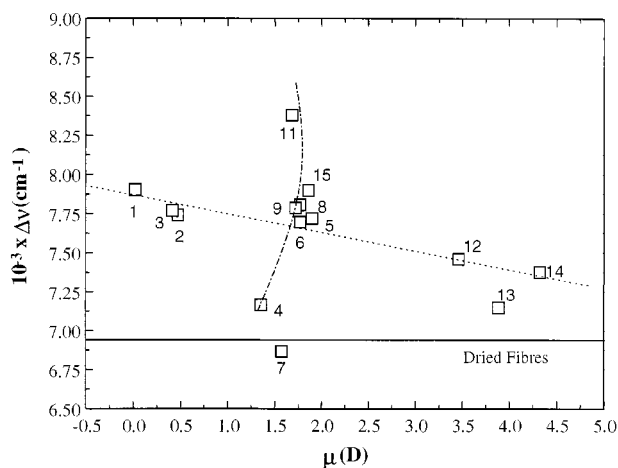

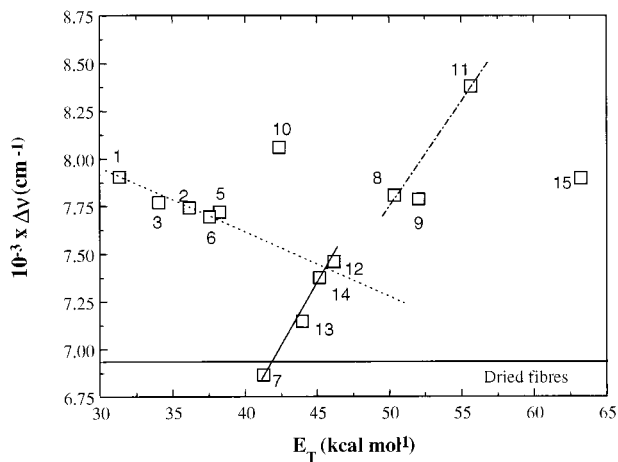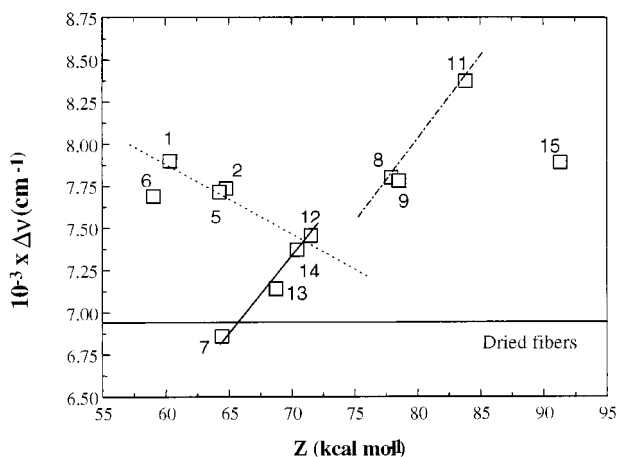**Fig. 5.** Stokes shift ($\Delta v = v_a - v_e$) of the dansylamide conjugate emission as a function of the Kosower parameter, Z, of several solvents.
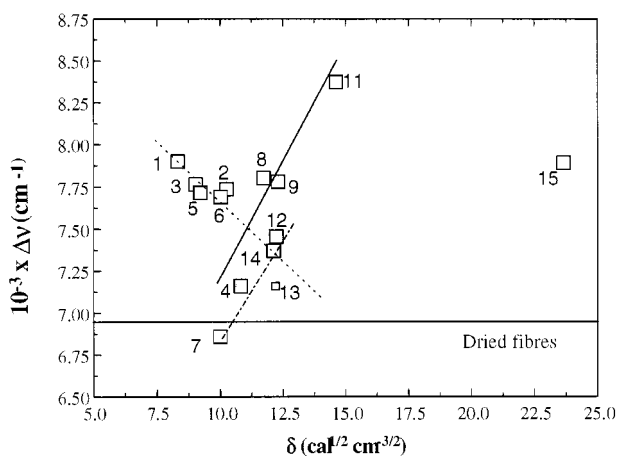

Fig. 3. Stokes shift ($\Delta v = v_a - v_e$) of the dansylamide conjugate emission as a function of the dipole moment, μ, of several solvents.

Fig. 6. Stokes shift ($\Delta v = v_a - v_e$) of the dansylamide conjugate emission as a function of Hildebrand's parameter, δ, of several solvents.

Fig. 4. Stokes shift ($\Delta v = v_a - v_e$) of the dansylamide conjugate emission as a function of the Dimroth parameter, E_T, of several solvents.

more stabilized. This behavior is similar to that of other polymeric systems where the dansyl moiety is labeled [11,15]. From the linear course a Stokes shift value for dansyl in water of $10.3 \times 10^{+3}$ cm^{-1} can be predicted; this value coincides fairly well with reported values for the dansyl moiety in water [18]. The fact that water deviates from the predicted values can be explained if nonfavorable interactions between the polymer and the solvent are taken into account. Contact angle results previously reported [3] support this hypothesis.

On the other hand, aprotic solvents (1–3, 5–7, 10, and 12–14) show an apparently opposite tendency, i.e., Δv decreases when ε increases. This result seems to be opposite to the expected behavior but it can be explained in terms of system mobility. Generally, when the dielectric constant of the solvent increases, both the ground and

the excited states of the fluorophore are stabilized. This dipolar stabilization requires a dipole reorientation of the solvent molecules [8]. This process needs the entire molecular motion of both the fluorophore and the solvent within the excited lifetime. As a result, the stabilization energy of the excited state of the fluorophore should depend not only on the dipole moments and intermolecular distances but also on the system rigidity, the latter being strongly dependent on the polymer swelling. Accordingly, the negative trend found for the Stokes shift variation reflects the slight tendency of polar solvents to interact with the coated fiber. A deeper analysis of the interactions in the labeled polymer/solvent system is done in terms of the solubility parameter, although correlations with μ and other polarity parameters (Z and E_T) illustrate some interesting aspects that are worthy of mentioned.

Dipole Moment. The Δv variation as a function of μ (Fig. 3) shows a tendency similar to that in the case of the dielectric constant (Fig. 2). For the protic solvent group it can be observed that very small changes in the dipole moment yield large Stokes shifts, therefore, charge separation in protic molecules does not seem to be related to the stabilization of both the excited and the ground states of the fluorophore. This result suggests that, for these solvents, some specific interaction between the solvent and the dansyl moiety must be in the origin of the excited-state stabilization. The results obtained for aprotic solvents show a behavior similar to that of the results for the dielectric constant: a slight decrease in the Stokes shift as the dipole moment increases.

Kosower's Z and Dimroth's E_T Parameters. In Figs. 4 and 5 Δv is plotted as a function of the well-known polarity scales [19] Z and E_T, respectively. In contrast with the previous plots (Figs. 2 and 3), these compare the fluorescence of the labeled dansyl moiety with the absorption of 1-ethyl-4-carbometoxypyridinum iodide (Z) or the intramolecular charge transfer band of pyridinum-N-phenolbetaine (E_T). Therefore, the compared magnitudes are much more similar and the correlations that can be obtained better express all of the effects associated with the fluorophore–solvent interaction. In fact, three groups of solvents can be clearly observed: (i) nonpolar aprotic solvents ($\varepsilon \leq 7.6$), where Δv decreases with Z and E_T; (ii) polar aprotic solvents ($\varepsilon \geq 8.9$), where Δv increases with Z and E_T; and (iii) protic solvents, where Δv has the highest values and increases with Z and E_T.

Solubility or Hildebrand's Parameter, δ. Spectral shifts of the DNS as a function of Hildebrand's parameter, δ_{SOL}, are depicted in Fig. 6. The solubility parameter of the coating polymer was estimated as $\delta_{POL} = 8.3$ cal$^{1/2}$ cm$^{-3/2}$ using the group contribution method [20]. Taking into account the miscibility predictions based on the dif-

ference between δ_{POL} and δ_{SOL} [20], those solvents with a solubility parameter similar to that of the polymer should solvate it. According to Table I, the nonpolar aprotic solvents (group i), have values of δ similar to that of the polyaminosiloxane. Similar intermolecular interactions should be expected, and therefore, all of them should yield a similar Δv value. Nevertheless, the Stokes shift for dried fibers is much lower (900 cm^{-1}) than the corresponding value for wetted fibers. This result suggests that the dansyl moiety is located in a rigid environment that cannot couple efficiently with the excited state. Solvating molecules such as those in group i swell the polymer, increasing the local flexibility, dielectric relaxation becomes possible, and the excited state is stabilized.

For polar aprotic solvents (group ii), except for CH_2Cl_2, $\delta_{solvent} > \delta_{polymer}$, the miscibility condition is not fulfilled, and therefore, these solvents do not swell the coating polymer. The wetting ability of these nonsolvents may be not enough to stabilize the excited state of the dansyl group and the "environmental rigidity" effect may predominate. This argument could be the explanation of the Stokes shifts found for this solvent group; they are lower than those found for group i.

Finally, protic solvents (group iii) behave as does group ii, although with higher Stokes shifts. This result might be due to the presence of specific interactions (hydrogen bonding) between protic solvents and the dansyl excited state or to a higher degree of polymer swelling. In the first case, hydrogen-bonding formation allows additional excited-state stabilization in the chromophore [17], while in the second case, a higher degree of swelling would allow local flexibility enhancement, easier dielectric relaxation, and, therefore, greater excited-state stabilization.

Analysis of the different types of polymer/solvent interactions can offer a way to decide which of the two possibilities mentioned above is more correct. Hanssen and Skaarup [21] assumed that the cohesive energy density between solvent molecules arises from dispersive, dipole–dipole, and hydrogen-bond forces; they expressed the solubility parameter as the sum of three terms (eq. 1):

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{1}$$

where δ_D, δ_P, and δ_H are the disperse, polar, and hydrogen-bond contributions, respectively. The contributions δ_D and δ_P for the polymer were estimated using the following empirical expressions [20]:

$$\delta_D = 9.55 n_D - 5.55 \tag{2}$$

$$\delta_P = (12,108/v^2) \cdot [(\varepsilon - 1)/(2\varepsilon - n_D^2)] \cdot (n_D^2 + 2) \cdot \mu^2 \tag{3}$$

where $n_D = 1.423$, $\varepsilon = 3.1$, and $\mu = 3.38$ D are the refraction index, dielectric constant, and dipole moment of the APES monomer. The molar volume, v, was estimated from the density, $\rho = 0.97$ g cm^{-3}, and the molecular weight, $M = 74.12$ g mol^{-1}, of the monomer. As an approximation, the contribution δ_H of the polymer was taken from the propylamine ($\delta_H = 5.9$ MPa$^{1/2}$).

To predict the degree of swelling of the poly-APES, a three-dimensional plot was used (Fig. 7), in which the fractional contributions to the solubility parameter for the polymer and all of the solvents are shown. The points that are nearest neighbors of the polymer should correspond to the best solvents of the polymer. As can be clearly observed, except for propylamine, protic solvents are far away from the polymer. It is therefore possible to conclude that the main cause for the long Stokes shifts presented by protic solvents (Fig. 6) must be specific interactions between the fluorophore and the solvent.

Comparison Between Free and Labeled Fluorophores

To study the accessibility of the solvents, the behavior of dansylpropylamide as a model compound (free fluorophore) was compared. From reported data on this molecule [15] the parameters of Taft and Kamlet's relationship [11] were obtained by a nonlinear fitting procedure. Results are shown in Eq. (4):

$$\lambda_{cal} = 61.88\pi^* + 28.38\alpha + 22.08\beta + 433.3 \quad (4)$$
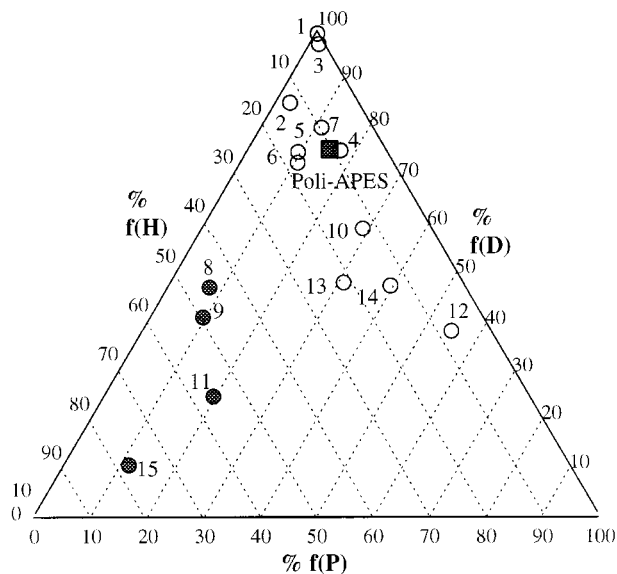
This expression estimates the wavelength at the max-

imum for the free probe (model compound) in solvents with known values of π^* (solvent dipolarity/polarizability), α (hydrogen-bond donor strength), and β (hydrogen-bond acceptor strength). A plot of λ_{cal} vs λ_{exp} is given in Fig. 8. The diagonal line corresponds to Eq. (4). In Fig. 8 the fluorescence emission maxima of the model compound in pure organic solvents are plotted jointly with the emission values of the labeled dansyl in both the dried and the wetted fibers, λ_{exp}. It can be observed that the λ_{exp} values are systematically far away from the Taft line. This result confirms the weak interaction of the labeled fluorophore with solvents.

For polar aprotic solvents such as AcN, DMF, and $(CH_3)_2SO$, λ_{exp} is even lower than for the dried fibers. This result can be understood in terms of a solvophobic effect. The intermolecular interactions between the polymer coating and these solvents are so unfavorable that they may induce the collapse of the polymer layer, therefore decreasing the fluorophore mobility.

Variation of the Stokes Shift with the Orientational Polarizability Function (Δf)

Figure 9 presents, for each studied solvent, the Stokes shift value, Δv, as a function of the orientational polarizability function [8,17], Δf. As in the case of Figs. 5 and 6, it is possible to classify the solvents into three groups where linear correlations can be drawn.

From the slope corresponding to the group of polar aprotic solvents (7 and 12–14), the change in the permanent dipole moment, $\Delta\mu = \mu_P^* - \mu_0$ can be obtained according to the Lippert approximation [8,17]; μ_P^* and μ_0 are the dipole moments in the excited and ground state, respectively. Taking the Onsager cavity radius as
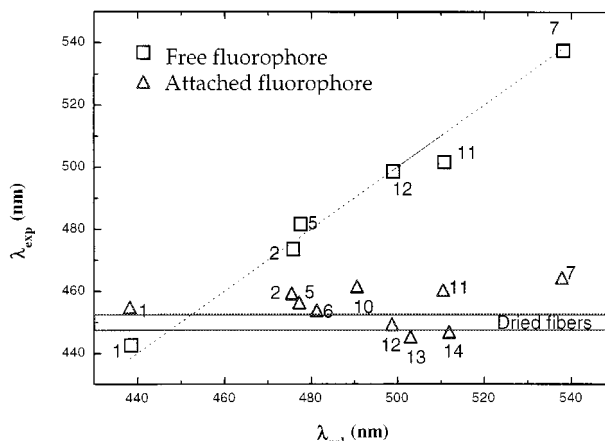

Fig. 7. Fractional contributions to the solubility parameter, $\%f(i) = \delta_i^2/\Sigma\delta_i^2$ (i = D, P, H), of the polymer and all the studied solvents.

Fig. 8. Experimental vs calculated λ_{max} in several solvents (the horizontal line is for dried fibers).
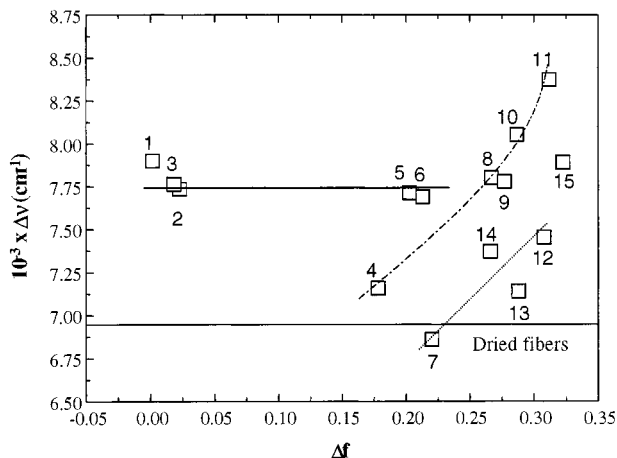
Fig. 9. Stokes shift values, Δv, as a function of the orientational polarizability function, Δf.

$a = 3.85$ Å [12], the change in the permanent dipole moment has been estimated as 6.0 D.

Using quantum mechanical calculations (AM1 method), it is possible to estimate the energy, $E(\phi)$, of the ground state, S_0, and both the first and the second excited states, $S_1(\phi)$ and $S_2(\phi)$, as a function of the torsion angle, ϕ, formed between the dimethylamino plane and the naphthalene ring. The dipole moment for each state was averaged according to the expression

$$\langle \mu^2 \rangle = \sum \mu_{\phi i}^2 \exp\{-E(\phi i)/kT\}/\sum \exp\{-E(\phi i)/kT\} \quad (5)$$

where $\mu_{\phi i}$ and $E(\phi_i)$ are the dipole moment and energy of the DNSA molecule, estimated by AM1, for each angle ϕ_i; k is the Boltzman constant; and T is the absolute temperature (293 K).

The root mean square dipole moment for the ground state of the model compound dansylpropylamide was estimated as $\langle \mu_0^2 \rangle^{1/2} = 5.9 \pm 0.3$ D. Assuming that this value can be taken as a measure of μ_0, the dipole moment of the dansyl excited state in a polar aprotic solvent can be estimated as $\mu_P^* = \Delta \mu + \mu_0 = 11.9 \pm 1.5$ D.

For nonpolar aprotic solvents the Stokes shift seems to be constant with the orientational polarizability function. This result suggests that the excited-state stabilization is due not to dipole–dipole interactions but to dipole-induced dipole interactions between the excited dansyl moiety and the high-polarizability solvent molecules. Therefore, in this case it is more convenient to study the stabilization energy in terms of Eq. (6) [17].

$$v_a - v_e = (\tfrac{1}{2} a^3 hc) \cdot (\mu_{NP}^{*2} - \mu_0^2) \cdot f(n^2) \quad (6)$$

where μ_{NP}^* and μ_0 are the dipole moments of the ground and excited states, respectively, h is Planck's constant, c

is the speed of light, a is the Onsager cavity radius, and $f(n^2)$ is the high-frequency polarizability function, $f(n^2) = 2(n^2 - 1)/(2n^2 + 1)$.

Fitting to Eq. (6) the Δv values as a function of $f(n^2)$ for solvents 1–6, the average dipole moment of the excited dansyl group attached to glass fibers under the effect of nonpolar aprotic solvents was estimated as $\mu_{NP}^* = 7.2 \pm 1.6$ D. This value is lower than that calculated for the excited state in the presence of polar aprotic solvents, μ_P^*.

By using Lippert's correction factors [8] due to solvent effects in the energy of the states (AM1 calculations), the square mean dipole moments for the two excited states S_1 and S_2, $\langle \mu_1^{*2} \rangle$ and $\langle \mu_2^{*2} \rangle$, of dansyl were calculated from Eq. (5) for each solvent. In all cases, it was determined that $\langle \mu_1^{*2} \rangle^{1/2} \approx 7.3 \pm 0.5$ D and $\langle \mu_2^{*2} \rangle^{1/2} \approx 9.3 \pm 1.4$ D. D. Comparison with experimental results yields that $\mu_{NP}^* \approx \langle \mu_1^{*2} \rangle^{1/2}$ and $\mu_P^* \approx \langle \mu_2^{*2} \rangle^{1/2}$.

The fact that the permanent dipole moment of the dansyl excited state, i.e., the emitting state, depends on the solvent polarity is in agreement with the interpretation of Hercules and co-workers [18] for the photophysics of dansyl. The results of our calculations show that in nonpolar solvents, fluorescence arises from the ^1L_b state (S_1), and in polar solvents, from the ^1L_a state (S_2). Although interactions between the dansyl excited and the dansyl ground states when it is attached to a solid support are not very favorable because of the chemical nature of the polymer coating, the relatively good coincidence between experiment and calculations is noteworthy. Therefore it seems that mobility restrictions imposed by the solid support have no important effect on the nature of the excited state.

Effect of Temperature

In Fig. 10, v_{MAX} is plotted as a function of absolute temperature. A gradual red shift is observed as the temperature increases, with an overall change of about 600 cm^{-1}, greater than the expected thermal energy for a 250 K temperature increase. These results are interpreted as following. The emission energy is high and nearly constant below the transition temperature, T_1, of the matrix, and the excited state is stabilized by electronic polarization only because the orientation polarization is restricted due to the frozen state of the matrix. The dipole orientation time is too long and emission comes from a nonrelaxed excited state of the chromophore. This transition temperature is 175 K, which agrees with the relaxation temperatures of other polysiloxanes [22]. Above T_1 the dipole orientation time becomes progressively shorter and the excited state is additionally stabilized by solvent relax-
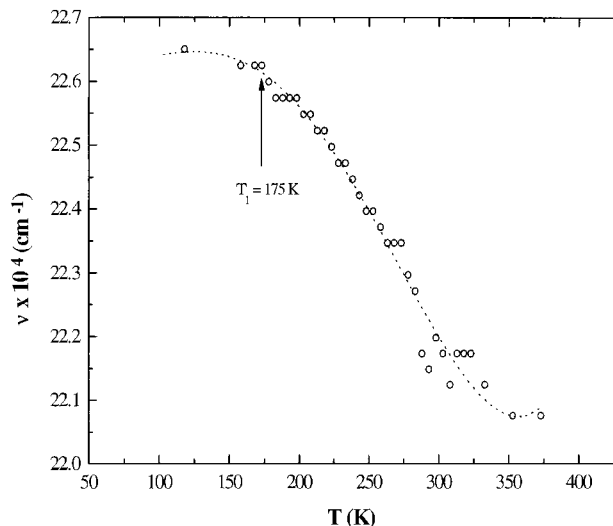
Fig. 10. Variation of the fluorescence emission band maximum wavelength for dansylsulfonamide as a function of temperature.

ation processes. As a consequence, the emission energy decreases strongly with temperature.

CONCLUSIONS

The use of the dansyl group as a fluorescence label is a very easy analytical method for understanding substrate coating microstructures such as polyorganosiloxane layers on glass fibers. Stokes shift variations when labeled fibers are impregnated in different solvents should allow determination of the thermodynamic compatibility and accessibility of polymer matrices and reinforcements in composite materials. Temperature-induced shifts allow also to study coating relaxations and, therefore, changes in coating rigidity. A transition temperature of 175 K was determined for the coating polymer used.

From the solvent accessibility study it was concluded that, for aprotic solvents, the solvent dipolar coupling relaxation mechanism is dominated by thermodynamic interactions between the solvent and the coating polymer, while for protic solvents, this mechanism is dominated by specific interactions between solvent molecules and the excited state of the chromophore.

The properties of the emitting state of the dansyl moiety depend on the solvent polarity. When a polar solvent is in contact with the fluorophore, the corresponding dansyl excited state is S_2 and its dipole moment value was estimated as $\mu_P^* = 11.9 \pm 1.2$ D. When a nonpolar solvent is used, the dansyl excited state corresponds is S_1 and its dipole moment was estimated as $\mu_{NP}^* = 7.2 \pm 1.6$ D.

ACKNOWLEDGMENTS

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