

Characteristic Features of the Matrix Effect on the Stokes Shift of Fluorescent Dye Molecules in Pure and Plasticized Polymers

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Synopsis

The influence of the chemical structure, composition, and physical properties of polymers [polyacrylates and -methacrylates, poly(vinyl acetate), polystyrene, and polybutadiene] and plasticized polymers [poly(methyl methacrylate) and polystyrene] on the Stokes shift of fluorescent dyes has been investigated. The results indicate that the structure and overall mobility of the polymer matrix as well as the nature of the dopant all together influence the separation of the absorption and emission band of a given fluorescent dye. In general, polar and highly flexible polymers favor the band separation. The effect of both polar and apolar dopants seems to be primarily a plasticization in case of polar polymers, whereas for apolar polymers the plasticizer effect can be neglected and the increased Stokes shift upon addition of polar dopants has to be attributed to particular dopant/dye interactions. These findings open some new routes to improve the efficiency of solar collectors based on fluorescent dyes.

INTRODUCTION

The use of the fluorescence of dye molecules for the collection of light has been demonstrated¹⁻⁴ and its application has been proposed for solar energy collection.^{5,6} The principle features of these systems, which are composed of fluorescent dye molecules embedded in polymer plates, have been described elsewhere.⁶⁻¹⁰ However, in order to achieve a maximum collection efficiency, i.e., for a high output of the incident light in form of fluorescent light, a complete separation of the absorption and emission bands of the fluorescent dye is desired. From the physical point of view, this requirement can only be satisfied if there is optimum stabilization of the excited dye molecule by the medium such that there is a large difference between the energy needed for excitation and the emitted energy, thus leading to a large difference between the wavelengths of the maxima of the absorption and fluorescence bands, the so-called Stokes shift.^{11,12}

Stabilization of the excited state by interaction with the environment is much easier in a medium of low viscosity than in a highly viscous medium, e.g., a glass or a polymer matrix (cf. Refs. 13 and 14). The energy of the excited state of the dye molecule in a low molecular weight liquid is lowered by reorientation of the solvent molecules around the dye due to its increased dipole moment in the excited state.

The degree of stabilization for a given fluorescent dye depends on several parameters, such as the polarity and steric features of the solvent molecules and, of course, the mobility of the solvent molecules within the life time of the excited state.¹¹ When going from a low molecular weight liquid to a polymer melt or glass, steric effects and especially the restrictions on the mobility of polymer segments are the most important factors, both of which greatly decrease the possibilities for stabilization of the excited molecules. As a consequence, one usually observes higher frequencies for the fluorescence maximum in a polymer matrix compared to those in a low molecular solvent of a similar chemical structure as the basic monomer unit of the polymer.¹⁴

In order to overcome these restrictions, attempts have been made to dope a polymer matrix with low molecular compounds.¹⁵⁻¹⁷ It was hoped that the dopant would act as a plasticizer or would be able to interact directly with the fluorescent dye, two effects which both should result in a better stabilization of the excited state of the dye. In fact, it was found that, by doping a rigid matrix with polar molecules, almost total separation of the absorption and fluorescent band can be achieved, the extent of separation varying with the nature (polarity, size, relaxation time) and also with the concentration of the dopant.^{15,17}

However, it is still unclear if, and to what extent, the dopant acts as a plasticizer by increasing the overall segmental mobility of the polymer matrix, and thus facilitating the interaction polymer/dye, or if the possible direct dopant/dye interaction is the decisive factor as it has been inferred from previous work.¹⁵ In order to get some indication of the role of the dopant in the polymer/dye system, we have performed some basic experiments using 4-dimethylamino-4-nitrostilbene (DMANS) as a fluorescent dye dissolved in pure polymers of different chemical and physical properties, and also in the same polymers doped with various low molecular weight compounds of different polarity.

EXPERIMENTAL

The fluorescent dye, 4-dimethylamino-4'-nitrostilbene (DMANS, Eastman Kodak) was used without further purification.

Poly(ethylacrylate) (PEA), poly(*i*-butylmethacrylate) (PiBMA) and poly(*n*-butylmethacrylate) (PnBMA) were synthesized by free radical polymerization in toluene at 70°C with AIBN as initiator, and were precipitated in methanol. Poly(methyl methacrylate), (PMMA, Röhm, Darmstadt), poly(vinyl acetate) (PVAc, Bayer AG, Leverkusen), polystyrene (PSt, Chemische Werke Hüls), and 1,4-*cis*-Polybutadiene (PBd, Chemische Werke Hüls) were commercial grade polymers.

The dopants camphor (Merck, Darmstadt), *n*-heptane (Uvasol, Merck, Darmstadt), and *n*-dodecane (Merck, Darmstadt), were used without further purification; methylisobutyrate (MIB, Merck, Darmstadt) and diethylphthalate (Merck, Darmstadt) were freshly distilled prior to use.

Polymer films were prepared by solution casting on glass plates from chloroform (p.a. Merck, Darmstadt) solution of the polymer/dye and the polymer/dye/dopant mixture. The thickness of the polymer films varied between 0.1 and 0.3 mm, the concentration of DMANS was lower than 10⁻⁵ mol/L.

The glass transition temperatures T_g of the polymer samples were determined with a Perkin-Elmer DSC-2 instrument at a heating rate of 20°C/min with indium as standard.

Excitation was achieved using monochromatic light (150-W Osram XPO Xenon lamp) in the wavelength range of the absorption maximum. The other experimental conditions were the same as previously described.¹⁵

RESULTS AND DISCUSSION

As a general feature, it was observed that the absorption spectrum and the wavelength of the absorption maximum of DMANS is little affected by the chemical structure and physical state of the polymer matrix varying between 420 and 438 nm, and there was also no significant temperature effect. The same can also be said for the absorption spectrum of the dye in a doped polymer and for the absorption maximum in low molecular weight solvents. As a consequence, any observed variation in the Stokes shift has to be attributed nearly exclusively to the change in the fluorescence band maximum, i.e., to the ability of the matrix elements (polymer chain, side groups, dopant) to lower the energy of the excited state of the dye molecules by particular reorientation and interactions.

Effect of Chemical Structure and Physical Properties of Pure Polymers and of Temperature on the Stokes Shift

The chemical structure of the polymer, i.e., the polarity of the polymer repeat unit affects the Stokes shift in the same way as is known to occur for low molecular weight solvents (cf. Ref. 11). This is evident from the data in Table I and particularly from comparison of the Stokes shift observed in PMMA as a polar polymer ($\Delta\lambda = 131$ nm) and PSt as an apolar polymer ($\Delta\lambda = 102$ nm) at room temperature, where both polymers are in the glassy state at nearly the same state of supercooling.

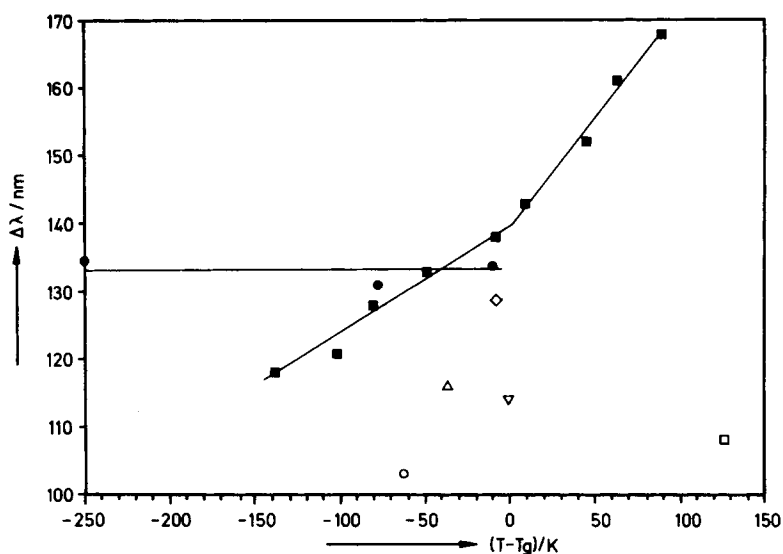


Fig. 1. Dependence of the Stokes shift $\Delta\lambda$ of DMANS in different pure homopolymers on temperature T normalized to the glass transition temperature T_g ; (●) PMMA ($T_g = 375$ K); (■) PEA ($T_g = 253$ K); (Δ) PiBMA ($T_g = 334$ K); (▽) PnBMA ($T_g = 298$ K); (◇) PVAc ($T_g = 306$ K); (○) PSt ($T_g = 360$ K); (□) PBd ($T_g = 173$ K).

Besides the polarity, steric factors are also important, as can be seen from the comparison of the Stokes shift in PMMA and either PiBMA or PnBMA and also in PMMA and PEA: The polar ester carbonyl group is much less shielded by the methyl ester group in PMMA than in PiBMA or PnBMA by the bulkier butylester group, therefore allowing a better interaction with the dye. Furthermore, additional substitution of the main chain decreases the accessibility of the carbonyl group and leads to a decrease in the Stokes shift, as one can see, e.g., from the comparison of the figures obtained for PnBMA and PEA. It is interesting to note that the Stokes shift in glassy PnBMA and PiBMA is similar to that found for rubbery PBd; this again clearly demonstrates the extensive restrictions in the possibilities of interaction of the carbonyl group with the dye due to the shielding effect of the aliphatic ester substituents, i.e., the fluorescent dye doesn't take notice of the polar side groups and behaves as if it were surrounded by pure aliphatic medium.

The effect of temperature on the Stokes shift seems to depend mainly on the change in the physical state and the corresponding change in the chain segmental mobility; in addition, some structural and steric features have to be considered. Figure 1 shows the temperature dependence of the Stokes shift in glassy PMMA and PEA and in rubbery PEA together with some figures obtained at room temperature for other polymers. Whereas for glassy PMMA no temperature dependence is found, over a broad temperature range a distinct increase in the

TABLE I
Absorption (λ_A) and Emission Band (λ_E) Maxima and Stokes Shift ($\Delta\lambda$) of DMANS in Pure PMMA, PiBMA, PnBMA, PEA, PVAc, PSt, PBd Matrix, and in PMMA Matrix Doped with Camphor at Room Temperature and of Glass Transition Temperature T_g of Corresponding Matrix

Polymer	Camphor (wt %) (T_g in K)	Temp (K)	λ_A (nm)	λ_E (nm)	$\Delta\lambda$ (nm)
PnBMA	0 (298)	298	432	546	114
PiBMA	0 (334)	298	425	541	116
		334	425	542	117
PMMA	0 (375)	298	438	569	131
		375	438	572	134
PEA	0 (253)	298	432	587	155
		253	432	574	142
PVAc	0 (306)	298	438	567	129
		306	438	567	129
PSt	0 (368)	298	435	537	102
		368	435	538	103
PBd	0 (173)	298	422	536	114
		173	422	534	112
PMMA	0 (375)	298	438	569	131
		375	438	572	134
	4 (336)	298	438	588	150
		336	438	590	152
	7.5(327)	298	438	594	156
		327	438	594	156
	17 (318)	298	440	602	162
		318	440	604	164

Stokes shift with increasing temperature is observed for PEA; this effect can only be attributed to the higher main chain mobility of PEA as compared to PMMA, due to the lack of the α -substituent (methyl group) in the former polymer which greatly hinders the rotation around the carbon-carbon bond in the backbone. This is also confirmed by the nearly constant figures compiled in Table I for the Stokes shift in various polymers at and below T_g .

When going from the glassy matrix to the liquid rubbery matrix, the temperature coefficient of the Stokes shift in the polar, highly flexible PEA is higher than in the glassy matrix; this finding is in agreement with the change of the temperature dependence of the specific volume in amorphous glassy polymers and polymer melts, and it reflects the faster increase of the free volume above the glass transition temperature which facilitates the chain segmental motions as compared to the glassy state, where the long range motions are largely frozen in. The comparison with the PBd matrix (see Table I), also a highly flexible polymer but without polar groups, demonstrates the combined effect of the polarity of the polymer side group and the increase in segmental mobility as a requirement for an increased absorption/emission band separation.

Effect and Role of Dopant on the Polymer/Dye System and the Stokes Shift

It was already evident from earlier studies¹⁵ that the Stokes shift of the fluorescent dye in a polymer (PMMA) could be increased greatly by addition of polar

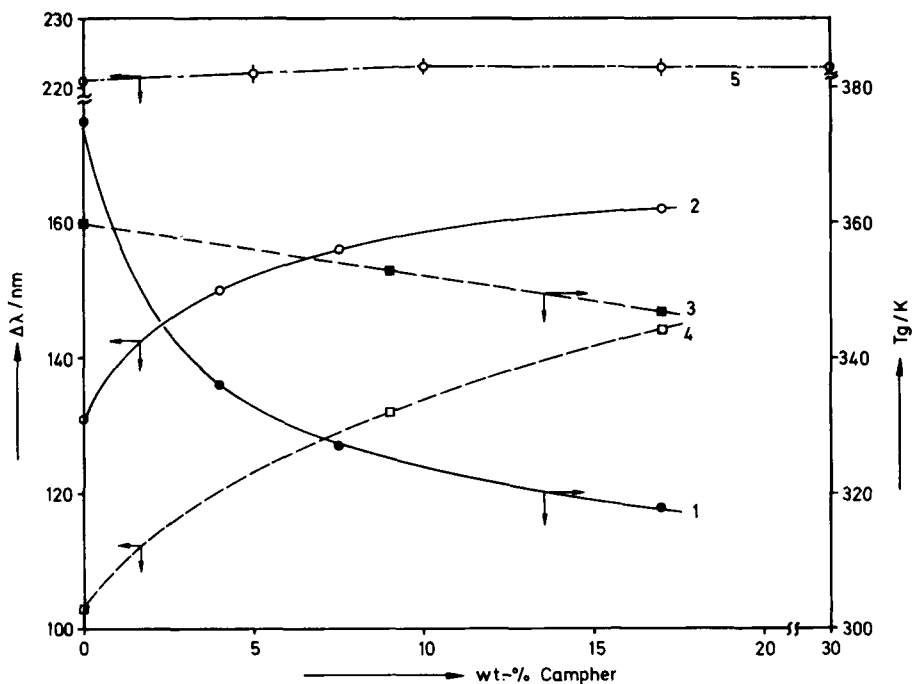


Fig. 2. Variation of the Stokes shift $\Delta\lambda$ of DMANS (open symbols) and the glass transition temperature T_g (solid symbols) on the camphor concentration in PMMA [---, curve 2 (O), 1 (●)], in PST [—, curve 4 (□), 3 (■)], and in MIB [---, curve 5 (◇)].

dopants such as either DMSO or camphor. In order to be able to discriminate between the action of the dopant as a pure plasticizer and the importance of a specific interaction of the dopant with the dye molecule, the effect of camphor as a dopant on the physical properties and the Stokes shift of DMANS was investigated for PST and PMMA as examples of apolar and polar polymers, respectively. It was found for both polymers that with increasing concentration of camphor the glass transition temperature T_g decreases (curves 1 and 3, Fig. 2) and simultaneously the Stokes shift in the glassy polymers increases (curves 2 and 4, Fig. 2). However, whereas in the case of the polar polymer PMMA the increase in the Stokes shift is direct proportional to the change in the T_g , in case of the relatively apolar PSt the increase in the Stokes shift upon doping with camphor clearly exceeds what would be expected from the decrease in T_g . This discrepancy between these two systems becomes even more evident when comparing the plots of the change of the Stokes shift with the change in T_g upon addition of the camphor dopant (Fig. 3) to PMMA (line 1) and PSt (curve 2). Even MIB, the low molecular weight analogue of the monomer unit, plays only the role of a plasticizer for PMMA (see Fig. 3), in spite of the fact that an optimal band separation is observed in this solvent, as can be seen from Figure 4, where some representative absorption and fluorescence spectra of DMANS in different media are depicted.

These findings point to the fact that, in a polar polymer, the dopant predominantly acts as a plasticizer by increasing the local segmental mobility and thus increasing the probability for a successful interaction of the polar side groups with the dye in regard to a lowering of the energy of the excited state of the dye molecule. In contrast, the role of the dopant in an apolar polymer with relatively little possibilities of strong polymer dye interactions is mainly a direct interaction with the dye itself, rather than the plasticizer effect seen for a polar polymer, and

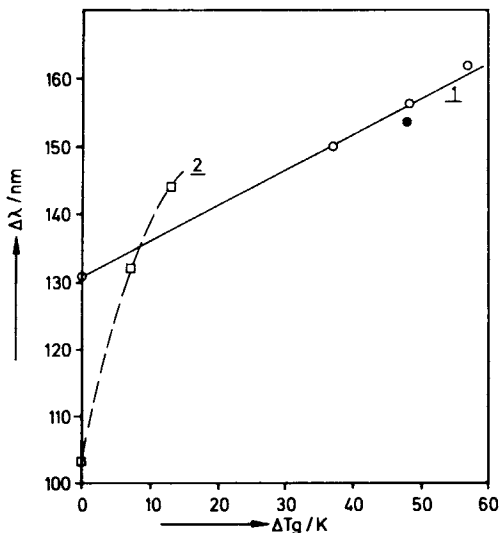


Fig. 3. Dependence of the Stokes shift $\Delta\lambda$ at room temperature on the glass transition temperature depression ΔT_g upon doping in PMMA [$T_g = 375$ K; dopant concentration 0, 4, 7.5 and 17 wt % camphor (O) and 9 wt % MIB (●)], curve 1, and in PSt [$T_g = 360$ K; dopant concentration 0, 9, and 17 wt % camphor (□)], curve 2.

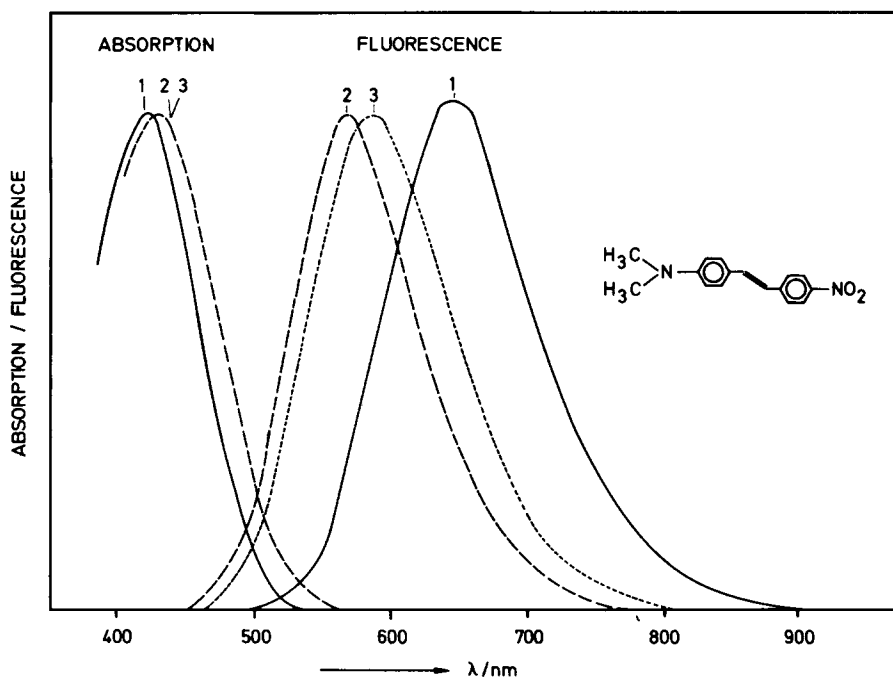


Fig. 4. Absorption and fluorescent spectra of DMANS at room temperature in different media; the spectra are normalized to the same maximum intensity: (1) (—) MIB solution; (2) (---) PMMA matrix; (3) (···) PMMA matrix doped with 9 wt % MIB.

the efficiency of the dopant depends on its solvation power for the dye (see below).

This view is supported by the constant value of the Stokes shift of DMANS in MIB solution, which can be considered as a model for the repeat unit in PMMA, and in MIB/camphor mixtures of varying camphor concentrations (curve 5, Fig. 2). Evidently, the Stokes shift is unaffected by the addition of camphor, since the MIB solvent alone allows an optimal band separation (see Fig. 4) due to its comparatively high polarity.

As already mentioned above, the characteristics of the dopant, i.e., its abilities to interact with the dye and to stabilize the excited state, determine the effectiveness of the dopant on the increase of the Stokes shift in an apolar polymer. This is further clarified by comparing the various dopants, which, as solvents alone, give very different Stokes shifts for DMANS solutions, and by relating both the change in T_g of the doped polymers and the observed change in the Stokes shift to the nature of the dopant.

In solutions of aliphatic dopants such as *n*-heptane or *n*-dodecane, a minimum Stokes shift is generally found, i.e., a maximum overlapping of the absorption/emission band. Therefore, as can be assumed from the results discussed above, no effect is to be expected on the Stokes shift in an apolar polymer, but only on the glass transition temperature T_g of the polymer matrix. As can be seen from curve 4 in Figure 5, the only effect of aliphatic dopants is to change the glass transition temperature; the Stokes shift remains constant. Surprisingly, the Stokes shift is slightly higher in the polystyrene and also the polybutadiene matrix than in the pure dopant solvent, probably due to the limited interaction

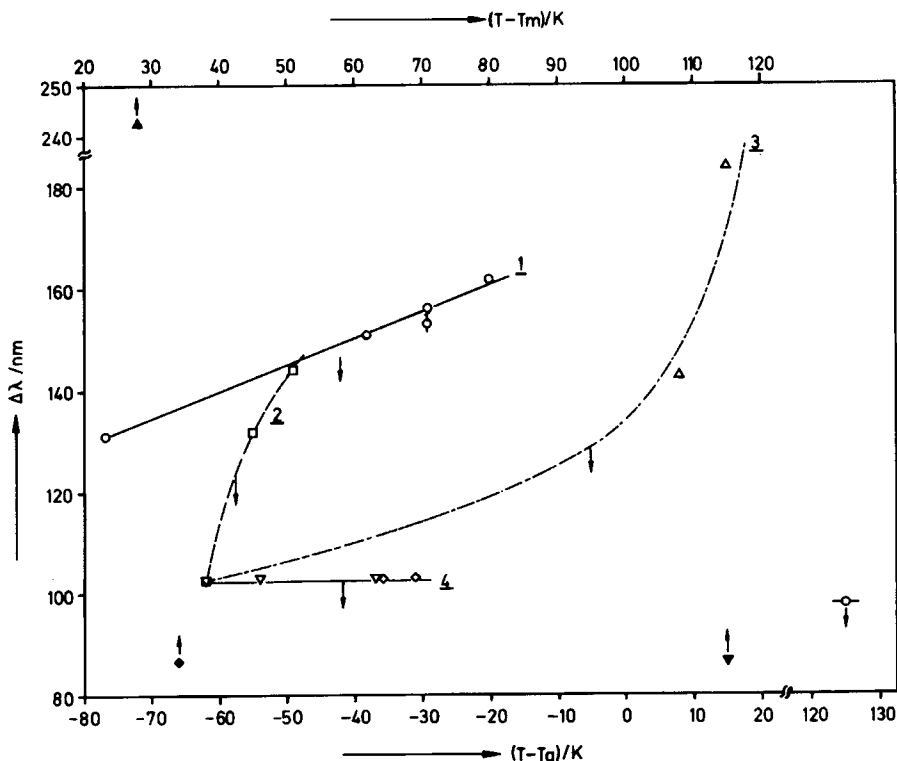


Fig. 5. Dependence of the Stokes shift $\Delta\lambda$ of DMANS at room temperature on $T - T_g$ for PMMA and PSt on the nature and concentration of different dopants; (1) (---) PMMA + 0, 4, 7.5, and 17 wt % camphor (O) and 9 wt % MIB (Φ); (2) (-·-·): PSt + 0, 9, and 17 wt % camphor (\square); (3) (-·-·) PSt + 20 and 35 wt % diethylphthalate (Δ); (4) (—) PSt + 20 and 40 wt % *n*-heptane (∇) and 20 and 40 wt % *n*-dodecane (\diamond); the full symbols indicate $\Delta\lambda$ of DMANS dissolved in the pure dopant at room temperature, i.e., above the melting temperature T_m of the dopant.

of the aromatic phenyl groups (or the olefin group in PBd) with DMANS. In contrast to this, the Stokes shift in PSt doped with camphor or diethylphthalate is much lower than in the pure dopant solvents but increases with increasing dopant concentration, and to a larger extent than the glass transition temperature is affected (see above). This is particularly evident for the camphor/PS system (compare with Fig. 3) and also for the system diethylphthalate/PS at temperatures above T_g . For the latter system it is interesting to note that, in the glassy state below T_g , the same behavior as for the system camphor/PMMA is observed, i.e., a variation of the Stokes shift proportional to the change in T_g . These observations together with the observed large change above T_g and also the differences in the effect of the dopant concentration on T_g and the Stokes shift clearly show the complex interactions of the different components in these systems. However, it is clear that, in an apolar polymer, only polar dopants effect the Stokes shift of a fluorescent dye.

CONCLUSIONS

The overlapping of the absorption and emission bands in a polymer matrix, i.e., the blue shift of the fluorescent band in comparison to a solution of the dye

in a low molecular weight solvent, is due mainly to the restrictions in the solvation and stabilization of the fluorescent dye in its ground and excited state by the polymer main chain and side groups. From the data presented here it is evident that both the chemical structure and physical properties of the polymer matrix and specific polymer/dye as well as dopant/dye interactions play important roles in the fluorescence behavior of the dye. Of course, besides this, the chemical structure and physical properties of the dye molecule itself determine the overall absorption and fluorescence behavior and are the controlling factors for the maximum Stokes shift that can be realized.

For a given fluorescent dye molecule, the overlapping of the absorption and fluorescent bands can be reduced by increasing the flexibility and polarity of the matrix. This can be achieved by changing the chemical structure of the polymer, by increasing the temperature, or by addition of polar dopants. By considering these parameters one should be able to solve the problem of minimum band overlap required for high efficiency of solar collectors based on fluorescent dyes. However, the question is yet unsolved as to how and to what extent the different parameters outlined above do influence the spectral behavior of the dye, particularly with regard to discrimination between the influence of the solvatochromic effects and the polymer dynamics.

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