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Spectroscopy of Dyes in Polymer Matrices: Dual Fluorescence of a [*p*-(Dialkylamino)benzylidene]malononitrile Dye in Poly(vinyl acetate) Matrices

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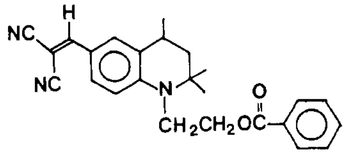
ABSTRACT: The dynamic behavior of a dye-in-polymer was revealed by electronic spectroscopy. Absorption, emission, and polarization spectra of [*p*-(dialkylamino)benzylidene]malononitrile 1 in poly(vinyl acetate) (PVAc) showed that the dye exists in monomeric form only at very low concentrations (<0.03 M). At higher concentrations and up to 0.6 M dye-in-polymer, dimeric species exists in equilibrium with the monomers, with an equilibrium association constant of 1.56 M^{-1}. Further increase in dye concentration leads to the formation of larger aggregates. The fluorescence quantum yields, ϕ_f, of the dye monomer, dimer, and amorphous solid were ~0.01, ~0.1, and 0.066, respectively. The higher ϕ_f of the dimer was attributed to a decrease in the rate of radiationless decay of 1 due to restricted molecular relaxation resulting from the binding of two monomer molecules. The polarization ratios (*P*) of the monomer, dimer, and amorphous solid were 0.5, 0.2, and 0.03, respectively. The value of 0.5 for the monomer indicates parallel absorption and emission transition moments with no molecular motion in the polymer within the lifetime of the singlet excited state (~30 ps).

Introduction

The idea of dispersing or dissolving small molecules into solid polymer matrices has attracted a great deal of interest in industry, mainly because such devices are simple to fabricate, are economical, and have wide technological applications. Applications in a carrier generation layer,[1,2] charge transport layer,[3] optical storage media,[4,5] and photoresist[6] have been documented. It has also been demonstrated that the concentration and the microscopic structure of these small molecules in the matrix have a profound effect on the performance of these devices.[1,2] In order to have better control over the performance of a given device, knowledge of the microscopic characteristics of the material package is essential.

In this work, the photophysical and photochemical behavior of a yellow dye ([*p*-(dialkylamino)benzylidene]-malononitrile 1) in a polymer matrix was studied. This material showed great potential in optical storage technology.[7] On the basis of spectroscopic and electrochemical data, we have assigned the $S_0 \rightarrow S_1$ transition of 1 in solution as a $\pi \rightarrow \pi^*$ transition with a considerable amount of charge transfer character.[8] The ground-state and excited-state dipole moments were estimated to be 9.0 and 16.0 D, respectively.[8] The increase in dipole moment on excitation indicates a further charge separation in the S_1 state. The rate of radiative decay (k_f) in ethyl acetate was calculated to be 2.8×10^8 s^{-1}. The lifetime of the S_1 state is estimated to be 6 ps in that solvent.[8] Molecular relaxation has been shown to play a dominant role in the deexcitation of the S_1 state. The quantum yield of internal conversion is estimated to approach unity in solution at room temperature. Most of the excitation energy absorbed by 1 is converted very rapidly and efficiently to heat. This phenomenon has thus been exploited for optical storage application.[7]



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In the present work, we use spectroscopic techniques to probe the microscopic properties of 1 in a poly(vinyl acetate) (PVAc) matrix. We observed dual fluorescence of 1 in PVAc. The concentration and polarization dependence of the dual fluorescence of 1 in PVAc will be discussed. High concentration of 1 in polymer (~2 M) can easily be achieved, rendering the polymer matrix a unique medium for simulating high-concentration conditions which cannot be achieved in solution. The advantage of the dye/polymer system over another high dye concentration condition prepared by incorporating dyes into the monolayer assembly is that the dye molecules in the former system are randomly orientated[9] whereas they have a specific orientation in the latter system.[10]

Experimental Section

Materials. [*p*-(Dialkylamino)benzylidene]malononitrile 1 was obtained from Eastman and was purified as described previously.[8] Poly(vinyl acetate) (PVAc) was a gift from the St. Lawrence Co. (B12 grade), methyl ethyl ketone was obtained from Baker and 9,10-diphenylanthracence (+99%) and low molecular weight poly(methyl methacrylate) (PMMA) were obtained from Aldrich and were used as received. Glass substrates were bought from Corning (7059) and were washed with soapy water and distilled water (twice) in an ultrasonic bath; they were then cleaned by ethanol vapor (refluxed over 95% ethanol) before use.

Preparation of the Dye-in-Polymer Films. Various concentrations of PVAc and 1 in methyl ethyl ketone were prepared by vibrating in an ultrasonic bath until a clear solution was achieved. The solutions were filtered through 1-μm Millipore filters and then spin-coated onto a precleaned 2 in. × 2 in. glass substrate, using a Model 1-EC-101 Headway Research photoresist spinner. Uniform and optically clear films were obtained. The film thickness was controlled by the spin rate, typically between 500 and 8000 rpm. The optical density and the thickness of the resulting films were measured with a Cary 17 spectrophotometer and a Talystep instrument, respectively.

Luminescence Measurement. Fluorescence and excitation spectra were recorded by front-surface illumination on a Perkin-Elmer MPF4 spectrofluorimeter which was equipped with a differential corrected spectral unit (DCSU-2). Fluorescence quantum yields were determined (in a corrected mode) by comparing with 9,10-diphenylanthracence fluorescence in PMMA (~3×10^{-3} M), which has been shown to have a quantum yield of 0.99.[11] The optical densities of all the dye-in-polymer samples were in the range 0.3–0.8 at the absorption maximum. Controlled experiments showed that the polymer film itself did not show any absorption or emission under the experimental conditions.

Polarization spectra were taken on the same spectrofluorimeter with polarization accessory 018-0054. The performance of the instrument has been checked against a Rhodamine B standard.

Results and Discussion

Absorption Spectroscopy. Figure 1 shows the concentration-dependent visible absorption coefficients of 1 in PVAc. The absorption bands become broader, less

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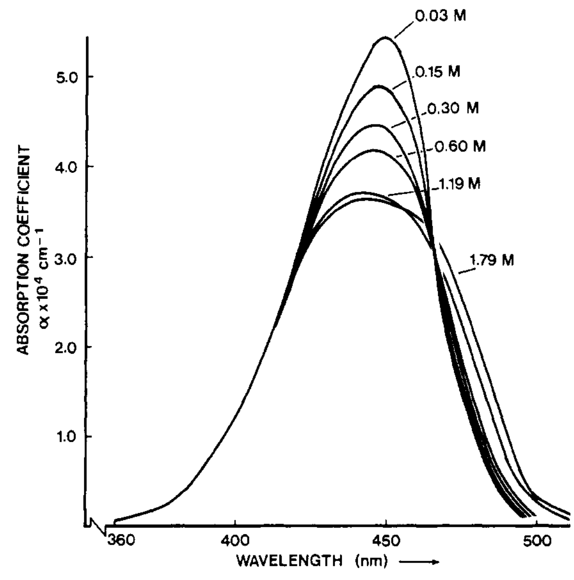

Figure 1. Absorption spectra of 1 in a PVAc matrix.

Table I
Absorption Spectra of 1 in PVAc

[1], M	λ_{max}, nm	$\alpha \times 10^4$, cm^{-1}	slope,[a] μm^{-1}
0.03	450.0	5.44[b]	
0.15	448.8	4.91	0.732
0.30	445.8	4.48	1.337
0.60	445.8	4.17	2.448
1.19	440.6	3.72	4.438
1.79	440.6	3.64	6.513

[a] See Figure 2. [b] Average of four samples.

intense, and blue shifted as the concentration of 1 in the polymer increases. The densities of these polymer films were found to be ~1.19 g/mL (independent of [1]). The molarity of 1 in the polymer was calculated, the absorption coefficients were calculated from the optical density, and the latter were plotted as shown in Figure 1. Plots of the optical density at the absorption maximum as a function of film thickness for various concentrations of 1 give straight lines (Figure 2). The absorption coefficient, α, of 1 in PVAc is calculated from the slopes of these lines according to eq 1, where MW is the molecular weight of

$$\alpha = (\text{slope} \times 10^4)\frac{\text{MW}}{C\rho}\ \text{cm}^{-1} \qquad (1)$$

1 (399 g/mol), C is the concentration of 1 in PVAc in weight percent, and ρ is the density of the film (1190 g/L). The dependence of the absorption coefficient and absorption maxima on the concentration of 1 is summarized in Table I. The results in Table I clearly show that there is a hypsochromic shift of the absorption maximum and a decrease in absorption coefficient as the concentration of 1 increases. An isosbestic point at ~465 nm was observed, indicating a specific stoichiometry of the aggregate. The only exception is the absorption curve of 1 at concentrations higher than 1.19 M. With the assumption that the concentration-dependent absorption change is due to the formation of a dimer, the data in Figure 1 were analyzed with a best-fit program to calculate the monomer and dimer spectra for a given equilibrium association constant K_{eq}.[12] Systematically varying K_{eq} yields the best-fit values of ϵ_m, ϵ_d, and K_{eq}, where ϵ_m and ϵ_d are the absorption coefficients of the monomer and dimer of 1, respectively. The best-fit ϵ_m and ϵ_d are then used to calculate K_{eq} and its error at each concentration. We observed a good fit of data for concentrations below 0.60 M. Incorporating higher concentrations leads to a larger deviation coefficient in the value of K_{eq}. The result indicates that true monomer–dimer equilibration exists only for dye concentrations below 0.60 M. For higher concentrations, larger aggregates of 1 are formed. The observed isosbestic point for concentrations up to 1.19 M of 1 may indicate that the resulting larger aggregates have an absorption very similar to that of the dimer. Reeves and co-workers[13] have also arrived at a similar conclusion in their spectrophotometric analysis of ionic azo dyes.

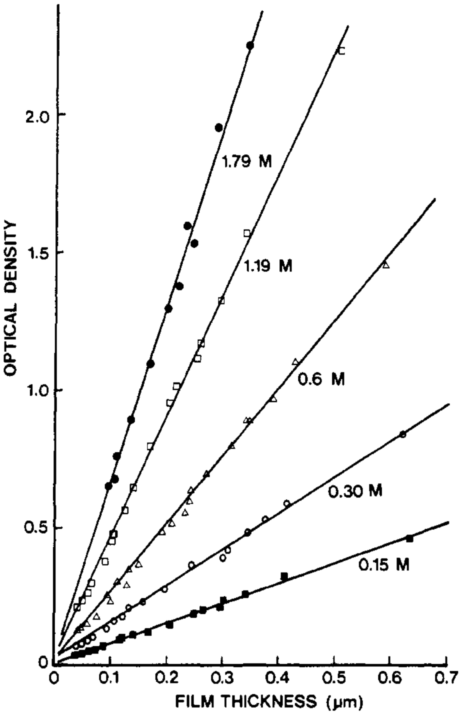

Figure 2. Plot of the optical density of the absorption maximum as a function of film thickness for various [1].

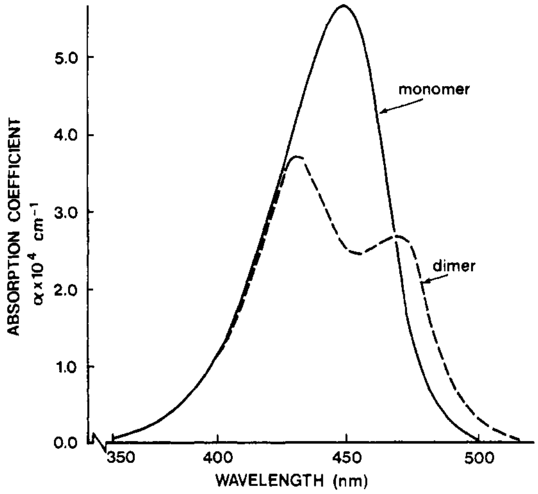

Figure 3. Calculated monomer and dimer spectra of 1: (—) monomer; (---) dimer.

The calculated monomer and dimer spectra of 1 for concentrations below 0.60 M are shown in Figure 3. The calculated monomer spectrum is identical with the absorption spectrum of 1 at [1] = 0.03 M. On the other hand, the calculated dimer spectrum shows two absorption maxima at ~430 and ~470 nm. The association constant, K_{eq}, of the dimerization process is 1.56 M^{-1}. The monomer,

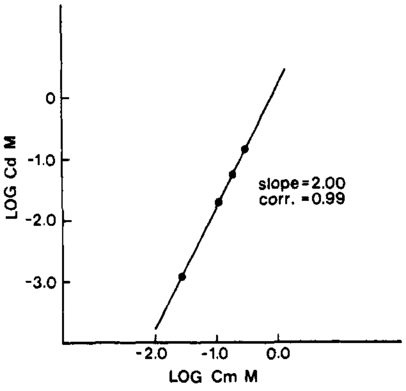

Figure 4. Plot of log C_d vs. log C_m.

Table II
Monomer and Dimer Concentrations of Various [1] in PVAc

[1], M	f	C_m, M	C_d, M
0.03	0.92	0.027	0.001
0.15	0.74	0.110	0.019
0.30	0.63	0.188	0.055
0.60	0.51	0.304	0.146

C_m, and dimer, C_d, concentrations present in the matrix at various concentrations of 1 can also be calculated:[12]

$$K_{eq} = (1 - f)/2f^2C_0 \qquad (2)$$

where f is the fraction of monomer in the matrix and C_0 is the total concentration of 1.

The calculated C_m and C_d for $K_{eq} = 1.56\ M^{-1}$ are tabulated in Table II. A plot (Figure 4) of log C_d vs. log C_m gives a straight line with a slope of 2.00, confirming the stoichiometry of the aggregate below 0.60 M.

Fluorescence Spectroscopy. The fluorescence spectra of various concentrations of 1 in PVAc are shown in Figure 5. The excitation wavelength was 400 nm, since at this wavelength, the absorption coefficients of various species in the matrix are very similar and these species will then be excited according to their concentrations. Dye 1 exhibits dual fluorescence for all the concentrations studied. The emission band can be resolved into two components, a short-wavelength emission band at ~490 nm from the monomer and a long-wavelength emission band at ~590 nm from the dimer (and other larger aggregates at higher concentrations). An isoemissive point at ~522 nm was observed for concentrations below 0.60 M. This observation gives firm support for the conclusion reached in the former section that monomer–dimer equilibrium only exists below 0.60 M. At higher concentrations, we observed a further bathochromic shift and a drop in fluorescence intensity, which are attributable to the formation of larger aggregations.

The fluorescence quantum yields, ϕ_f, at the 400-nm excitation were measured and are summarized in Table III. From the f values in Table II, ϕ_f of pure monomer and pure dimer of 1 in PVAc can be calculated to be ~0.011 and ~0.11, respectively. The ϕ_f of the monomer of 1 is ~6 times larger than that in solution, which is in the range $(1.5–2) \times 10^{-3}$.[8] This is not due to an increase in radiative decay rate (k_f) in the PVAc matrix since the calculated k_f in the PVAc matrix is identical with that in solution. We have previously established that molecular relaxation is a predominant decay pathway of the S_1 state of [*p*-(dialkylamino)benzylidene]malononitriles.[8] This molecular relaxation process can be slowed down to a different extent, depending on the rigidity of the chromophore or the matrix. It can also be completely frozen in a 2-methyltetrahydrofuran glass matrix at 77 K. We therefore conclude that the increase in ϕ_f of 1 in the PVAc matrix compared to that in solution is attributable to an increase in rigidity of the microenvironment which reduces the rate of molecular relaxation and consequently increases ϕ_f.

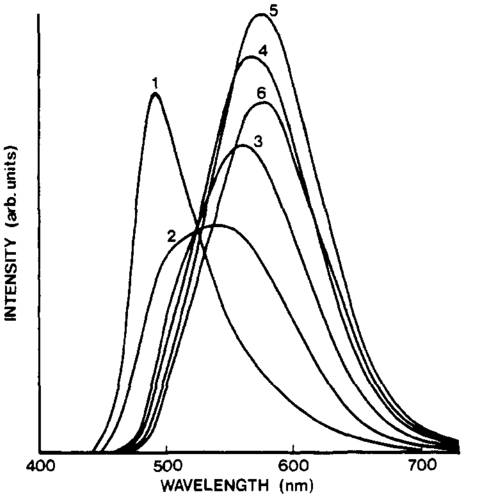

Figure 5. Fluorescence spectra (uncorrected) of 1 in a PVAc matrix: (1) 0.03 M; (2) 0.15 M; (3) 0.30 M; (4) 0.60 M; (5) 1.19 M; (6) 1.79 M.

Table III
Fluorescence Quantum Yields (ϕ_f) of 1 in PVAc

[1], M	ϕ_f[a]	[1], M	ϕ_f[a]
0.03	0.016	1.19	0.044
0.15	0.019	1.79	0.037
0.30	0.026	2.98 (solid film)	0.066
0.60	0.039		

[a] Estimated error ~±10%.

The ϕ_f of the dimer of 1 (~0.11) is an order of magnitude larger than that of the monomer in the same matrix. This is in contrast to the results of other dyes in solution, which, upon dimerization, normally show an enhancement of phosphorescence and a reduction of fluorescence.[15-19] Recently, Marx and Schiller[20] also reported on the fluorescence quenching of a number of cationic dyes in a poly(vinyl alcohol) matrix. The increase of ϕ_f in the present case is not due to an increase in radiative decay rate since the calculated k_f value of the dimer of 1 is ~$2 \times 10^8\ s^{-1}$. It cannot possibly be due to an increased rate of intersystem crossing since this will decrease ϕ_f rather than increase it. We hence conclude that the larger increase in ϕ_f for the dimer of 1 is attributable to the dramatic reduction in the rate of nonradiative decay via restricted molecular relaxation when two monomeric species are associated to form a dimer. This probably implies that the dimer has a rigid sandwich structure similar to those recently proposed by Inoue and Itoh.[21,22] Our results are also in agreement with those of Inoue and Itoh,[21] who showed that the fluorescence emission of the dimers of (3,5-dialkyl-4-methoxybenzylidene)malononitriles is greater than that of the corresponding monomers.

The fluorescence quantum yield of 1 decreases at concentrations higher than 1.19 M, indicating the formation of some new species (larger aggregates) whose fluorescence efficiency is less than that of the dimer. Indeed, the ϕ_f of evaporated solid films of 1 (2.98 M) is only 0.066, less than that of the dimer. The smaller ϕ_f of solid 1 compared to that of the dimer may be due to the amorphous and highly

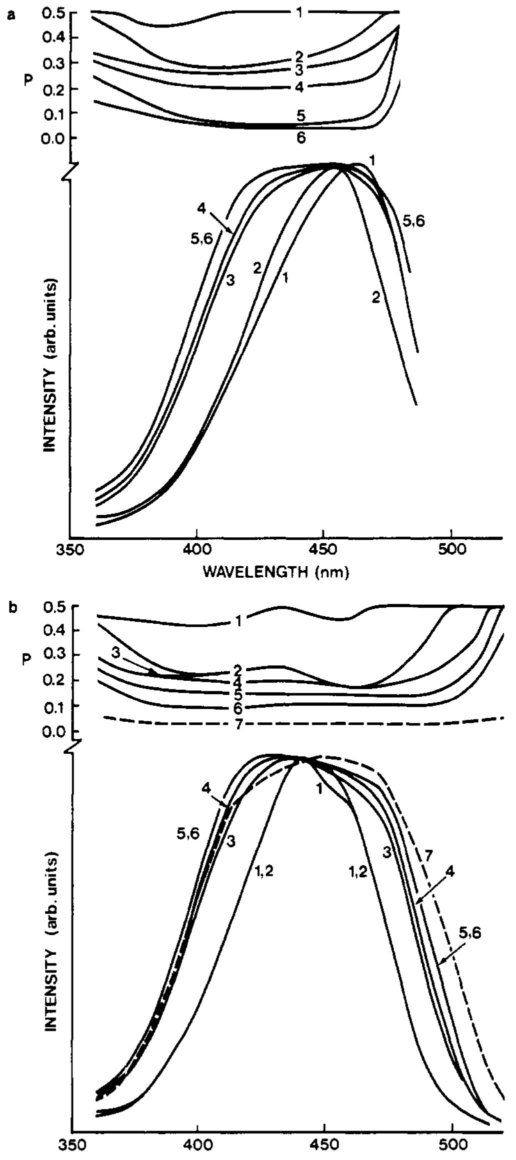

Figure 6. Excitation and polarization spectra (uncorrected) of 1 in a PVAc matrix: (a) monitored at 490 nm; (b) monitored at 590 nm. (1) 0.03 M; (2) 0.15 M; (3) 0.30 M; (4) 0.60 M; (5) 1.19 M; (6) 1.79 M; (7) 2.98 M.

aggregated nature of the solid film, a situation which is approached for concentrations of 1 higher than 0.60 M in polymer matrix. In conclusion, the ϕ_f of 1 decreases in the order dimer > solid 1 (or larger aggregates) > monomer, which is in the same direction of decreasing rigidity of the chromophore. This is again an indication that molecular relaxation is dominating the deexcitation process of the S_1 state of 1.

Excitation and Polarization Spectroscopy. Figure 6 shows the excitation and polarization spectra of various concentrations of 1 in PVAc matrices monitored at two different emitting wavelengths, 490 and 590 nm, respectively. Spectra of solid films of 1 are also included for comparison (Figure 6b). At the lowest dye concentration used (0.03 M), the excitation spectrum, as monitored at 490 nm, is similar to the monomer absorption spectrum and the polarization is +0.5 (Figure 6a, curve 1). The maximum polarization value observed means that the absorption and emission transition moments are parallel and there is no molecular rotation during the lifetime of the singlet excited state (30 ps). On the other hand, when the emission was monitored at 590 nm, which corresponds to the emission wavelength maximum of the dimer, both excitation and polarization spectra reveal contributions from the dimer (Figure 6b, curve 1) despite its low concentration (0.0012 M) present in the matrix. The excitation spectrum shows a hypsochromic shift relative to the monomer spectrum and the polarization spectrum shows two depolarized bands corresponding to the absorption maxima of the dimer.

As the concentration of 1 increases, both excitation and polarization spectra show increased contribution from the dimer. For instance, the excitation spectra become broader and shift to shorter wavelengths. Also the polarization ratio is decreased. At 0.60 M, the polarization is ~+0.2, regardless of the monitoring wavelength. We attributed this to the polarization of the dimer of 1 according to the results from absorption and fluorescence spectroscopy. The polarization ratio is further decreased and approaches that of the solid film ($P \sim +0.03$) at concentrations of 1 higher than 0.60 M for both monitoring wavelengths. These results again confirm the formation of larger aggregates of 1 at these concentrations.

We have also examined the spectroscopic properties of 1 in a variety of polymers: poly(vinylcarbazole), polycarbonate, poly(methyl methacrylate), copoly(styrene–acrylonitrile), copoly(styrene–*n*-butyl methacrylate), poly(*sec*-butyl methacrylate), poly(isobutyl methacrylate), and poly(*tert*-butyl methacrylate). Dimer and monomer emissions were observed in all polymers. The tendency to form dimer and higher aggregates was greater in polymers which are poor solvents for the dye, e.g., polystyrene and copoly(styrene–acrylonitrile).

Conclusion

We have combined absorption, fluorescence emission, fluorescence excitation, and polarization spectroscopic techniques to identify different forms of dye 1 present in PVAc matrices as a function of concentration. [*p*-(Dialkylamino)benzylidene]malononitrile 1 exhibited a definite affinity to form dimers in polymer matrices at concentrations below 0.60 M. The association constant of the dimerization was determined to be 1.56 M^{-1}. At dye concentrations higher than 0.60 M in the polymer matrix, larger aggregates are formed. This result implies that there may be a constant amount of free volume within the polymer matrix. For low concentrations, the molecule can distribute itself to follow a thermodynamic equilibrium. Once the volume is occupied, further addition of molecules will force formation of dimer or larger aggregates. Under the microscope, no evidence of microcrystal formation was observed in any of the films studied. If present, these microcrystals must be less than 0.1 μm in diameter.

The fluorescence quantum yields of the dimer, larger aggregates (solid), and monomer of 1 are ~0.11, 0.066, and ~0.011, respectively. ϕ_f increases as the rigidity of the chromophore increases, further illustrating the influence of molecular relaxation on the decay process(es) of the S_1 state of 1. Moreover, the fluorescence spectrum of ~0.03 M 1 in ethyl acetate is identical with that of 0.03 M 1 in the PVAc matrix. The fluorescence quantum yield is, however, ~6 times higher in the polymer film and the retardation of molecular motion in a more rigid microenvironment is again revealed. Another added advantage of dye-in-polymer studies is the fact that absorption and excitation spectroscopy at high dye concentration can be studied, since the thickness and optical density of the polymer film can be easily and accurately controlled. The present study has demonstrated that microscopic properties of dyes-in-polymer can be determined spectroscopically. Thus one can use polymer matrices as a solvent for studying physicochemical properties under high concentration conditions.

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A Modified Technique for Measurement of Orientation from Polymer Surfaces by Attenuated Total Reflection Infrared Dichroism

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ABSTRACT: For a sensitive measurement of surface molecular orientation by attenuated total reflection (ATR) IR dichroism, a modified sample holder was developed, utilizing a symmetrical, double-edged internal reflection crystal. This modified sample holder allows the sample to be rotated without the disassembling and reassembling operations which change the contact area between the polymer and the ATR crystal. Therefore correction of the reflectivities to an internal standard absorption band which is insensitive to orientation is not necessary with this modified apparatus. This was tested on two types of polypropylene. Results with uniaxially drawn polypropylene show that the surface orientation is similar to the bulk, as expected. On the other hand, the orientation as measured by this technique was greater on the surface than in the core of an injection-molded polypropylene plate, a tendency confirmed by birefringence. This technique can be used for estimating bulk orientation of a thick sample without sectioning when the surface has similar orientation to the bulk. In cases where the surface differs significantly in orientation from the bulk, our technique should provide a surface-sensitive estimation of orientation, since the surface probed is only about 1 μm in this technique.

Introduction

The surface of polymers can be represented by different structures and compositions from the bulk, for example, as a result of processing conditions or photodegradation. Therefore, careful characterization of the polymer surface is essential to understand and improve surface-related properties.

Although many techniques are available for the determination of the structure of polymers in the bulk, IR spectroscopy appears to be one of the most amenable for surface characterization. We have directed our attention in this study to the measurement of surface molecular orientation in comparison to bulk values by employing IR spectroscopy. Measurement of bulk molecular orientation by transmission IR dichroism with thin polymer films is a well-established technique.[1] However, the use of attenuated total internal reflection spectroscopy (ATR) for measurement of orientation on polymer surfaces is experimentally more difficult, in spite of the well-developed theoretical basis for ATR of anisotropic polymers. According to Fluornoy and Schaffers,[2] three optical constants, k_x, k_y, and k_z of the polymer film, are related to the reflectivities for the transverse electric (TE) and the transverse magnetic (TM) waves, where the x axis is the axis of drawing with the y and z axes parallel and normal to the film plane, respectively, as defined in Figure 1. With the film sample oriented with its x axis normal to the plane of incidence, the following two equations for the reflectivities are obtained by rotating the polarizer by 90°:

$$\ln R_{\mathrm{TE}_x} = -\alpha k_x \tag{1}$$

$$\ln R_{\mathrm{TM}_x} = -\beta k_y - \gamma k_z \tag{2}$$

where α, β, and γ are the functions of the refractive indices of the sample and the reflection crystal and the angle of incidence. A rotation of the film sample about the z axis by 90° will place the y axis normal to the plane of incidence, which will result in two additional equations

$$\ln R_{\mathrm{TE}_y} = -\alpha k_y \tag{3}$$

$$\ln R_{\mathrm{TM}_y} = -\beta k_x - \gamma k_z \tag{4}$$

In theory, a measurement of any three of the four reflec-

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