

Fluorescence probes for polymer free-volume

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Abstract - A series of fluorescence Probes (p-(N,N-dialkylamino)benzylidene malononitriles) which belong to a class of organic compounds known as "molecular rotors" has been developed. The internal molecular rotation of these compounds can be slowed down by increasing the surrounding media rigidity, viscosity or decreasing the free-volume available for molecular relaxation. Inhibition of internal molecular rotation of the probe leads to a decrease in the non-radiative decay rate and consequently enhancement of fluorescence. Therefore, the fluorescence emission of this class of compounds allowed us to study both the static and dynamic changes in free-volume of polymers as a function of polymerization reaction parameters, molecular weight, stereoregularity, crosslinking, polymer chain relaxation and flexibility. In addition, the dependence of the fluorescence emission maximum of these probes on media polarity allow continuous monitoring of the probes location in the polymer matrix. Therefore, these fluorescence materials are capable of simultaneously probing the flexibility and polarity of the surrounding media.

INTRODUCTION

There has been a long history of theoretical and experimental papers which are concerned with the development of the free-volume concept to explain transport and diffusion in polymer systems. The original work is probably that of Batschinski (1913)(ref.1). who postulated that the viscosity of a liquid was inversely proportional to the amount of free space in the system. Much later, Doolittle (1951) (ref.2) utilized an empirical exponential representation for the dependence of viscosity on free-volume to describe the temperature variation of viscosity for low molecular weight liquids. Bueche (1953) (ref.3) derived an expression for polymer segmental mobility by considering free volume fluctuations. Fujita (1960) (ref.4) formulated a free-volume description of diffusion in concentrated polymer solutions. Williams, Lendel and Ferry (WLF) (1955) (ref.5) demonstrated that the temperature dependence of molecular mobility and relaxation in glass-forming liquids is controlled by the available free-volume not only in the melt region but also in the "glassy region". The WLF empirical formula relating the viscosity, η , at a given temperature T to those at the glass transition temperature T_g is entirely based on the relationship between viscosity and free-volume and is given as:

$$\log \left(\frac{\eta}{\rho T} / \frac{\eta_g}{\rho_g T_g} \right) = - \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

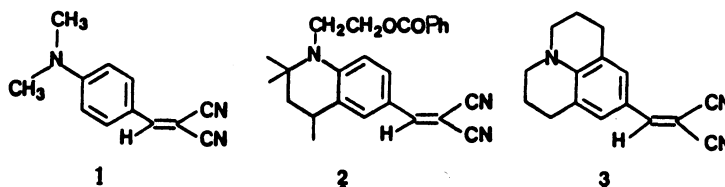
The left-hand side is commonly expressed in terms of just η/η_g in as much as the product ρT is insensitive to temperature variations. Thus, we obtain the familiarly derived form:

$$\log (\eta/\eta_g) = -17.44 (T - T_g) / [51.6 + (T - T_g)] \quad (2)$$

where the values of the universal constants C_1 and C_2 have been inserted. The WLF equation has been shown to describe the temperature dependence of viscosity and relaxation rate in many polymer systems, polymer solutions and for many glass-forming liquids. In these systems, the free-volume fraction shrinks with decreasing temperature to about 0.025 at the glass transition temperature, T_g , and both $\eta(T)$ and time-temperature shift factors are correlated in terms of free-volume expansion between T_g and T. The objective of this work is to develop a method to study the distribution and changes in free-volume in polymer systems.

RESULTS AND DISCUSSION

In recent years the application of luminescence spectroscopy for the study of a diversity of phenomena occurring in synthetic and natural polymers has become widespread (ref.6-11). The versatility and sensitivity of luminescence as a technique in polymer chemistry stem from the multiple aspects of the interaction of electronically excited states with their immediate environment. We have recently described a novel phenomenon associated with the effect of media rigidity on the fluorescence intensities of a series of donor-acceptor dyes, [p-(N,N dialkylamino)-benzylidene]malononitriles 1-3 (ref.6). The singlet-excited-state lifetime of these dyes is estimated to be 3-10 ps in solution, which corresponds to a nonradiative decay rate, k_{NR} , of the order of $10^{11}s^{-1}$. The extremely fast deactivation rate of the singlet state of these materials was attributed to rapid torsional relaxation. We have shown that environmental factors restricting the internal molecular rotation of these dyes lead to a decrease in k_{NR} and consequently an increase in fluorescence yield. These dyes are, therefore, excellent microscopic probes for measuring the torsional rigidity of the surrounding polymer media, and their fluorescence yield is very sensitive to dynamic structural changes occurring over a wide temperature range.



The fluorescence properties of these probes permits us to study the rotational relaxation in various polymers and even during polymerization reactions and thereby obtain information on the microscopic rigidity of the media. In the following discussion a description of the photophysical properties of the dyes 1-3 will be given, with particular emphasis on the excited-state conformational relaxation in various media. This will be followed by a discussion related to the application of these probes to study polymerization reactions, the effect of polymer molecular structure on free-volume, the dependence of polymer chain relaxation on molecular weight and the effect of temperature on polymer conformation and free-volume.

Photophysical properties of the fluorescent probes

Fig. 1 displays the absorption and emission spectra of dyes 1-3 in ethyl acetate at 25°C. The dyes exhibit an intense ($\epsilon_{max} = 5 \times 10^4 M^{-1} cm^{-1}$) absorption band in the blue and a weak fluorescence emission in the green region of the spectrum. The S_1 state of these dyes is a

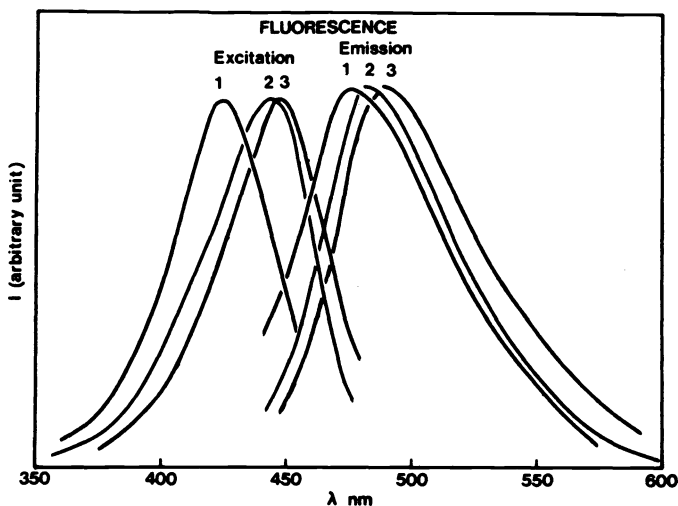


Fig. 1. The fluorescence emission and excitation spectra of di-alkylaminobenzylidenemalononitriles. 1, 2, and 3 is ethyl acetate at room temperature.

n, π^* state with a considerable amount of charge transfer (CT) character. The ground state, dipole moment, μ_g , is about 9 Debyes which increases to about 24 Debyes upon excitation (ref.10). The absorption maximum (λ_{max}) and fluorescence maximum (λ_F) of the dyes 1-3 shift to longer wavelength when the dielectric constant of the media increases, which is consistent with the high CT character of S_1 state. Actually, the fluorescence emission maximum (λ_F) correlate well with the solvent dielectric constant, as shown in Fig. 2 for dye 1. This correlation is important because it can be used as tool to determine the polarity of the surrounding media.

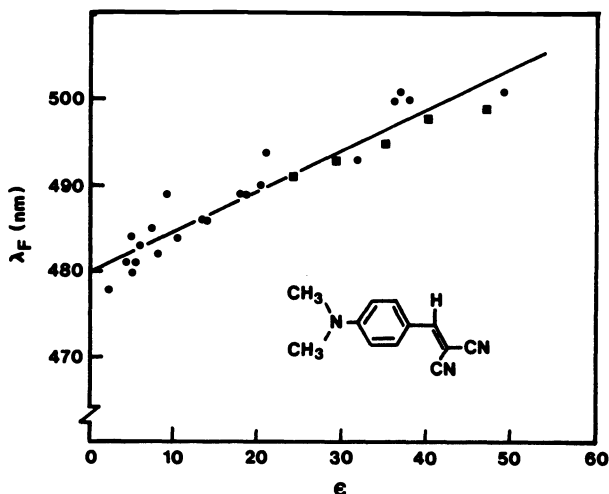


Fig. 2. Correlation between the fluorescence emission maximum of dye 1 and the dielectric constant of the solvent.

Despite the similarity of the calculated radiative decay rate of dyes 1-3 ($\sim 3 \times 10^8 \text{ s}^{-1}$) their quantum yields of fluorescence, ϕ_f , are different in any given media. In non-viscous media (ethyl acetate, vinyl monomers) ϕ_f of 1,2 and 3 is 0.89×10^{-3} , 2.1×10^{-3} and 3×10^{-3} respectively, at room temperature. ϕ_f increases as the dimension of the molecular probe increases. In more rigid media at RT, such as poly (methyl methacrylate), ϕ_f of 1,2 and 3 are 0.012, 0.057 and 0.12, respectively. Further experiments with these dyes at 77K in 2-methyl tetrahydrofuran glass matrix give ϕ_f of nearly unity, an increase of over 300 times. A media-dependent excited state relaxation must be proposed to explain these dramatic changes in ϕ_f of these dyes. Since these dyes exhibits very little triplet yields, the main pathway for non-radiative deactivation of the excited state is internal conversion. The absence of change in fluorescence emission maximum between room temperature and 77K and the approach of ϕ_f to unity at 770K indicates that the emitting states must be those excited states which maintain a ground-state conformation. Previous work at Xerox (ref.10-12) has shown that for molecular rotors such as 1-3 torsional motion in the excited state is capable of inducing radiationless decay, $S_1 \rightarrow S_0$. It has also been suggested that the torsional motions responsible for inducing radiationless decay are hindered by the viscous drag of the solvent. Rotation of the aryl group in the excited state is considered to be the rate-determining step, leading to rapid internal conversion to the ground state. The effect of media is to hinder or slow down the torsional relaxation of molecular rotors, thus decreasing the radiationless decay rate, k_{nr} , and increasing ϕ_f .

Fluorescence probe in bulk polymerization reactions

We investigated the dependence of the fluorescence intensity of 3 on polymerization reactions. The polymerization reactions investigated were those of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, ethyl acrylate, styrene and copolymerization of styrene/n-butyl methacrylate with the fluorescent probe 3 simply dissolved in the monomer at 10^{-5} M concentration. Bulk polymerization was initiated using AIBN (0.5% by weight) at 70°C. The fluorescence intensity of the probe (λ_{ex} 430 nm) was continuously monitored at 500 nm at the polymerization temperature. Fig. 3 shows the change in fluorescence intensity (I_f) of 3 as a function of polymerization time for each of MMA, EMA and BMA. Fig. 4 shows the dependence of I_f of 3 on the polymerization time of styrene. Similar results were obtained with ethyl acrylate and co-styrene (65%) /n-butyl methacrylate (35%). A curious behavior was observed. The fluorescence intensity remained almost constant in time until a critical moment is reached where a sharp rise in fluorescence intensity occurs, followed by a levelling-off as the polymer limiting conversion is reached. The S shaped fluorescence intensity dependence on polymerization time is a common behavior to all polymerizations studied. However, the lag period, the slope of the fluorescence rise and the magnitude of

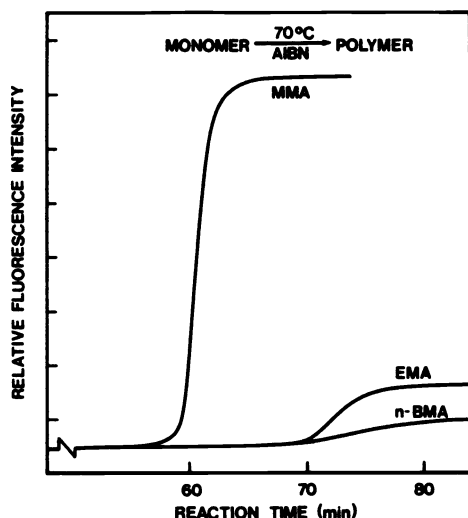


Fig. 3. Dependence of fluorescence intensity on the polymerization of methyl methacrylate (MMA), ethyl methacrylate (EMA), and *n*-butyl methacrylate (*n*-BMA).

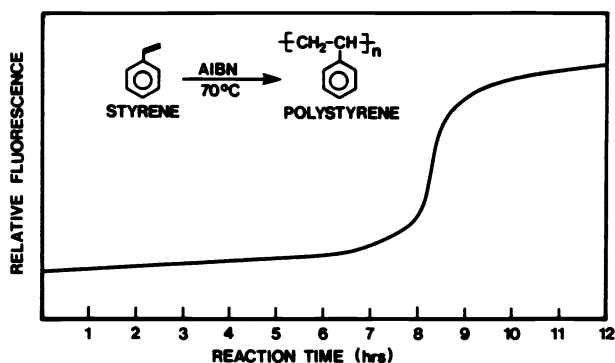


Fig. 4. Fluorescence intensity change as a function of styrene polymerization time.

fluorescence increase, all depend strongly on the rate of polymerization (temperature, initiator concentration and monomer reactivity) as well as on the particular polymer formed. In Table 1 the fluorescence yield, ϕ_f , of 3 at the limiting conversions are listed. The observed increase in ϕ_f going from the fluid monomer to the glassy polymer at 70°C was a factor of 17, 3.4, 1.8 and 4.7 for MMA, EMA, *n*-BMA and styrene respectively. The polymerization region in which fluorescence intensity increases sharply appears to correspond to the increase of medium viscosity from fluid to rigid glass.

TABLE 1. Spectroscopic Data for Julolidine Malononitrile in Various Media

	Dye Absorption λ_{\max} (nm)	Dye fluorescence			
		In monomer		In polymer ϕ_f	
		λ_f (nm)	$\phi_f (\times 10^{-3})$	70	23°C
methyl methacrylate	450	493	3.0	0.05	0.12
ethyl methacrylate	449	492	3.0	0.01	0.046
<i>n</i> -butyl methacrylate	448.5	486	2.8	0.005	0.02
styrene	454.5	485	3.0	0.014	0.04
vinylacetate	449.5	490	2.9
ethyl acrylate	449	491	2.9
styrene/butyl methacrylate	450	490	2.9

The importance of viscosity and free volume in the molecular relaxation processes of excited dyes has been well documented in the case of polymethines, di and triphenylmethanes and coumarin dyes (ref.13-21). For dyes in which rotation-dependent non-radiative decay (k_{nr}) links the excited state conformation to the media free-volume, V_f , one can express k_{nr} in terms of solvent free volume as:

$$k_{nr} = k_{nr}^0 \exp\left(-\beta \frac{V_0}{V_f}\right) \quad (3)$$

Here k_{nr}^0 is the intrinsic rate of molecular relaxation of the dye, V_0 is the occupied (Van der Waals) volume of the dye and β is a constant for the particular dye. The non-radiative decay rate, k_{nr} is related to the fluorescence yield according to:

$$k_{nr} = k_r \left(\frac{1}{\phi_f} - 1\right) \quad (4)$$

Equation (4) can be substituted in Equation (3) to yield the fluorescence dependent free-volume.

$$\phi_f = \left(\frac{k_r}{k_{nr}^0}\right) \exp\left(\beta \frac{V_0}{V_f}\right) \quad (5)$$

An expression of viscosity in terms of the free-volume of the media has been derived by Doolittle (ref.14):

$$\eta = A \exp\left(\frac{V_0}{V_f}\right) \quad (6)$$

Combining Equations (6) and (5), the relationship between the dye fluorescence quantum yield and viscosity can be derived as:

$$\phi_f = B\left(\frac{\eta}{T}\right)^x \quad (7)$$

where $B = (k_r/k_{nr}^0)(T/A)^x$. Here x is a constant between zero and one.

The above relationships indicate that the fluorescence yield of dyes which exhibit rotation-dependent non-radiative decay (3 is one of the dyes) will increase with decrease free-volume Equation (5) and/or increase viscosity of the media Equation(7). Therefore, to determine the link between the fluorescence intensity changes and the physical changes occurring during the polymerization reactions, we need to obtain the change in free-volume, viscosity, and glass temperature of the polymer/monomer mixture as a function of conversion. Bueche (ref.22,23) has developed general expressions for the variation of V_f , T_g and η of a polymer diluent system:

$$V_f = 0.025 + \alpha_p(T - T_{gp})V_p + \alpha_d(T - T_{gd})V_d \quad (8)$$

$$V_f = \left[\alpha_p V_p T_{gp} + \alpha_d (1 - V_p) T_{gd} \right] / \left[\alpha_p V_p + \alpha_d (1 - V_p) \right] \quad (9)$$

where V_p is the volume fraction of the polymer, η_g is the viscosity at the glass temperature and η is the polymer or glass forming liquid viscosity at temperature T . These relationships have been tested for several polymer-diluent systems and have been found to be reasonably accurate.(ref.23) Application of these relationships require the knowledge of the glass temperature of the polymer, T_{gp} and the diluent, T_{gd} the expansion coefficient of the polymer α_p and of the diluent, α_d . The value of α_p is very close to 4.8×10^{-4} per $^{\circ}C$ for most polymers and 10^{-3} per $^{\circ}C$ for most diluents. We studied, for example, the polymerization of $MMA \rightarrow PMMA$. Here $T_{gp} = 110^{\circ}C$, $T_{gd} = -102.8^{\circ}C$.

From conversion-time measurements for MMA bulk polymerization initiated by AIBN at $T = 70^{\circ}C$ we could determine the volume fraction of the polymer V_p . One can thus compute the change in V_f and η of MMA/PMMA mixtures as a function of conversion, using Equations (8) and (9) respectively.

Fig. 5 shows the dependence of the fluorescence yield of 3 on the viscosity of PMMA/MMA systems. A gradual increase in fluorescence occurs as the viscosity increases from 0.1 to 2cp. This is followed by a sharp rise in fluorescence as the viscosity of the medium changes from 2 to 100 cp. The slope of this portion of the plot corresponds to $\phi_f \propto \eta^{2.5}$ which is in agreement with the Foster and Hoffmann (ref.16) model, and also with Law's (ref.11) recent

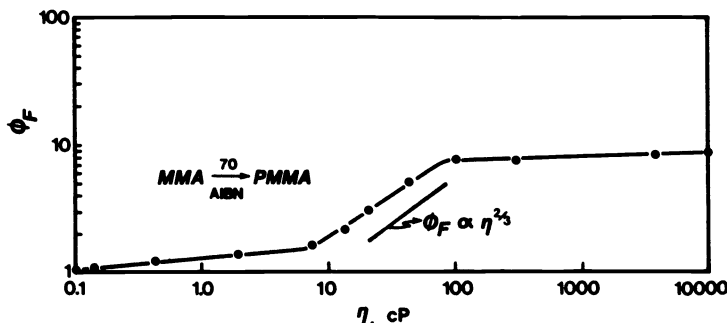


Fig. 5. Dependence of fluorescence yield of 2 (at $70^{\circ}C$) on the viscosity of PMMA/MMA mixture.

results on a similar probe. Further increase in conversion leads to rapid increase in the macroscopic viscosity, as the glassy state is approached. Once T_g exceeds the reaction temperature no further change in fluorescence occurs; the fluorescence in this region levels off.

The viscosity dependent ϕ_f arises from the dependence of η on the free-volume for the media. At polymer conversion of 60% and less the free-volume is plentiful and only small changes in fluorescence is seen. However, as the bulk polymerization approach the glassy status rapid reduction in the free-volume occurs which leads to the observed rapid rise in fluorescence. According to Eq. 5 a plot of $\ln\phi_f$ vs $1/V_f$ should give a straight line, the slope of which gives $V_0\beta$ and the intercept $\ln(k_r/k_{nr}^0)$. Fig. 6 shows such a plot which gives a value of $V_0\beta = \frac{1}{2}$.

The phenomenon observed here, which is common to most polymerization reactions, demonstrates that polymers can interfere sterically with processes involving movement of parts of the guest molecules (fluorescent probes). As the polymer glassy state is approached the relative free volume diminishes sharply and the medium viscosity increases rapidly; mobility becomes restricted and the deactivation rate of the probe becomes controlled by the microscopic free volume provided by the polymer. This accounts for the abrupt increase in fluorescence until the limiting conversion is reached, at which point fluorescence levels off.

One can imagine the use of these dyes to monitor, on-line, the progress of bulk polymerization to prevent run-away reactions. Such an application could be of commercial importance.

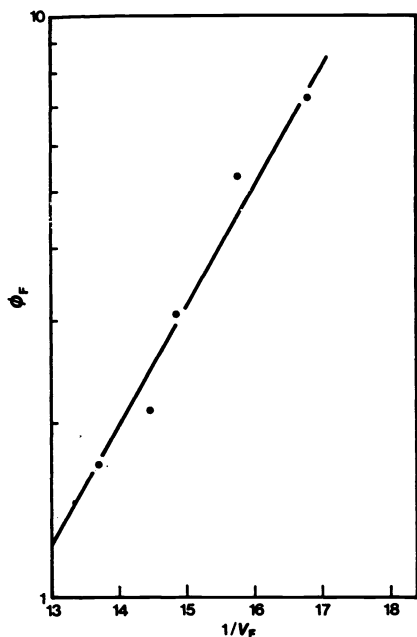


Fig. 6. Dependence of fluorescence yield of 2 (at 70°C) on PMMA/MMA mixture free volume.

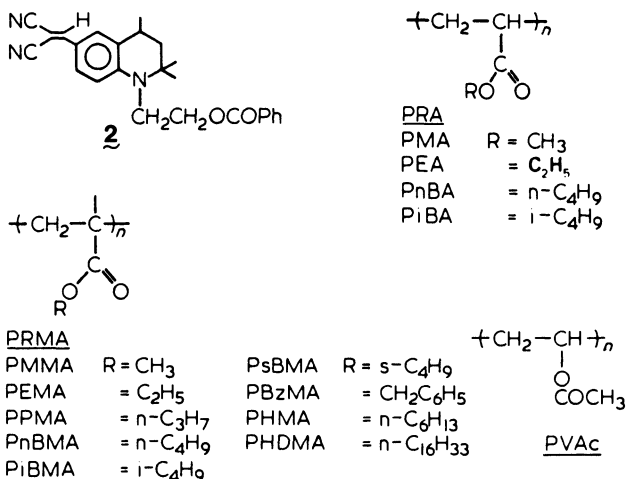


Fig. 7. Structure of dye 2 poly(alkylmethacrylate), PRMA, poly(alkylacrylate), PRA and poly(vinyl acetate), PVAc.

Effect of polymer molecular structure on the fluorescence of the molecular rotors

We have investigated the effect of poly(alkylmethacrylate), PRMA, and poly(alkylacrylate), PRA, matrices on the fluorescence quantum yield (ϕ_f) of dye 2 to study the effect of polymer molecular structure on free-volume and to study polymer segmental relaxation processes. Fig. 7 shows the chemical structure of the polymers used. Table 2 lists the absorption and fluorescence spectral data of dye 2 in the various matrices. The glass transition temperatures of the polymers chosen varied from -54 to 105°C. No direct correlation between the glass transition relaxation temperature (T_g) of the polymer binder and the ϕ_f of 2 is observed. Instead, ϕ_f of 2 is related to the fluorescence emission frequency (ν_f) of 2, a parameter which has been shown to exert little influence on the ϕ_f values in organic solvents (ref.11). Since ν_f is correlated to the polarity of a medium, our results suggest that 2 is located in different sites in various polymer matrices. The variation of ϕ_f with ν_f is an indirect reflection of the difference in free volume (polymer chain flexibility) in these various sites of the polymers studied. This finding demonstrates the power of these probes and the utilization of the dual functionality, ν_f to probe the location of the dye and ϕ_f to probe the rigidity of that environment.

TABLE 2. Absorption and fluorescence emission spectral data of in PRMA, PRA and PVAc matrices.

Polymer	T_g^a	ν_{abs}^b	ν_F^c	$\phi_f \times 10^3^d$
PRMA:				
PMMA	105	22341	20325	12.3
PEMA	65	22396	20450	3.6
PPMA	35	22426	20408	5.1
PnBMA	20			5.1
PiBMA	53	22533	20450	3.1
PsBMA	60	22426	20534	3.4
PBzMA	54	22163	20367	5.2
PHMA	-5	22426	20661	1.1
PHDMA	15	22532	20877	0.96
PRA:				
PMA	9	22222	20408	13.0
PEA	-24	22311	20533	4.2
PnBA	-54	22426	20876	2.1
PiBA	-24	22431	20920	2.8
PVAc	35	22222	20408	11.0

^a Glass transition temperature, in $^{\circ}\text{C}$, values either taken from J. Brandrup and E. H. Immergut, 'Polymer Handbook' 2nd Edition, John Wiley and Sons Inc., or specified by suppliers.

^b Absorption maximum frequency, in cm^{-1}

^c Fluorescence emission maximum frequency, in cm^{-1}

^d Better than $\pm 10\%$

When the ϕ_f of 2 is plotted as a function of ν_f (Fig. 8), we observe two nearly parallel curves. One curve belongs to the PRMA family and the other curve belongs to the PRA family. The data for 2 in PVAc is incorporated into the PRA family because of their similarity in structure. The ϕ_f versus ν_f curve of PRMA is always on the low frequency side of PRA. This implies that, for the same R group, 2 is located in a more polar microenvironment in PRMA polymers, a probable consequence of the conformational effect produced by the methyl groups on the polymer backbone.

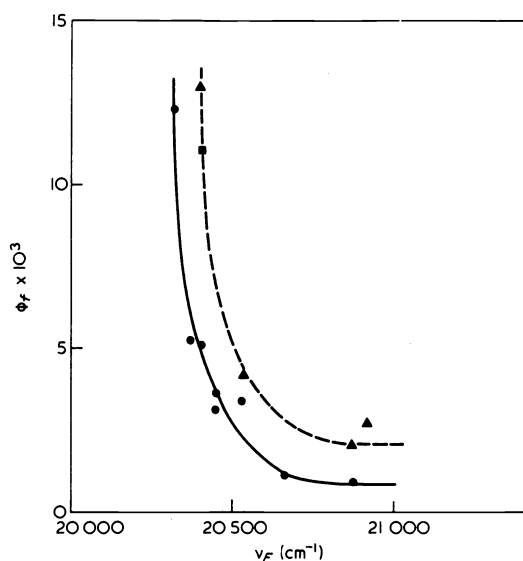


Fig. 8. Plot of ϕ_f of 1 as a function of ν_f of (● PRMA; ▲ PRA and ■ PVAc).

The variation of ν_f values shown in Table 2 indicates that 2 prefers different microenvironments within a family of polymers. In PMMA, PMA and PVAc matrices, 2 is basically located in the vicinity of the polymer backbone (the polar carboalkoxy group). This is confirmed by the low ν_f values (20325–20408 cm^{-1}) observed in these three polymers, which have an effective dielectric constant of ~ 20 . The ϕ_f of 2 in PMMA, PMA and PVAc are 0.0123, 0.013 and 0.011, respectively, despite their large differences in T_g values. The

similar ϕ_f values in these three polymers suggests that the polymer chain flexibility (or free volume) around the polymer backbones of PRMA, PRA and probably poly(vinyl alkanoate) is probably very similar.

For PRMA and PRA polymers with longer alkyl side chains, the increase in v_f values observed within a family of polymers indicates that 2 tends to gradually penetrate deeper and deeper into the alkyl chain as its chain length increases. Using the v_f of 2 as an indicator for the location of 2 in these polymers, the change in ϕ_f values within a family of polymers will then give some information on the flexibility of segments of known locations along the alkyl side chain. For example, in PHDMA matrix, v_f of 2 is 20877 cm^{-1} , indicating that 2 is basically located in a hydrocarbon environment (v_f of 2 in benzene is 20921 cm^{-1}). Information on the free volume (or chain flexibility) of the hydrocarbon chain in these polymers is then obtainable. The ϕ_f of 2 in PHDMA is 0.96×10^{-3} , indicating that the free volume in the hydrocarbon chain region in these polymer is very similar to those of low viscosity solvents (ref.10).

These results indicate that the flexibilities of the polymer backbones of PRMA, PRA and PVAc are very similar. However, local polarity and local flexibility of polymer segments vary from site to site and from polymer to polymer. Great care should be exercised in using probes or labels in studying polymeric systems, especially when the location of the probe is difficult to determine.

In the next section the effect of polymer molecular weight on the fluorescence of dye 2 will be described which illustrate the dependence of polymer chain entanglement on molecular weight.

Probing polymer chain relaxation as a function of molecular weight

The effect of the molecular weight of monodispersed atactic polystyrene as non-fluorescent host polymer on the fluorescence yield of dye 2 was investigated. Films of dye 2 (0.5 wt.%) in atactic polystyrene (a-PS) of various molecular weight were prepared by solvent casting from 10% methylene chloride solution. The fluorescence data of dye 2 in polystyrene films with molecular weight from 10^2 to 10^6 are given in Table 3 and plotted in Fig. 9. The fluorescence yield of dye 2 increases gradually with the increase of polystyrene molecular weight up to $M_n = 10,000$. Between $M_n = 10^4$ and 10^5 , ϕ_f increases rapidly by about a factor of 2 to a plateau that extends to $M_n = 1.8 \times 10^6$. This fluorescence behavior of the molecular probe is qualitatively very similar to that observed for poly(2-vinylnaphthalene) guest in PS solution.(ref. 24) However, the origin of the change in the fluorescence of the two probes with PS molecular weight must be different, since in our experiment a molecular rather than a polymeric probe was used. Probe miscibility with the host polymer is not an issue here.

The gradual increase in fluorescence efficiency of dye 2 with increase in the molecular weight of the host polystyrene to $M_n < 10^4$ can be attributed to inhibition of radiationless decay by rigidization of the probe by the local environment. This arises entirely from a decrease in the available free volume as the molecular weight of PS increases. Since the change in the glass transition temperature, T_g , with M_n is due to changes in free volume, a correlation between ϕ_f of 2 and T_g of the host polymer is expected and is observed, supporting the validity of the free-volume concepts as the controlling factor of torsional motion of the excited dye.

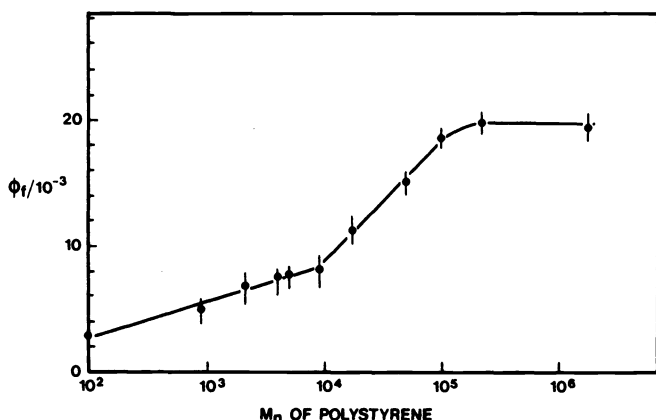


Fig. 9. Variation of 2 fluorescence with polystyrene molecular weight, M_n .

TABLE 3. Dye Fluorescence in Polystyrene with Varying Molecular Weight

polystyrene		dye fluorescence
M_n	$T_g, ^\circ\text{C}$	$\phi_f / 10^{-3a}$
1.04×10^2	-130	3.0
8.0×10^2	27	4.9
2.0×10^3	49	6.8
4.0×10^3	59	7.5
5.0×10^3	64	7.6
9.0×10^3	83	8.2
1.75×10^4	94	11.1
5.0×10^4	100	15.0
1.0×10^5	104	18.5
2.23×10^5	105	19.6
1.8×10^6	107	19.3

^aMeasured at 23°C; estimated error $\pm 10\%$.

The situation is quite different for $M_n > 10^4$ and $M_n < 10^5$; the fluorescence of 2 abruptly increases by a factor of 2 and then levels off at $M_n > 10^5$. In that molecular weight range the glass transition temperatures of PS hardly changes. It should also be noted that all films prepared were optically clear; thus it might be argued that no phase separation has occurred.

The simplest possible explanation of the sudden rise in the fluorescence of the molecular probe 2 in PS above a critical molecular weight, $M_c \sim 10^4$, is due to an abrupt change in the morphology of the bulk polymer resulting from chain contraction, or coiling. Since the torsional motion of the probe becomes progressively restricted by chain contraction, this process effectively decreases the non-radiative decay rate, k_{nr} , of the probe, leading to the sudden rise in fluorescence above that critical M_n . At PS molecular weight greater than 10^5 a polymer network will form and at this point the fluorescence levels off.

In the next section the temperature-dependence on the fluorescence of the dyes in solid polymer films will be described. This study was motivated to determine the effect of temperature on polymer free-volume and polymer conformation in the solid.

Effect of temperature on the probe fluorescence in solid polymer films

To test the validity of the free-volume restriction imposed by a polymer matrix on the dye internal relaxation, we studied the effect of temperature on the fluorescence yield of dye 2 and 3 in stereoregular polymethyl methacrylates.

The fluorescence intensity, I_F , of 2 in atactic PMMA decreases with increasing temperature as shown in Fig. 10. A break in the I_F vs. temperature plot occurs at 106°C , the glass transition temperature of a-PMMA. Similarly, the fluorescence intensity of 3 in syndiotactic PMMA decreases gradually with increasing temperature with a break in I_F vs. T occurring at 125°C , the T_g of S-PMMA as shown in Fig. 11.

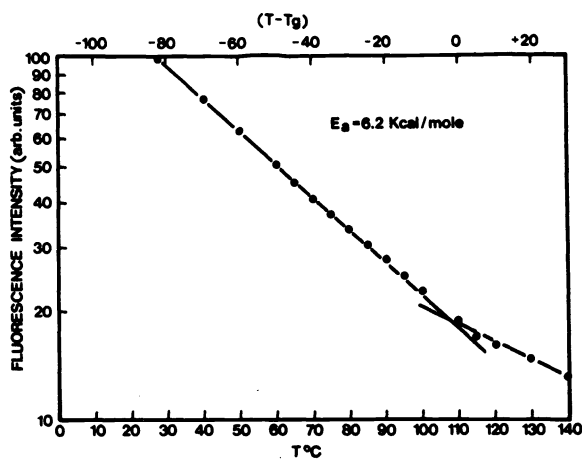


Fig. 10

Fig. 10. Dependence of fluorescence of 2 on temperature in a-PMMA.

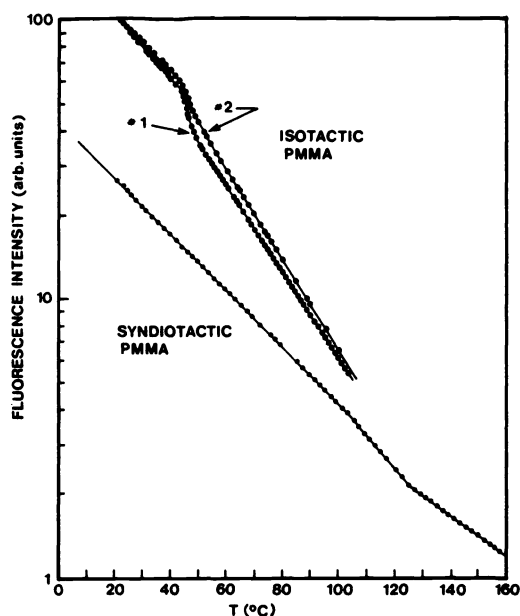


Fig. 11

The fluorescence-temperature behavior of 3 in isotactic PMMA is radically different (See Fig. 11). A sharp drop in the fluorescence occurs at $\sim 43^\circ\text{C}$, followed by the normal decrease in I_F with increased temperature. A remarkable resemblance of the I_F vs. T plot to the DSC thermogram of isotactic PMMA is observed; that is a well defined transition occurs at 43°C . This transition cannot be a glass transition but is rather consistent with a change in the conformation of the polymer chains from a tight, less flexible, to an open, more flexible, conformation. The activation energy for the relaxation process of isotactic PMMA at temperatures below 43°C is 4.2 kcal/mol, consistent with side-group motion. Above 43°C , the activation energy is 8.5 kcal/mol, which corresponds to localized main-chain motions. On the basis of the above information, one must conclude that the conformational transition at 43°C for isotactic PMMA is triggered by rotations of the side groups, which change the choice of the preferred conformation.

To summarize in atactic and syndiotactic PMMA, we observe a continuous increase in polymer free-volume with the increase of temperature up to the glass transition temperature, whereas with isotactic PMMA, a conformational transition was noted.

FUTURE WORK

We have shown that the fluorescence intensity of molecular rotor fluorescence probes is highly dependent on media free-volume, while their fluorescence emission maxima are sensitive to media polarity. This dual functionality of these probes makes them useful in the study of a variety of polymer science problems such as curing of epoxy polymers, photocrosslinking of polymers, the dynamics of formation of sterically stabilized colloidal particles, polymer relaxation phenomena and many others. By expanding the series of fluorescence probe to cover probes with different sizes one should be able to determine free-volume distribution in polymeric systems.

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