Fluorescence probe for microenvironments: On the fluorescence properties of *p-N,N*-dialkylaminobenzylidenemalononitrile in polymer matrices

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(Received 6 *April* 1982*; revised* 1 *June* 1982*)*

The effect of an alkyl group (R) in a series of poly(alkylmethacrylate) and poly(alkylacrylate) polymers on the fluorescence properties of *p-N,N*-dialkylaminobenzylidenemalononitrile derivative, **1**, has been studied. The fluorescence emission maximum shifts to the blue and the fluorescence quantum yield decreases as the chain length of R increases. These results are interpreted in terms of a model which assumes that the location of **1** is dependent on R and the change in quantum yield reflects the difference in free volume or polymer chain flexibility in various locations in these polymers.

Keywords Fluorescence probe; segmental relaxation; poly(alkylmethacrylate); poly(alkyl acrylate); microenvironmental effect; fluorescence quantum yield

INTRODUCTION

Relaxation behaviour of polymer chains has been the subject of intensive investigation for many years. A tremendous amount of work has been carried out in an effort to try and understand the details of the relaxation processes, both in solution[1] and in bulk polymers[2]. Among the various physical techniques employed, photophysical and photochemical probes have been very attractive because polymer chain motion occurring over a wide range of time scales (from millisecond to nanosecond) can be studied using probes of various reference time scales[3-5]. A number of key questions towards the use of these techniques are: (i) is the observed relaxation due to the whole 'molecule' or due to a polymer segment? (ii) which segment (or functional group) is responsible for the observed relaxation? In addition, the exact location of the probe molecule and the possible perturbation it could cause to the original environment are of concern when a chemical probe (or label) is used in these studies. Despite all these difficulties, relaxation times associated with polymer motion (relaxation) over a wide range of time scales have been reported in the literature[4-10].

We have recently reported[11] a study on the photochemistry of *p-N,N*-dialkylaminobenzylidenemalononitriles. The S_1 state of these materials is a charge-transfer π,π^* state which undergoes predominantly radiationless decay via molecular relaxation. The rate of this molecular relaxation process was found to be free-volume-dependent; it decreases as the ambient temperature decreases[11], as the molecular rigidity of the chromophore increases[11] and as the solvent viscosity increases[12]. Because of the high sensitivity of this molecular relaxation process towards a microenvironment, it has been exploited as a probe to study properties of various microenvironments[13,14].

Here, we report the results of a systematic investigation of the effect of poly(alkylmethacrylate), PRMA, and poly(alkylacrylate), PRA, matrices on the fluorescence quantum yield (φ_f) of *p-N,N*-dialkylaminobenzulidenemalononitrile, **1**, as a fluorescence probe to study polymer segmental relaxation processes. No direct correlation between the glass transition relaxation temperature (T_g) of the polymer binder and the φ_f of **1** is observed. Instead, φ_f of **1** is related to the fluorescence emission frequency (ν_F) of **1**, a parameter which has been shown to exert little influence on the φ_f values in organic solvents[11,13]. Since ν_F is correlated to the polarity of a medium in organic solvents[13], thus our results indicate that **1** 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 various sites of the polymers studied.

EXPERIMENTAL

Materials

Compound **1** was obtained from Eastman Chemicals and was purified as previously described[11]. Poly(methylmethacrylate), PMMA, $M_w = 250\,000$, $M_w/M_n = 1.04$; poly(ethylmethacrylate), PEMA, $M_w = 340\,000$, $M_w/M_n = 2.70$; poly(benzylmethacrylate),

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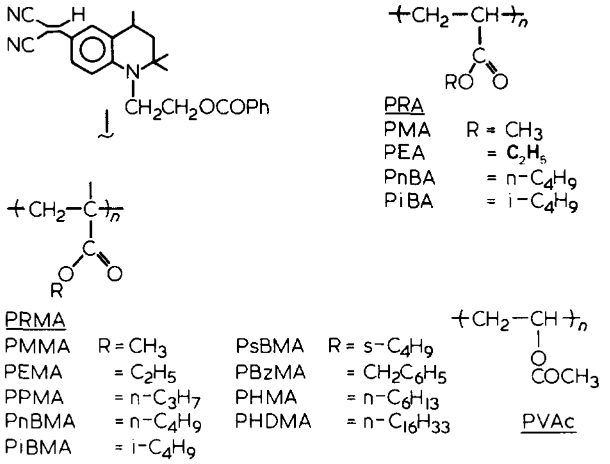

Figure 1 Structures of dye **1**, poly(alkylmethacrylate), PRMA, poly(alkylacrylate), PRA, and poly(vinyl acetate), PVAc

PBzMA, $T_g = 54°C$; poly(n-propylmethacrylate), PPMA; and poly(n-butylmethacrylate), PnBMA, high molecular weight were bought from Polysciences, Inc. Poly(isobutylmethacrylate), PiBMA, $M_w = 369\,000$, $M_n = 128\,000$; poly(hexylmethacrylate), PHMA, $T_g = -5°C$; and poly(sec-butylmethacrylate), PsBMA, $T_g = 60°C$; were obtained from Aldrich Chemical Co. Poly(methylacrylate), PMA, $M_w = 200\,000$, $M_n = 63\,200$; poly(ethylacrylate), PEA, $M_w = 125\,000$, $M_n = 38\,000$; poly(isobutylacrylate), PiBA, $M_w = 116\,000$, $M_n = 31\,600$; poly(n-butylacrylate), PnBA, $M_w = 119\,000$, $M_n = 33\,000$; and poly(hexadecylmethacrylate), PHDMA, $T_g = 15°C$; were obtained from Scientific Polymer Product Inc. All of these materials were used without further purification. Methylene chloride was spectroscopic grade from Fisher. Glass substrates (2in. x 2in.) were from Corning (7059) and were cleaned as previously described[15].

Preparation of dye–polymer films

About 2 mg of **1** was added to a methylene chloride solution containing ~250 mg polymer in a 5 ml volumetric flask. The mixture was vibrated in an ultrasonic bath until a clean solution was achieved. The dye–polymer solution was then cast onto pre-cleaned glass substrates. The wet film was covered with a crystallizing dish and was dried at room temperature for ~20 h. The air-dried polymer film was vacuum-dried in a vacuum oven at 50°C for another 48 h. Controlled experiments indicated that the resulting polymer film was free from the coating solvent. The absorbances of the resulting films were in the range of ~0.2–0.4 at the absorption maximum.

General techniques

The methodology and instruments for recording absorption and corrected fluorescence spectra have been described previously[15].

RESULTS AND DISCUSSION

Similar to the electronic spectral data of compound **1** in solution[11,13], compound **1** exhibits an intense absorption band in the blue region and a weak fluorescence emission band in the green in the visible region in polymer matrices. Both the absorption band and fluorescence emission band bandwidths of compound **1** in polymer matrices are essentially identical to those in homogeneous organic solvents, except in the PnBMA matrix. This indicates that the solvating situation of compound **1** in polymer matrices is very similar to those in organic solvents and compound **1** basically occupies one kind of site in each matrix. In the PnBMA matrix, both absorption and fluorescence emission bandwidths are ~30% broader than expected and this is presumably due to the multi-location of compound **1** in this matrix. The absorption and fluorescence emission spectral data of compound **1** in PRMA and PRA (structures shown in *Figure 1*) are listed in *Table 1*. The T_g values of the polymers used are also listed. During the course of this work, a larger variety of PRMA and PRA polymers were examined. However, the quality of the resulting dye–polymer films confined our studies to those reported in *Table 1*.

As noted in the introductory section, the S_1 state of **1** undergoes mainly radiationless decay via a free-volume-dependent molecular relaxation process. The validity of using the S_1 state of **1** as a probe to study the flexibility of its surrounding environment has been demonstrated by these authors previously where we have shown that φ_f of **1** increases as the solvent viscosity increases (or as the free volume of the solvent decreases)[12]. Here, we have used φ_f of **1** to study the flexibility of various polymer chains in polymer matrices. Before we discuss the results in *Table 1*, let us first consider some possible artifacts which may be present in polymeric systems.

It has been shown previously that **1** forms dimer and higher aggregates at high dye concentration in polymer matrices[15]. Although both dimer and higher aggregates of **1** emit in an entirely different spectral region compared with the monomer emissions and the monomer emission intensity can be evaluated accurately, owing to the similarity in their optical absorptions, the exact amount of light absorbed by the monomer of **1** is hard to calculate. The φ_f values thus obtained may not be very reliable. In

Table 1 Absorption and fluorescence emission spectral data of **1** 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	[e]	[e]	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[f]	35	22222	20408	11.0

[a] Glass transition temperature, in °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 ±10%

[e] Broad absorption and fluorescence emission bands, see text for details

[f] Data taken from ref 15

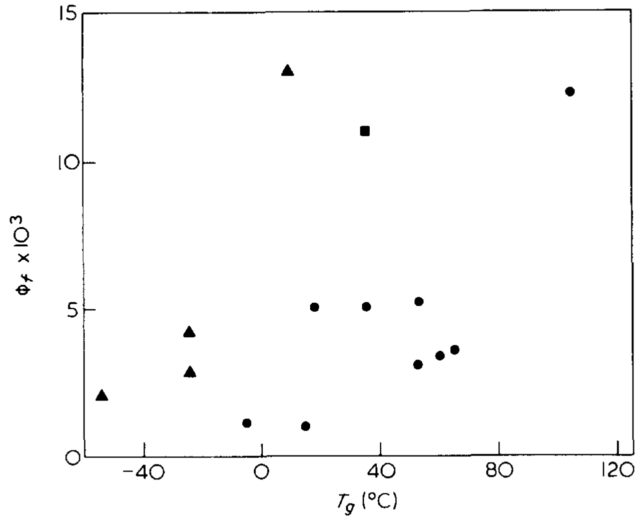

Figure 2 Plot of ϕ_f of **1** as a function of T_g (●, PRMA; ▲, PRA and ■, PVAc)

order to avoid this problem, a very low **1** concentration (<0.003 M) is used and consequently only the monomer emission is observed throughout. Moreover, the use of low dye concentration also reduces the potential plasticizing effect produced by **1** towards the binding matrix, further minimizing any possible perturbation on the relaxation of the polymer chain.

In a recent study of **1** in polystyrenes of varying molecular weight, Loutfy found that the φ_f of **1** increases as the molecular weight of polystyrene increases in the low molecular weight region ($M_n < 20 \times 10^3$ g mol^{-1}) and becomes constant in the high molecular weight region ($M_n > 20 \times 10^3$ g mol^{-1}). The increase in φ_f of **1** in the low molecular weight region was attributed to the decrease in free volume (produced at the end of each polymer chain) as the molecular weight of polystyrene increases. We have used polymers of molecular weight $> 20 \times 10^3$ g mol^{-1}, so that φ_f of **1** is in the molecular weight independent region[17]. We are thus certain that any variation of the φ_f of **1** in various polymer matrices is not caused by the use of low molecular weight polymers. Moreover, any variation is also not due to the change in the effective polarity in various polymer matrices, since we know that φ_f of **1** is not sensitive to the dielectric constant of any particular medium[11,13].

The free volume of a polymeric material generally increases as the temperature increases. Below the glass transition temperature (T_g), the polymer is in a glassy state and only subgroup motions can occur. Above T_g, the polymer is in a rubbery state, additional free volume becomes available due to the occurrence of motion of very long segments of polymer chain consisting of 20–40 carbons. The free volume of a polymer at ambient temperature should, therefore, qualitatively relate to its T_g value, e.g. a low T_g polymer should have a large free volume. Because of the free-volume-dependence of the molecular relaxation of the S_1 state of **1**, in an attempt to identify a universal probe for T_g's of various polymers, we have tried to correlate φ_f of **1** with the T_g's of PRMA and PRA. As shown in *Figure 2*, the data is very scattered and no correlation can be obtained, even within a family of polymers[18]. As discussed earlier, the data presently observed is not caused by any artifacts. The failure to observe any correlation may be due to the fact that the T_g describes the relaxation processes of a very long polymer chain whereas φ_f of compound **1** only probes the relaxational process of a very short segment (e.g., two to three carbons) immediate to it. It is conceivable that the segmental relaxation process observed with **1** is different from the relaxation responsible for the T_g relaxation. In any event, the nearly constant φ_f of **1** in PMMA, PVAc and PMA, where the T_g values vary from 9°C to 105°C, is quite striking.

However, when the φ_f of **1** is plotted as a function of ν_F (*Figure 3*), 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 **1** in PVAc is incorporated into the PRA family because of their similarity in structure (*Figure 1*). The φ_f *versus* ν_F curve of PRMA is always in the low frequency side of PRA. This implies that, for the same R group, **1** 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. We have to emphasize again that, in organic solvents, φ_f of **1** is only sensitive to factors that affect the molecular relaxation of the excited state (e.g. solvent viscosity) and is not sensitive to solvent polarity[11,13]. The difference in effective polarity produced by the same carboalkoxy group in PRMA and PMA polymers should therefore have no adverse effect on the use of the φ_f of **1** as a measure for polymer chain flexibility.

Since the fluorescence emission maximum wavelength has been found to shift to the red region of the spectrum as the dielectric constant of the solvent increases[13] and since the only polar functional group in PRMA, PRA and PVAc polymers is the carboalkoxy group, which lies very close to the polymer backbone, the effective polarity of a particular location in polymer matrix is thus expected to decrease as its distance from the polymer backbone (or the carboalkoxy group) increases. The variation of ν_F values shown in *Table 1* indicates that **1** locates differently within

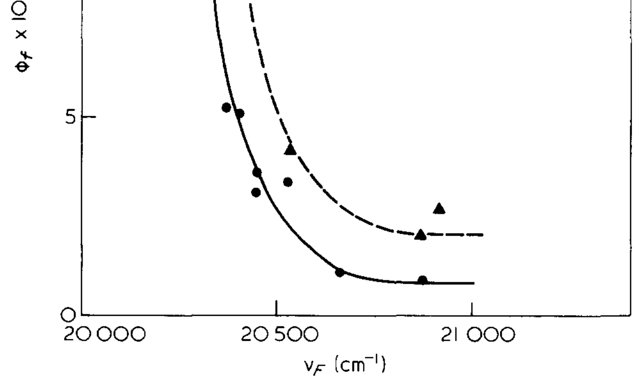

Figure 3 Plot of ϕ_f of **1** as a function of ν_F of **1** (●, PRMA; ▲, PRA and ■, PVAc)

a family of polymers. The location of **1** gradually shifts towards the end of the alkyl side chain, a less polar environment, as its length increases. This is attributable to the increased contribution of the hydrophobic interaction between the non-polar phenyl ester group of **1** and the R group of the polymer as the length of R increases.

In PMMA, PMA and PVAc matrices, **1** 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[13]. The φ_f of **1** in PMMA, PMA and PVAc are 0.0123, 0.013 and 0.011, respectively, this is 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 ν_F values observed within a family of polymers indicates that **1** tends to gradually penetrate deeper and deeper into the alkyl chain as its chain length increases. Using the ν_F of **1** as an indicator for the location of **1** 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. Despite the difference in effective polarity produced by the same carboalkoxy group ($-CO_2R$) in PRMA and PRA polymers, owing to the similarity in solvation towards **1**, the distance between the segment where **1** locates and the polymer backbone is expected to be very similar. Consequently, similar polymer chain flexibility should be recorded by **1**. In practice, similar φ_f values, which suggest a similar free folume in these locations are observed, e.g. φ_f's are 0.0036 and 0.0042 in PEMA and PEA, respectively, φ_f's are 0.0031 and 0.0028 in PiBMA and PiBA, respectively. A proper comparison between PnBMA and PnBA cannot be made because of the multilocation of **1** in a PnBMA matrix. In PHDMA matrix, ν_F of **1** is 20877 cm^{-1}, indicating that **1** is basically locating in a hydrocarbon environment (ν_F of **1** in benzene is 20921 cm^{-1}). Information on the free volume (or chain flexibility) of the hydrocarbon chain in these polymers is obtained. The φ_f of $^{\Delta}$ 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 polymers in low viscosity solvents[11,13].

In conclusion, the overall results presented in *Table 1* reveal that the polymer chain flexibility varies along the alkyl side chain. The flexibility increases as its distance from the polymer backbone increases. This effect is attributable to the friction provided by the more rigid, stiff polymer backbone as the C–C bond of individual segment rotates, and is diminished as the distance between the rotating C–C bond and the backbone increases.

SUMMARY

We have used compound **1** as a fluorescence probe to study the relaxation behaviour of polymer segments of bulk PRMA, PRA and PVAc. Owing to the increased interaction between the phenyl ester group of **1** and the alkyl side chain of.PRMA and PRA, **1** penetrates deeper and deeper into the alkyl side chain as its length increases. Consequently, segmental relaxation behaviour (or free volume) along the alkyl side chain was studied. Our results indicate that the flexibilities of the polymer backbones of PRMA, PRA and PVAc are very similar. Polymer backbones are found to have a great influence on the relaxation processes of the alkyl side chains in these polymers. The extent of this influence decreases as the segment-backbone distance increases. This is attributable to the friction produced by the relatively rigid polymer backbone towards the rotating C–C bond during the relaxation and this frictional force decreases as the distance between the backbone and the rotating C–C bond increases.

Finally, the present study shows clearly that the local polarity and the local relaxation (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.

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16 Loutfy, R. O. to be published
17 We have also examined the φ_f of **1** in PMMA of molecular weights ranging from 33 300 to 490 200 and in PVAc of molecular weights ranging from 45 000 to 1 500 000, and we have observed no molecular weight effect in these two series of polymers
18 A large variety of polymers of different functional groups and different T_g's were also examined and we found no correlation between the T_g of the polymer and φ_f of **1**