

# Fluorescence Probes as Molecular Weight Detectors of Polymers

K. A. Al-Hassan,<sup>1,2</sup> M. A. Meetani,<sup>1</sup> and Z. F. M. Said<sup>1,3</sup>

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It is shown that the relative intensity of the twisted intramolecular charge transfer (TICT) band of ester and benzonitrile derivatives of dialkylaniline in polymethylmethacrylate polymer matrices of different molecular weights (MW) to increase with increasing MW of the polymer. Our results emphasize the role of local free volumes (mobility in the matrix cage) and focus attention on the role of the MW of the polymer on the fluorescence of various TICT probes. These observations are confirmed by the red edge effect and fluorescence decay results.

**KEY WORDS:** Fluorescence probes; molecular weight; polymers; electron transfer; red edge effect; dimethylaminobenzonitrile; free volume.

## INTRODUCTION

The dual fluorescence of 4-dimethylaminobenzonitrile (DMABN), first discovered by Lippert *et al.* [1], was found to fit the twisted intramolecular charge transfer (TICT) hypothesis proposed by Grabowski and co-workers [2]. Its mechanism, during the electronic excited state lifetime, involves rotation of the dimethylamino (donor) group to a perpendicular configuration relative to the acceptor (rest of the molecule), transfer of the electronic charge from the donor to the acceptor, and reorientation of the solvent cage beside the self-nonradiative transitions. The competition between these processes determines the lifetime and the quantum yield of the TICT fluorescence band [3].

The relative positions and intensities of the normal and TICT fluorescence bands are determined by the solvent polarity and medium viscosity [2,4]. This makes

DMABN and other TICT compounds useful probes for polymers [5–10] and cyclodextrins [11–13].

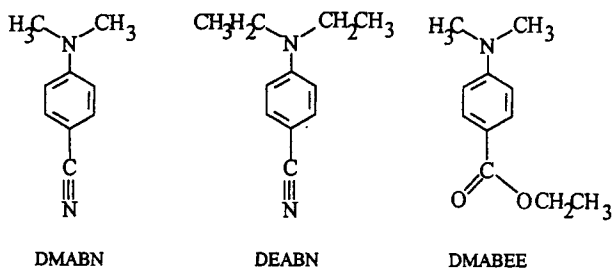
In cyclodextrins ( $\alpha$ ,  $\beta$ , and  $\gamma$ ), small cyclic polymers made of amylose units, with a structure like a cone and hydrophobic from inside [14–17], the dual fluorescence of DMABN was found to depend on both the polarity and the size of the cavity [11–13]. These studies confirm the role of the microenvironmental free volume as a driving force, besides the polarity, in controlling the TICT fluorescence of DMABN and related compounds, in rigid media.

In polymers we studied the fluorescence of DMABN and related compounds in PVA polymer matrices of different molecular weights (MW) [8] and in polyalkylmethacrylate polymer matrices of various alkyl side chain lengths [9]. We found the TICT fluorescence band of DMABN to be enhanced compared to the b-band in PVA polymer matrices of lower MW. In polyalkylmethacrylate polymers, however, the relative intensity of the TICT band was hardly observed or changed relative to the b-band by changing the polymers from polymethylmethacrylate (PMMA), to polyethylmethacrylate (PEMA), or to polybutylmethacrylate (PBMA) or to polyhexylmethacrylate (PHMA).

<sup>1</sup> Department of Chemistry, Yarmouk University, Irbid, Jordan. Fax: 962-2-247983 or (274725).

<sup>2</sup> To whom correspondence should be addressed.

<sup>3</sup> Present address: Faculty of Technology, University of Qatar, Doha, Qatar.



Scheme I

Table I. Approximate Average MW of PMMA Polymer Matrices Determined by GPC

Sample No.	Initiator conc. [I]	Measured MW of PMMA
1	0.0000	$3.2 \times 10^5$
2	0.00228	$8.6 \times 10^4$
3	0.00913	$5.5 \times 10^4$
4	0.06385	—
5	0.11965	—
6	0.17328	—
7	0.22914	$2.9 \times 10^4$
8	0.3567	$2.1 \times 10^4$

These observations were attributed to the opposite roles of the local polarity and local free volume of a polymer site on the TICT emission of DMABN and related compounds [8,9]. On one hand, as the polarity of the methacrylate polymers decreases from PMMA to PHMA, the TICT band is expected to be suppressed. On the other hand, as the rigidity (which reflects the local free volume) of these polymers decreases from PMMA to PHMA, the TICT fluorescence is expected to be enhanced. Therefore it was suggested that the enhancement of the TICT band of DMABN caused by the increase in free volume is suppressed by the decrease in polarity as one moves from PMMA to PHMA polymers, and vice versa. The TICT fluorescence of DMABN in this series of polymers was detected only by the use of either red edge effect (REE) [9] or time-resolved fluorescence (TRF) [10] techniques.

The purpose of the present study was to separate the effect of the local polarity from that of the local free volume of polymer matrices on the dual fluorescence of DMABN and related compounds (Scheme I). As a step in this direction we prepared samples of DMABN, DEABN, and DMABEE and measured their fluorescence spectra in PMMA polymer matrices of different MW.

## EXPERIMENTAL

### Materials

Pure, recrystallized, and sublimed samples of DMABN, DEABN, and DMABEE (Fluka or Aldrich) were used in this study.

Methylmethacrylate (MMA; BDH Chemicals) was purified by fractional distillation under reduced pressure with nitrogen bubbling (b.p., 30°C). The middle fraction of the monomer was collected and kept in a refrigerator until used.

1,1'-Azobis cyclohexanecarbonitrile (ABCHC) from Aldrich Chemical, 98%, was used as the initiator for polymerization.

### Polymerization

Polymerizations were carried out at 60°C in a glass rod-sized tube (5-mm width inside). About 5.0 cm<sup>3</sup> of the monomer with the probe,  $\sim 3.0 \times 10^{-5}$  M, and initiator (varying from one tube to another) was poured into these tubes through a narrow orifice, and the tubes were sealed after being flushed with N<sub>2</sub> gas. The tubes were left in an oven, fixed at 60°C for 3 days to achieve complete polymerization (full conversion to a bulk solid polymer).

The concentration of the initiator in the tubes was varied from 0.0 to 0.0357 mol dm<sup>-3</sup>. This produced polymers of different molecular weights.

### Procedure for MW Determination of Polymers

Molecular weights of PMMA polymers were determined, at Qatar Petrochemical Company (QAPCO, Umsaed, Qatar), by GPC (Water Associates, UK) using  $\mu$ -Styragel columns 500, 10<sup>3</sup>, 10<sup>5</sup>, 10<sup>5</sup>, and 10<sup>6</sup> Å in pore size, with a differential refractometer detector. The solvent used was 1,2,4-trichlorobenzene; flow rate, 1 ml/min; injection volume, 2500  $\mu$ l; and temperature, 30°C. The columns were calibrated by the universal calibration method with different standard polystyrene samples (MW  $3.0 \times 10^3$ – $1.0 \times 10^7$ ) from pressure chemicals (U.S.A.). The mean molecular weights  $M_n$  as a function of the initiator concentration, obtained using the above procedure, are listed in Table I.

### Spectroscopic Measurements

Fluorescence spectra (corrected) were measured using FS 900 CDT steady-state L-geometry Spectrofluorometer from Edinburgh Analytical Instruments (EAI).

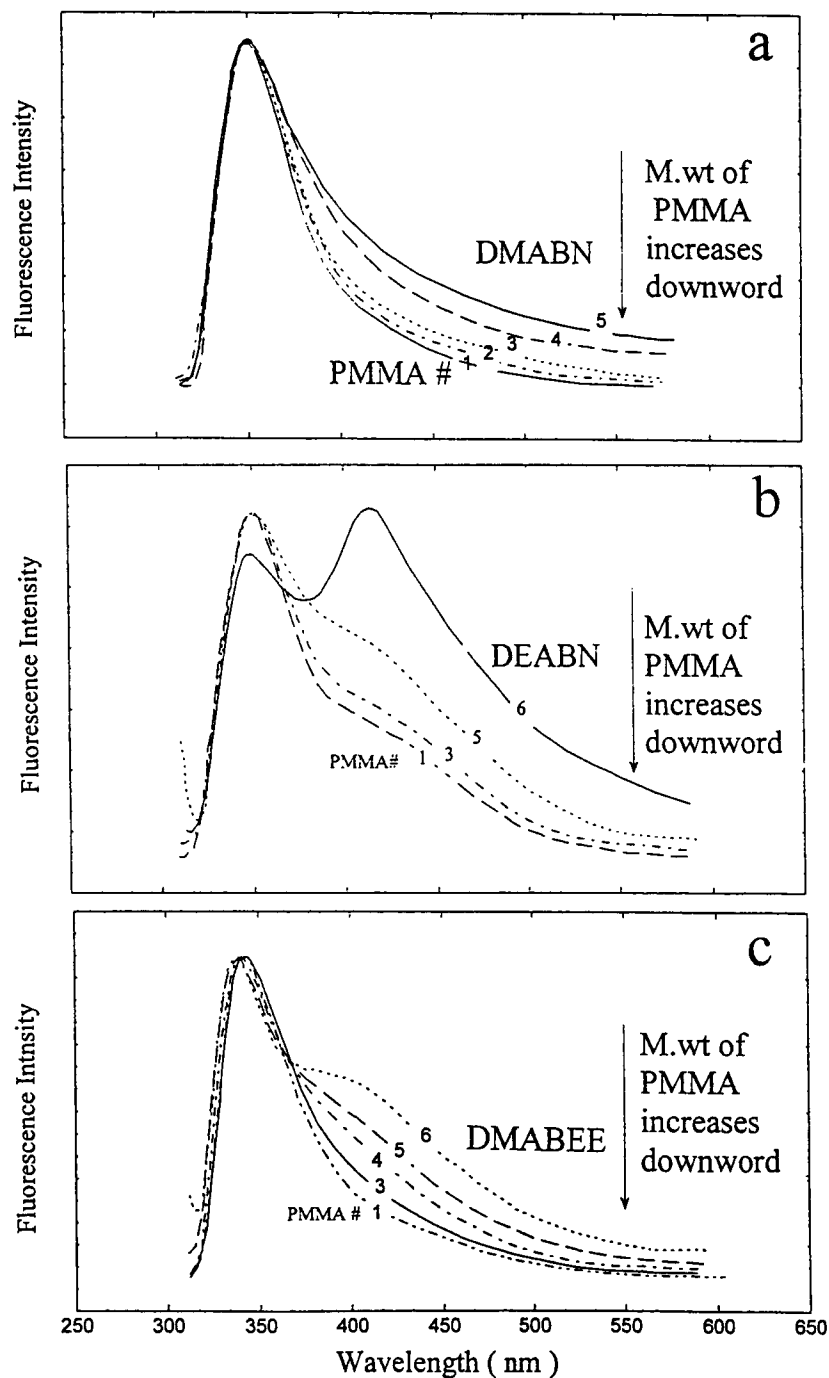


Fig. 1. Fluorescence spectra of (a) DMABN, (b) DEABN, and (c) DMABEE in PMMA polymer matrices of different MW [from 320,000 g/mol (No. 1) to ~29,000 g/mol (No. 6); see Table I] at room temperature;  $\lambda_{exc} \sim 300$  nm.

Fluorescence decay times measurements were obtained by the technique of time-correlated single-photon counting using an Edinburgh Instruments 199 M. The details of the instrument and method of measurements were described earlier [7].

## RESULTS AND DISCUSSION

Variation of the MW of PMMA polymers was obtained by introducing different amounts of the initiator, ABCHC, to solutions of the probe,  $3 \times 10^{-5}$  M, in meth-

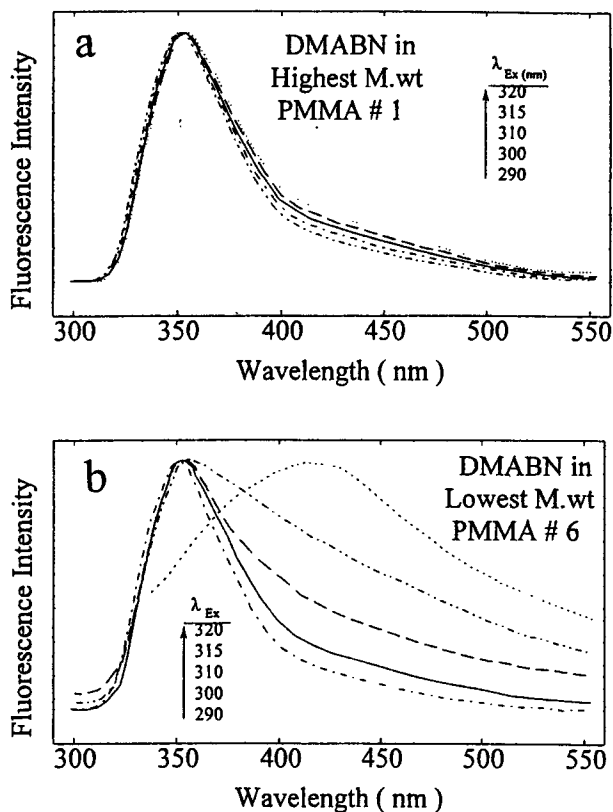


Fig. 2. Room-temperature fluorescence spectra of DMABN in a PMMA polymer matrix of MW 320,000 g/mol (a) and in a PMMA polymer matrix of MW  $\sim$ 29,000 g/mol at different excitation wavelengths.

ylmethacrylate monomer and were allowed to polymerize at a temperature  $\leq 60^\circ\text{C}$ . The details of the experiment are given under Experimental. The approximate mean average MW,  $M_n$ , as a function of initiator concentration are listed in Table I [18,19].

Figure 1 shows the fluorescence spectra of DMABN, DEABN, and DMABEE in different PMMA polymer matrices of different MW (range, 320,000 to  $<29,000$  g/mol) at room temperature. It is clear that the relative intensity of the TICT band increases with decreasing MW of the polymer and with increasing size of the dialkylamino moiety. It is also evident that the ester shows a larger TICT band compared to the corresponding nitrile derivatives.

This is consistent with our previous observations made for these compounds in PMMA polymer matrices of undetermined MW [8]. The enhanced TICT band in DEABN compared to DMABN is due to the larger diethylamino group, which is pretwisted (as photoelectron spectroscopy data and other spectroscopy techniques

show) by  $15\text{--}20^\circ$  compared to the dimethyl amino group [20,21].

The enhanced TICT band in DMABEE compared to DMABN is attributed to the presence of conical intersections (CI) along the reaction coordinate (during the excited-state lifetime) of DMABN and other nitrile derivatives. These CI are absent in DMABEE and other ester derivatives [22–26].

The enhancement of the TICT band in DMABN, DEABN, and DMAEE (Figs. 1a, b, and c, respectively) with decreasing MW of the PMMA polymer matrix is attributed to the free volume effect, which gains importance as the MW of the polymer decreases. As these polymers have the same chemical character and are assumed to have the same polarity effect on the TICT band, it is therefore the rigidity of these polymers that becomes important in controlling the TICT emission. PMMA polymer of MW 320,000 (No. 1, Figs. 1a, b, and c) is highly rigid compared to the softer PMMA polymer of MW  $\sim$ 29,000 (No. 5 and/or No. 6). The dialkylamino group will have more freedom (free volume) to rotate (during the excited state life time) in softer polymers compared to rigid ones. This is consistent with our previous observations and interpretations made for DMABN in different PVA polymer matrices of different MW. These results are also consistent with the observations made by Tazuke and co-workers for the same probes as a sensor of free volume in an acetate solution of a methacrylate copolymer [27,28]. They concluded that the longer the side chain of a polymer matrix, the larger is the free volume and the larger is the TICT quantum yield, despite the slight decrease in the local polarity. Moreover, our results are in line with Loutfy [29], who used the concept of free volume and correlated it with differences in the glass transition ( $T_g$ ) temperatures of the polymers. He concluded that the smaller the  $T_g$ , the larger is the free volume.

The relative intensity of the TICT band in DMABN and related compounds in PMMA polymer matrices of different MW is enhanced upon excitation at the red edge of the first absorption band. These observations are attributed to the red edge effect (REE), which has been explained in detail elsewhere [7]. Figures 2, 3, and 4 show the REE results for DMABN, DEABN, and DMABEE in PMMA polymer matrices of MW 320,000 and 29,000 g/mol, respectively. It is evident that for longer-wavelength excitation, the relative contribution of the TICT band is strongly enhanced. This is because pretwisted ground-state species contribute mainly to the long-wavelength tail of the absorption band [30]. Actually the distribution of these subclasses of rotamers in the ground state and their corresponding crossrelaxation times as

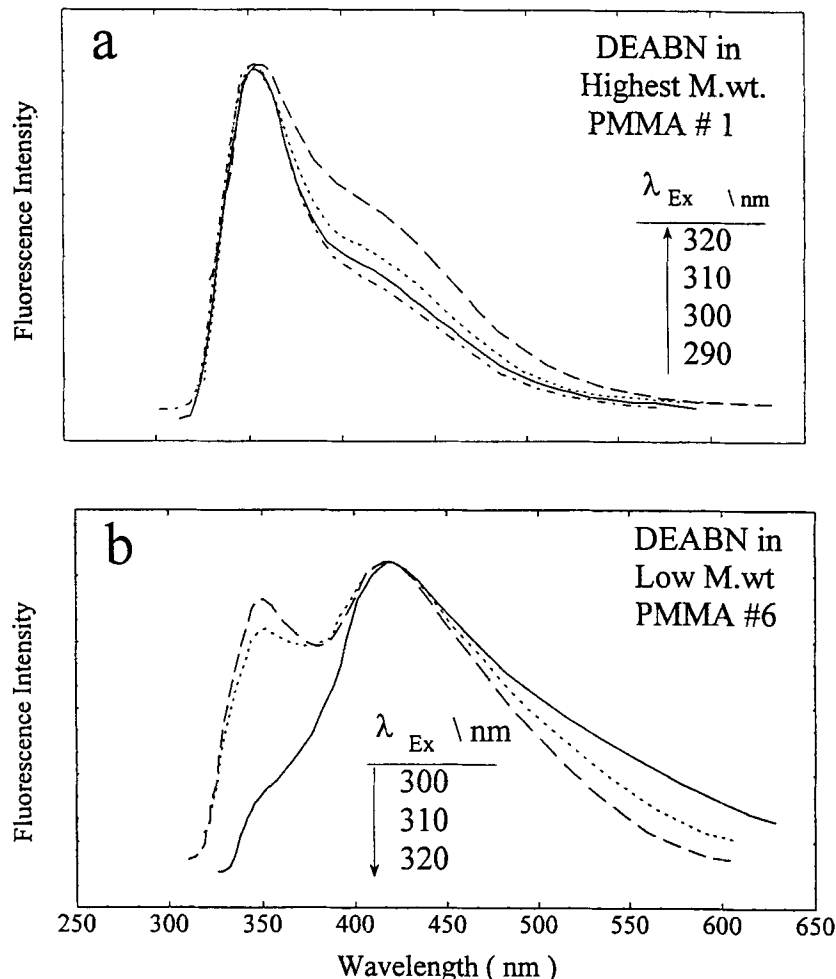


Fig. 3. Room-temperature fluorescence spectra of DEABN in a PMMA polymer matrix of MW 320,000 g/mol (a) and in a PMMA polymer matrix of MW  $\sim$ 29,000 g/mol at different excitation wavelengths.

compared with the fluorescence lifetimes in the excited state vary from one polymer to another, depending on their rigidities. Polymer 1 is the most rigid and is expected to trap conformers which, on average, have larger pretwist angles and hence absorb (as seen from the excitation spectra) at longer wavelengths compared with softer polymers, e.g., Nos. 2, 4, and 6. After excitation each subclass of rotamers will relax toward the TICT conformation with different probabilities. The excitation spectra shown for the case of DMABEE (Fig. 5) are good representatives of these subclasses of rotames. This is consistent with our previous results and interpretations [5–10].

The role of molecular weight of polymers on the emission properties of DMABN and related compounds

is confirmed by the fluorescence decay results. Figure 6 shows the fluorescence decay of DMABN in PMMA polymer matrices of different MW monitored at the normal band ( $\sim$ 350 nm) (Fig. 6a) and at the TICT band ( $\sim$ 430 nm) (Fig. 6b). The decay at either the 350- or the 430-nm band becomes faster in lower MW polymers. The corresponding lifetimes together with those measured for DMABEE in some of the polymers are listed in Table II. The mean lifetimes were calculated using a biexponential fit according to the following relation:  $\langle\tau\rangle = \Sigma\tau_i Q_i$ , where  $Q_i = \tau_i A_i / \Sigma\tau_i A_i$  are the quantum yields of the decay components, and  $A_i$  the preexponential factors in the fluorescence decay function. The biexponential model is only an approximation to the multiexponential decay of different conformers of the

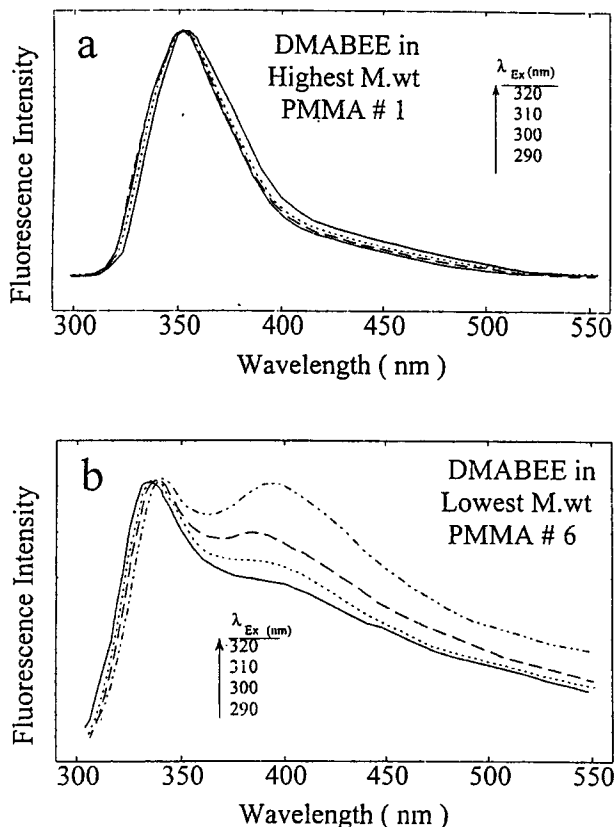


Fig. 4. Room-temperature fluorescence spectra of DMABEE in a PMMA polymer matrix of MW 320,000 g/mol (a) and in a PMMA polymer matrix of MW  $\sim$ 29,000 g/mol at different excitation wavelengths.

probe trapped in the large distribution of different sites of the polymer. The quality of the fits are determined by the distribution of residuals, the autocorrelation function, and the  $\chi^2$  value. The fluorescence lifetimes presented in Table II are consistent with our previous results for these probes in PMMA polymer matrices of undefined MW [9]. The somewhat shorter lifetimes obtained in the case of lower MW PMMA compared to higher MW PMMA polymer matrices is probably due to differences in their rigidities and therefore can be rationalized to the free volume effects. The PMMA polymer matrix of MW = 29,000 is much softer and therefore has a larger free volume compared to the rigid PMMA polymer matrix of MW = 320,000 (we assumed them to have similar polarities). Most probably in rigid media some nonradiative deactivation processes are slowed down. One can expect the torsional motions, determining the overlap of  $D^+$  (donor) and  $A^-$  (acceptor) moieties in the TICT state,

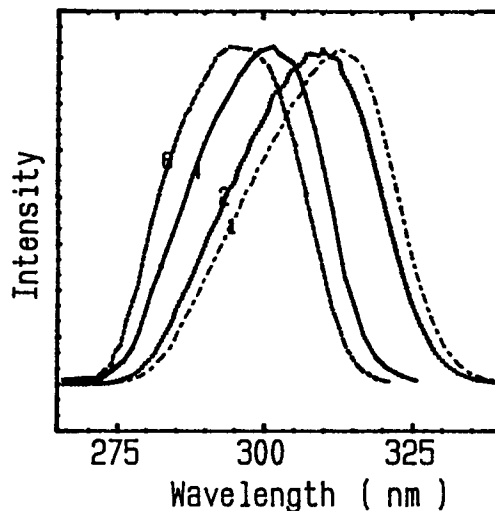


Fig. 5. Excitation spectra (normalized) for DMABEE ( $\lambda_{Fl} = 350$  nm) in various PMMA polymer matrices of different MW (see Table I for MW values).

to be responsible both for the emission rate and for the nonradiative rate [3]. Such motion would depend critically on the free volume available at the site.

In conclusion, we believe that we have shown that the fluorescence of DMABN and other TICT probes can be used to rationalize polymers according to their molecular weights and hence can be used as molecular weight detectors of polymers.

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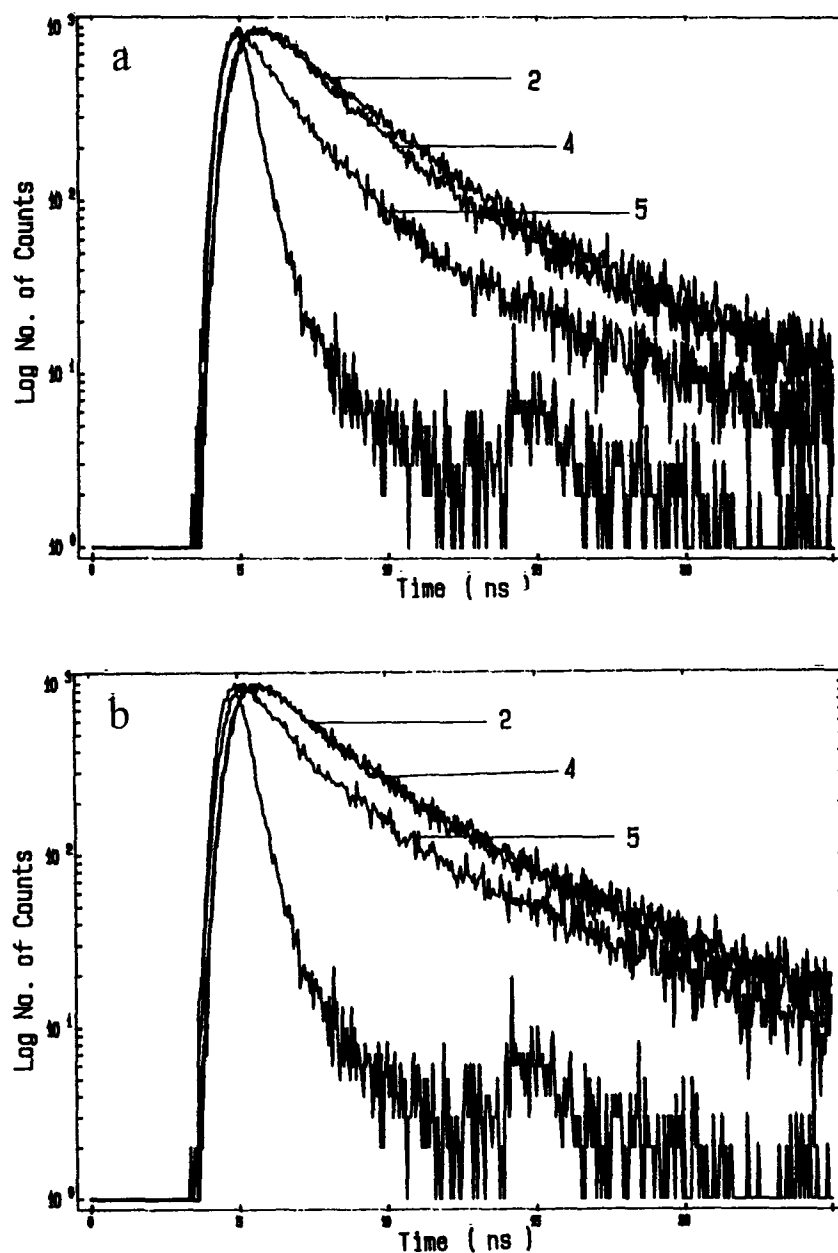


Fig. 6. Fluorescence decay curves of DMABN in various PMMA polymer matrices of different MW (see Table I for MW values) at room temperature monitored at 350 nm (a) and at 430 nm (b).  $\lambda_{exc} = 315$  nm.

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Table II. Fluorescence Decay Parameters [ $\tau$ -(ns)] of DMABN and DMABEE in Different Polymethylmethacrylate Polymer Matrices of Different Molecular Weights Monitored at 350 and 430 nm,  $\lambda_{\text{ex}} = 316 \text{ nm} (\pm 20 \text{ nm})$

Probe	Polymer sample No.	$\lambda_{\text{em}}$ (nm)	$\tau_1$ (ns)	$Q_1$	$\tau_2$ (ns)	$Q_2$	$\chi^2$	Mean $\tau$ (ns)	
DMABN	1	350	1.1	0.25	3.3	0.75	1.2	2.8	
	2	350	1.1	0.11	3.1	0.89	1.2	2.9	
	4	350	1.6	0.36	3.3	0.64	1.0	2.7	
	5	350	0.8	0.47	2.6	0.53	1.3	1.8	
	1	430	1.1	0.14	3.6	0.86	1.0	3.3	
	2	430	1.4	0.28	3.9	0.72	1.0	3.2	
	4	430	0.9	0.16	3.3	0.84	1.1	2.9	
	5	430	0.8	0.38	3.8	0.62	1.3	2.7	
	DMABEE	1	350	1.3	0.55	2.8	0.45	1.1	2.0
		4	350	1.3	0.69	3.3	0.31	1.1	1.9
5		350	0.9	0.59	2.4	0.41	1.1	1.5	
1		430	1.7	0.37	4.2	0.63	1.1	3.3	
4		430	1.3	0.25	3.8	0.75	1.1	3.2	
	5	430	1.8	0.70	5.7	0.30	1.2	3.0	

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