

# Intramolecular excimer formation in 1-naphthylmethyl methacrylate/methyl methacrylate copolymers

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Intramolecular excimer formation of poly(1-naphthylmethyl methacrylate) and a series of 1-naphthylmethyl methacrylate/methyl methacrylate copolymers has been investigated using steady-state fluorescence spectroscopy and the time-correlated single-photon counting technique. A linear relationship between the ratio of excimer to monomer emission intensities and the copolymer composition was established. The monomer fluorescence decays in these copolymers could be characterized by sums of exponential terms (single, double or triple), depending upon composition, while the excimer decays were poorly described by either single- or double-exponential fits. Some unusual phenomena for the photophysical processes in this polymer system are presented and discussed.

(Keywords: naphthalene fluorescence; energy migration; fluorescence decay measurements)

## INTRODUCTION

The fluorescence of polymers incorporating aromatic chromophores in the repeat unit is characterized by excimer emission. In order to clarify the intramolecular processes of excimer formation, the influences of various factors such as solvent, microstructure and conformation of polymers have been studied extensively by many research groups. Soutar has reviewed this topic and commented extensively on the role of energy migration on excimer formation<sup>1</sup>. It is well documented that the ratio of excimer to monomer emission intensities,  $I_e/I_m$ , increases with increasing mole fraction of chromophore<sup>1</sup>. This phenomenon was observed originally in styrene copolymers<sup>2,3</sup>. In many systems, this increase is proportional to the fraction of chromophore pairs  $f_{nn}$  in the polymer backbone. Nakahira *et al.*<sup>3</sup>, Geuskens *et al.*<sup>4</sup> and Hill *et al.*<sup>5</sup> have all observed a linear dependence of  $I_e/I_m$  on  $f_{nn}$ . Monnerie *et al.*<sup>6</sup> examined a series of phenyl-substituted alkanes and showed that  $I_e/I_m$  increases from the model compounds with two phenyl groups to the model compounds with three phenyl groups, but does not increase further for the tetraphenyl compound. Morawetz *et al.*<sup>7</sup> have observed that  $I_e/I_m$  is slightly influenced by the sequence length.

Soutar and his group have studied a series of homopolymers and copolymers, e.g. poly(1-vinylnaphthalene-co-methyl methacrylate)<sup>8,9</sup>. They invoked energy migration among naphthalene groups to explain their observation that  $I_e/I_m$  did not increase linearly with  $f_{nn}$ . To fit

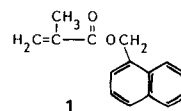
their data, they derived the expression:

$$I_e/I_m = kf_{nn}\bar{l}_n \quad (1)$$

Here  $\bar{l}_n$  is the mean sequence length of chromophores. This expression assumes that excimer formation is dominated by nearest-neighbour interactions ( $f_{nn}$ ) and that  $\bar{l}_n$  properly describes energy migration in the system.

MacCallum<sup>10</sup> has proposed alternative models to explain these data without the need for energy migration. He points out, for example, that the two chromophores at the end of an  $\bar{l}_n$  sequence are statistically less liable to form an excimer than those within the sequence. The different types of behaviour observed for different polymers, and the variety of models put forth to explain these observations, emphasize the complexity of the problem.

In this context we report a new kind of behaviour for copolymers of 1-naphthylmethyl methacrylate (1-NMMA; **1**) with methyl methacrylate (MMA),  $I_e/I_m$  increasing in proportion to  $f_n$ , the mole fraction of naphthalene (N) groups in the polymer.



## EXPERIMENTAL

The preparation, purification and characterization of these polymers have been described in detail elsewhere<sup>11,12</sup>. Chloroform (CHCl<sub>3</sub>) and ethyl acetate (EA)

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were distilled and middle fractions were collected. Each polymer was dissolved in sufficient solvent to have a naphthalene chromophore concentration of  $2 \times 10^{-5} \text{ mol l}^{-1}$ . The solutions were then transferred into 13 mm o.d. cylindrical quartz tubes, which were connected to the Pyrex cells via graded seals, degassed on a vacuum line by five freeze-pump-thaw cycles and sealed under a vacuum less than  $3 \times 10^{-5}$  Torr.

Steady-state fluorescence spectra in  $\text{CHCl}_3$  or EA were run on a Spex spectrofluorometer ( $\lambda_{\text{ex}} = 290 \text{ nm}$ ). Fluorescence decay profiles were obtained using the time-correlated single-photon counting<sup>13</sup> method ( $\lambda_{\text{ex}} = 282 \text{ nm}$ ;  $\lambda_{\text{em}} = 338 \text{ nm}$  for monomer;  $\lambda_{\text{em}} = 440 \text{ nm}$  for excimer). Sample decays in  $\text{CHCl}_3$  and the lamp profiles were recorded until the maximum counts in the early channel reached more than 20 000. Observed decay traces were fitted by an iterative deconvolution 'match and compare' technique using a non-linear least-squares algorithm.

## RESULTS AND DISCUSSION

Table 1 presents all of the data pertinent to these experiments. The samples are listed, along with their composition, and values of the parameters  $f_{\text{nn}}$ ,  $\bar{l}_{\text{n}}$  and  $f_{\text{nn}}\bar{l}_{\text{n}}$ . Each of the polymers had molecular weights (by gel permeation chromatography, based upon PMMA standards) close to 50 000. Values of  $I_{\text{e}}/I_{\text{m}}$ , obtained from steady-state fluorescence measurements in chloroform and in ethyl acetate, are also presented in Table 1.

To appreciate the amount of excimer formed, it is best to look directly at the fluorescence spectra themselves. The spectra for samples in  $\text{CHCl}_3$  are presented in Figure 1. It can be seen that in the lower NMMA composition range (samples 1–4, 1-NMMA content 0.59–4.65 mol%) no excimer emission spectra appears.

However, at aromatic contents of 6.19 mol% and greater, the spectra exhibit excimer emission in the region 370–390 nm. It is evident that the copolymer with the highest 1-NMMA content (largest  $f_{\text{n}}$ ) has the highest relative excimer intensity.

The plots of  $I_{\text{e}}/I_{\text{m}}$  vs.  $f_{\text{n}}$  were built up using the data for copolymerization of 1-NMMA and MMA given in Table 1. A linear relationship for the copolymers was obtained for samples in both  $\text{CHCl}_3$  and ethyl acetate (Figure 2). The correlation coefficients were 0.9965 and 0.9970, respectively. Figure 2 shows that the slopes of

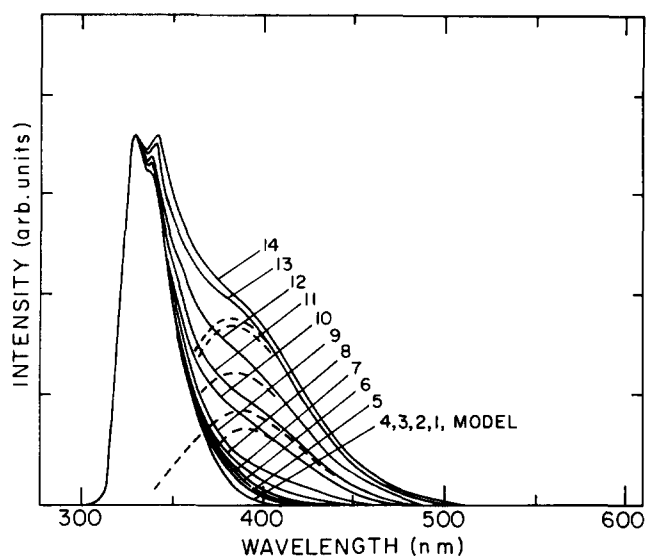


Figure 1 Fluorescence spectra of copolymers of 1-NMMA and MMA in  $\text{CHCl}_3$ ;  $\lambda_{\text{ex}} = 280 \text{ nm}$ ; chromophore concentration,  $2 \times 10^{-5} \text{ mol l}^{-1}$ . Excimer areas are obtained by subtracting the normalized spectrum of the model from each curve

Table 1 Composition and fluorescence data for 1-NMMA/MMA copolymers

| Sample | $f_{\text{n}}$ (mol%) | $f_{\text{nn}}$ | $\bar{l}_{\text{n}}$ | $f_{\text{nn}}\bar{l}_{\text{n}}$ | $I_{\text{e}}/I_{\text{m}}$ |      |
|--------|-----------------------|-----------------|----------------------|-----------------------------------|-----------------------------|------|
|        |                       |                 |                      |                                   | $\text{CHCl}_3$             | EA   |
| Model  | 100.00                | 0.0             | 0.0                  | 0.0                               | 0.0                         | 0.0  |
| 1      | 0.59                  | 0.0             | 1.0                  | 0.0                               | 0.0                         | 0.0  |
| 2      | 1.09                  | 0.01            | 1.01                 | 0.01                              | 0.0                         | 0.0  |
| 3      | 2.44                  | 0.02            | 1.02                 | 0.02                              | 0.0                         | 0.0  |
| 4      | 4.65                  | 0.04            | 1.04                 | 0.04                              | 0.0                         | 0.01 |
| 5      | 6.19                  | 0.05            | 1.05                 | 0.05                              | 0.03                        | 0.02 |
| 6      | 9.74                  | 0.08            | 1.09                 | 0.09                              | 0.04                        | 0.03 |
| 7      | 12.35                 | 0.10            | 1.12                 | 0.11                              | 0.05                        | 0.06 |
| 8      | 15.97                 | 0.14            | 1.16                 | 0.16                              | 0.06                        |      |
| 9      | 22.36                 | 0.19            | 1.29                 | 0.25                              | 0.10                        | 0.08 |
| 10     | 43.17                 | 0.39            | 1.63                 | 0.64                              | 0.21                        |      |
| 11     | 56.79                 | 0.52            | 2.09                 | 1.09                              | 0.26                        | 0.28 |
| 12     | 76.63                 | 0.73            | 3.72                 | 2.72                              | 0.37                        | 0.35 |
| 13     | 92.13                 | 0.91            | 10.72                | 9.76                              | 0.49                        | 0.41 |
| 14     | 100.0                 | 1.0             |                      |                                   | 0.49                        | 0.48 |

$f_{\text{n}}$ , mol% of 1-NMMA units in the copolymers

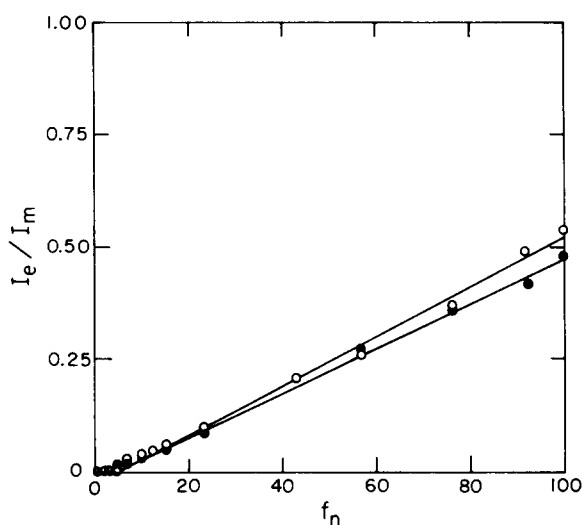
$f_{\text{nn}}$ , fraction of (1-NMMA)-(1-NMMA) diads in the copolymers

$\bar{l}_{\text{n}}$ , mean length of sequences of 1-NMMA units

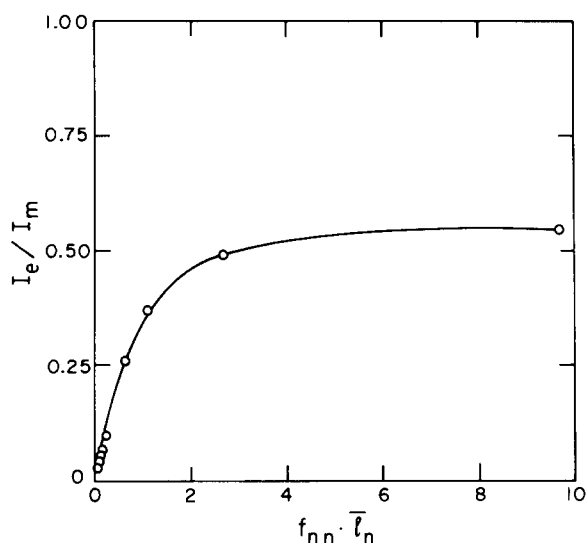
$I_{\text{e}}$ , excimer fluorescence emission intensity

$I_{\text{m}}$ , monomer fluorescence emission intensity

EA, ethyl acetate model, 1-naphthylmethyl pivalate



**Figure 2** The variation in the relative fluorescence intensity ( $I_e/I_m$ ) with the content (mol%) of 1-NMMA ( $f_n$ ). ○,  $\text{CHCl}_3$ ; ●, EA



**Figure 3** The variation in the relative fluorescence intensity ( $I_e/I_m$ ) with the product ( $f_{nn} \cdot \bar{l}_n$ ) of the diads of 1-NMMA units and the mean sequence length of 1-NMMA

the straight lines describing the dependence of  $I_e/I_m$  on  $f_n$  for this polymer system in both solvents are almost the same. This shows that the relationship between excimer and monomer emission in this series of work is a very simple one and is determined mainly by the content (mol%) of 1-NMMA in the copolymers. When our data are plotted against more complicated functions such as  $f_{nn}$ , or  $f_{nn} \bar{l}_n$ , we obtain curved plots (e.g. *Figure 3*). One possible explanation for the difference between our results and those reported previously<sup>3-5</sup> is that here the naphthalene chromophore is attached to the polymer chain through a longer 'leash'<sup>14</sup> and might be able more freely to attain the excimer geometry. Therefore, in this case, it is possible that the influence of  $f_{nn}$  or  $\bar{l}_n$  on the excimer formation is weaker. It is possible that the excimers in P(1-NMMA) and in MMA copolymers containing 1-NMMA could be formed either by nearest or non-nearest neighbours of naphthalene chromophores.

Naphthalene monomer fluorescence decay profiles from deoxygenated samples of copolymers in ethyl acetate at 23°C are displayed in *Figure 4*. In the lowest

1-NMMA composition range (samples 1-3, 1-NMMA content 0.59-2.44 mol%), the emission intensity decay of monomer  $I_m(t)$  could be described well by a single-exponential function:

$$I_m(t) = A_1 \exp(-t/\tau_1) \quad (2)$$

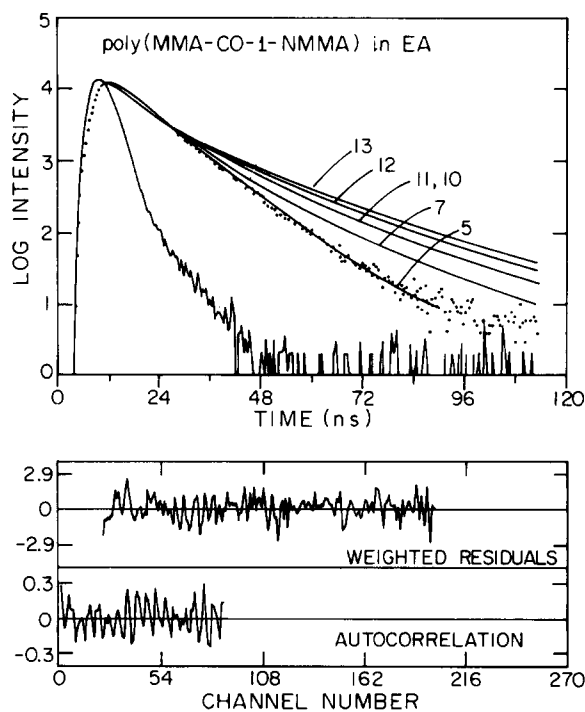
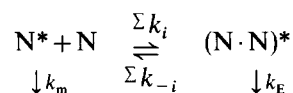
The fluorescence lifetime (44.8 ns) is identical for the three samples<sup>11</sup>. In sample 5 (1-NMMA content 6.19 mol%) the fluorescence decay profile is non-exponential, but could be fitted to a sum of two exponential terms:

$$I_m(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (3)$$

However, at aromatic chromophore contents of 12.35 mol% and greater (samples 7-14), we needed to use a sum of three exponential terms to fit the data. The excimer decays  $I_e(t)$  were poorly described by single- and double-exponential fits. The characteristic decay times and pre-exponential factors obtained from analysis of the fluorescence decay profiles of these copolymers are listed in *Tables 2* and *3*. It should be emphasized that the lifetimes themselves are not physically significant; they serve only to parametrize the fluorescence decay data. It was frequently convenient to calculate mean decay time  $\langle \tau \rangle$ , which is defined as:

$$\langle \tau \rangle = \frac{\int_0^{\infty} t I_m(t) dt}{\int_0^{\infty} I_m(t) dt} \quad (4)$$

The data and the  $\langle \tau \rangle$  for naphthalene emission calculated using equation (4) are listed in *Table 2*. The rise times (cf  $\tau_1$ , *Table 3*) for excimer emission are estimated to be of the order of 4 ns. These results provide further evidence for the formation of excimers via diffusive encounters.



**Figure 4** A plot of  $\log I_m(t)$  vs.  $t$  for 1-NMMA/MMA copolymers with varying 1-NMMA content:  $\lambda_{ex} = 282$  nm,  $\lambda_{em} = 338$  nm

**Table 2** Decay data for (1-NMMA/MMA) copolymers

| Sample | $f_n$ (mol%) | $A_1$  | $\tau_1$ (ns) | $A_2$  | $\tau_2$ (ns) | $A_3$  | $\tau_3$ (ns) | $\langle\tau\rangle$ (ns) |
|--------|--------------|--------|---------------|--------|---------------|--------|---------------|---------------------------|
| 5      | 6.19         | 0.0133 | 20.52         | 0.2010 | 7.46          | 0.0619 | 11.70         | 8.85                      |
| 7      | 12.35        | 0.0133 | 20.52         | 0.1366 | 5.19          | 0.1253 | 10.48         | 10.01                     |
| 10     | 43.17        | 0.0272 | 21.12         | 0.1546 | 4.33          | 0.1060 | 10.61         | 11.36                     |
| 11     | 56.79        | 0.0262 | 21.25         | 0.1667 | 4.62          | 0.0901 | 11.14         | 11.38                     |
| 12     | 76.63        | 0.0298 | 22.72         | 0.1888 | 4.04          | 0.0836 | 11.61         | 12.35                     |
| 13     | 92.13        | 0.0459 | 22.08         | 0.1790 | 2.63          | 0.1126 | 8.22          | 12.96                     |

**Table 3** Excimer fluorescence ( $\lambda_{em}=440$  nm) growth and decay data for copolymers in  $\text{CHCl}_3$ 

| Sample | $f_n$ (mol%) | $A_1^2$ | $\tau_1$ (ns) | $A_2$  | $\tau_2$ (ns) | $A_3$  | $\tau_3$ (ns) |
|--------|--------------|---------|---------------|--------|---------------|--------|---------------|
| 7      | 12.35        | -0.3015 | 3.74          | 0.0435 | 34.90         | 0.3324 | 17.58         |
| 10     | 43.17        | -0.2641 | 3.68          | 0.0716 | 32.31         | 0.2856 | 17.42         |
| 11     | 56.79        | -0.2878 | 3.61          | 0.0564 | 33.11         | 0.3134 | 17.39         |
| 12     | 76.63        | -0.2254 | 3.34          | 0.0507 | 35.90         | 0.2788 | 18.43         |
| 13     | 92.13        | -0.2261 | 2.65          | 0.0645 | 36.67         | 0.2423 | 19.24         |

These results are consistent with the general mechanism given in the above scheme, where excimer formation is depicted as being largely diffusive, with a possible energy migration component, and a distribution of excimer formation rates described by  $\sum k_i$ . Excimer dissociation rates are described by  $\sum k_{-i}$ . One of the most striking features of our fluorescence decay measurements is that we can demonstrate the importance of excimer dissociation in our system.

In *Figure 4* we observe that the monomer decay rate decreases and  $\langle\tau_M\rangle$  increases with increasing 1-NMMA content in the polymers. This result is unusual in that, as the N content goes up, excimer formation should become faster.  $I_e/I_m$  increases, and one anticipates a corresponding decrease in  $\langle\tau_M\rangle$ .

When the excimer decay rate is slower than that of the monomer, the excimer can serve as a reservoir of excited states. Under these circumstances, excimer dissociation provides a feedback step to excited monomer and contributes a slowly decaying tail to the monomer decay profile. This is the feature that appears in *Figure 4*. While the system is too complex to analyse quantitatively in terms of the above scheme, there is no doubt that excimer dissociation is important to the excited-state behaviour of 1-NMMA copolymers, and becomes increasingly more important with increasing N content.

## ACKNOWLEDGEMENTS

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