Intramolecular energy migration in polyesters from 2,6-naphthalene dicarboxylic acid: polarization of fluorescence in the polymers and in bichromophoric model compounds

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The fluorescence has been measured in dilute solution and in glassy poly(methyl methacrylate) for polyesters in which 2,6-naphthalene dicarboxylate is the rigid unit, and $(CH_2)_m$ ($m = 2$–6) is the flexible spacer. Bichromophoric compounds in which the same flexible spacer connects two molecules of 2-naphthoate were also studied. The anisotropy in the rigid medium demonstrates the existence of intramolecular energy migration, which becomes more important as m decreases from 6 to 2. The Förster radius is ~12 Å in the bichromophoric compounds and 14 Å in the polyesters.

(Keywords: anisotropy; conformation; energy migration; excimer; fluorescence; polyester)

INTRODUCTION

A wide range of properties in dilute solution and in the solid state are exhibited by polymers that have a repeating sequence in which a rigid unit alternates with a flexible spacer. One local property of the chain that is subject to control is the ease with which the polymer forms a tight bend. The tightest bend would involve the fragment A-B_m-A, where A denotes the rigid unit, B is a flexible unit and m denotes the number of flexible units in the spacer. If A contains a chromophore that is capable of forming an excimer, the dependence of the intensity of excimer emission on B and m in poly(A-B_m) provides information about the tendency for formation of a tight bend in the chain[1–5]. These tight bends have important consequences for the types of ordered structures that might be formed by ensembles of chains[6,7].

The interpretation of the excimer formation is simplest in systems where an excited A has a very short fluorescence lifetime, τ, and a very small radius, R_0, for energy transfer to an A in the ground state. These conditions are well approximated in polyesters where A is either terephthalate or isophthalate[4].

A more complicated situation is presented when A is derived from a dicarboxylic acid of naphthalene because of the larger values of τ and R_0. The influence of R_0 on the population of the excimer can be suppressed by substitution of the bichromophoric model compounds, A-B_m-A, for the polymers, poly(A-B_m). This approach has recently been used for several systems in which A contains a naphthyl unit[8–11]. The dependence on m of the measured values of the ratio of the intensities of excimer and monomer emission, I_D/I_M, in media of very high viscosity, η, was interpreted with a rotational isomeric state analysis[12] of the population of the conformations of the flexible spacer at equilibrium.

Here we consider polymers in which A contains 2,6-naphthalene dicarboxylate. The flexible spacer is $(CH_2)_m$, $m = 2$–6. Measurements of the anisotropy of the fluorescence in a rigid medium are used to provide information about the manner in which the influence of energy migration depends on m. The results are interpreted using rotational isomeric state theory to evaluate the distribution of conformations in the static system.

METHODS

The glycols, $HO(CH_2)_mOH$ ($m = 2$–6), 1,2-dichloroethane, methanol, 1,1,2,2-tetrachloroethane, methyl methacrylate and the dimethyl ester of 2,6-naphthalene dicarboxylic acid (DMN) were purchased from Aldrich. The DMN was recrystallized from methanol, and the methyl methacrylate was distilled before use. The 2,6-naphthalene dicarboxylic acid was purchased from Amoco.

The 2,6-naphthalene dicarboxylic acid was converted to the diacid chloride by reaction with thionyl chloride.

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Polymers were synthesized under N_2 with stoichiometric amounts of the diacid chloride and glycol in chloroform in the presence of triethylamine. After reflux for several hours, the polymer was collected by washing sequentially with water and aqueous sodium bicarbonate. The polymer was precipitated from chloroform by the addition of methanol, reprecipitated from 1,1,2,2-tetrachlorethane/methanol, and characterized by n.m.r. The polymers are abbreviated as P*m*, where the numerical value of *m* denotes the number of methylene groups in the flexible spacer. A similar synthetic route, which is described elsewhere[8], was used for the bichromophoric compounds, $C_{10}H_7COO(CH_2)_mOOCC_{10}H_7$, $m=2$–6, abbreviated as N*m*N, where the numerical value of *m* denotes the number of methylene groups. The methyl ester of 2-naphthoic acid is abbreviated as 2MN.

Dilute samples of the naphthyl-containing molecules in glassy poly(methyl methacrylate) were prepared using as a mould a test tube with a diameter of ~3 cm. Solutions of the polyester or the model compound were prepared in freshly distilled methyl methacrylate so that the optical density was 0.5–1.0 at the wavelength to be used for excitation (usually 294 nm for the bichromophoric model compounds and 296 nm for the polyesters). Approximately 3 ml of the solution was introduced into the test tube. In order to minimize the formation of voids and the quenching by O_2 of the free radicals at the ends of the chains, the sample was placed in an ultrasonic bath for ~45 min, and dry N_2 was bubbled through the solutions. Then the solutions were thermally polymerized under N_2, in the absence of initiator. The polymerization was accomplished by heating the solution slowly to 70°C over 3 h, during which time the mixture formed a viscous fluid. The temperature was then increased to 90°C and the polymerization continued for 12 h. The vitrified samples were retrieved by hitting the test tube with a hammer. Blanks that contained only poly(methyl methacrylate) were prepared in the same fashion.

Absorption spectra were measured with a Hewlett-Packard 8451 A diode array spectrophotometer. Similar absorption spectra are observed for P*m* and DMN, and for N*m*N and 2MN. The features in the first series are shifted slightly to the red of the features of the second series. In ethylene glycol at ambient temperature, peaks are observed at 286, 296, 338 and 352 nm with DMN, and they occur at 284, 294, 324 and 336 nm in 2MN.

Fluorescence measurements were performed at 25°C using an SLM 8000C fluorometer, equipped with a double monochromator in the excitation path. Slit widths were 8 nm for excitation, and 4 nm (solutions) or 8 nm (vitrified samples) for the emission paths. With the exception of the measurements of the anisotropy, the polarizers were set to magic angle conditions. Typical absorbances for solutions at the wavelength of excitation, 294 or 296 nm, were in the range 0.05–0.15. Right angle geometry was used for measurements in solution, and front face illumination (at an angle of 35°) was used for measurements in the vitrified glass. Solvent signals were subtracted from the observed spectra for all measurements.

The anisotropy of the fluorescence, *r*, was measured as described by Lakowicz[13]:

$$r=\frac{I_{vv}-GI_{vh}}{I_{vv}+2GI_{vh}} \qquad (1)$$

where I_{vv} is the intensity of the emission that is measured when both polarizers are vertical, I_{vh} is the intensity of the emission when the excitation polarizer is vertical and the emission polarizer is horizontal, and *G* corrects for any causes of depolarization in the optical system.

$$G=\frac{I_{hv}}{I_{hh}} \qquad (2)$$

The polarizers in the excitation and emission paths are horizontal and vertical, respectively, for measurement of I_{hv}, and they are both horizontal for measurement of I_{hh}.

The rotational isomeric state calculations were performed in a manner similar to that employed in recent work for closely related compounds[11]. The bond lengths used were 1.34, 1.40, 1.44, 1.51 and 1.53 Å, respectively, for C^*–O, C^{ar}–C^{ar}, C^{ar}–C^* and C–C, where C^* denotes the carbonyl carbon atom and C^{ar} denotes a carbon atom in the naphthyl group. Bond angles were 110, 112, 114.4, 119.1, 120 and 120°, respectively, for C–C–O, C–C–C, C^*–O–C, C^{ar}–C^*–O, C^{ar}–C^{ar}–C^{ar} and C^{ar}–C^{ar}–C^*. Naphthyl and ester groups are planar. There are two principal rotational isomeric states, with $\Phi=0$ and 180°, at the C^{ar}–C^* bond. All other rotatable bonds in the chain have three principal rotational isomers with $\phi=180$ and $\pm 60°$. These three principal rotational isomers are elaborated into a set of nine isomers by adding to each principal rotational isomer two subsidiary states, displaced by $\Delta\phi=20°$ in either direction from the principal state. Conformational energies are not distinguished for subsidiary and principal rotational isomers.

RESULTS AND DISCUSSION

Excitation spectra

Figure 1 depicts excitation spectra for 2MN, N3N, DMN and P3 in 1,1,2,2-tetrachloroethane at 25°C. The emission was monitored at 400 nm. The major features in the excitation spectra occur at the same positions as the features in the absorption spectra.

Emission spectra

Figure 2 depicts emission spectra, normalized at 363 nm, for 2MN and N*m*N ($m=2$–6) in methanol at 25°C. Spectra obtained in other solvents were normalized at the distinct peak of highest energy. This peak is in the range 340–346 nm in some solvents, such as 1,1,2,2-tetrachloroethane. In other solvents, as illustrated by the cases of methanol and ethylene glycol, the transition near

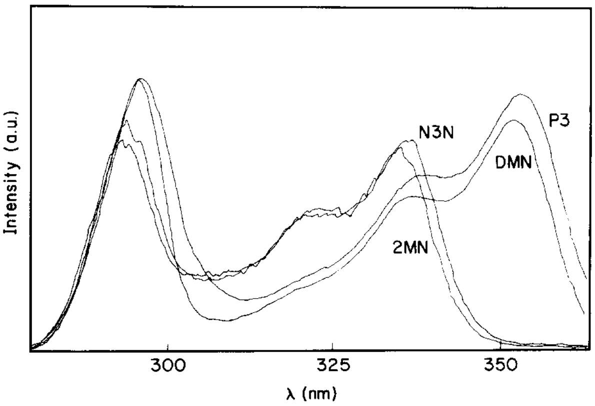

Figure 1 Excitation spectra for 2MN, N3N, DMN and P3 at 25°C in 1,1,2,2-tetrachloroethane. The emission was monitored at 400 nm

Table 1 Values of I_D/I_M

	Solvents					
Components	CH_3OH	$(CH_2Cl)_2$	$(CHCl_2)_2$	$(HOCH_2)_2$	MMA	PMMA
N2N	0.31	0.18	0.12	0.22	0.13	0.041
N3N	0.87	0.52	0.36	0.43	0.45	0.073
N4N	0.56	0.22	0.13	0.16	0.19	0.004
N5N	0.48	0.26	0.20	0.25	0.17	0.002
N6N	0.72	0.36	0.24	0.25	0.25	0.004
P2	0.19	0.38	0.40	0.14	0.24	0.42
P3	1.67	0.57	0.32	0.28	0.73	0.42
P4	0.66	0.60	0.32	0.067	0.49	0.19
P5	0.82	1.43	1.13	0.30	0.81	0.17
P6	0.86	0.64	0.54	0.19	0.47	0.13

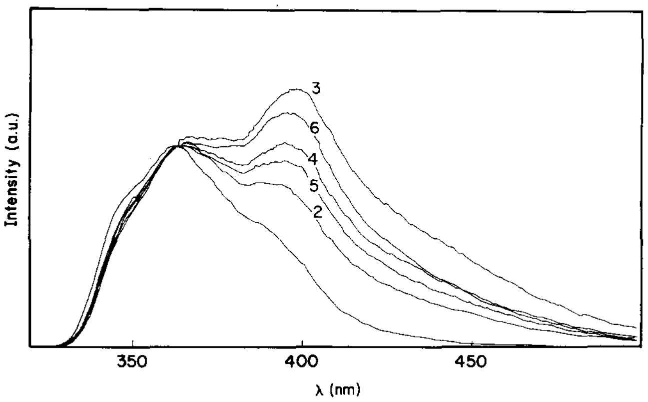

Figure 2 Normalized (at 363 nm) emission spectra for 2MN and for N*m*N ($m=2$–6) in methanol at 25°C, using excitation at 292 nm

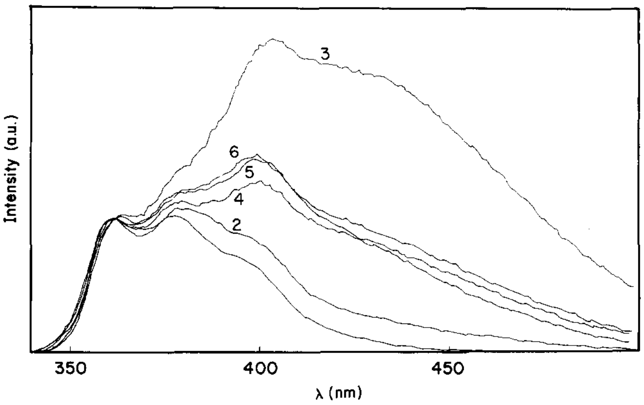

Figure 3 Normalized (at 363 nm) emission spectra for DMN and for P*m* ($m=2$–6) in methanol at 25°C, using excitation at 296 nm

343 nm becomes a shoulder for a more prominent transition at 363 or 367 nm, respectively. Then the spectra are normalized at the peak at 363–367 nm, as shown in *Figure 2* for results obtained in methanol.

The intensity to the red of the wavelength selected for normalization is smallest for 2MN, which contains only one chromophore. The enhanced intensity to the red in the bichromophoric model compounds, the N*m*N, is attributed to the intramolecular formation of an excimer. A simple means for comparing the relative intensities of excimer emission by different compounds, and in different solvents, is by the ratio denoted as I_D/I_M and defined as:

$$\frac{I_D}{I_M}=\frac{I_{NmN,400}-I_{2MN,400}}{I_{norm}} \qquad (3)$$

where the intensities in the numerator are evaluated at 400 nm and the intensity in the denominator is evaluated at the wavelength chosen for normalization. A similar equation will be used for evaluation of I_D/I_M for the DMN and the P*m*. *Table 1* presents the results obtained in the different solvents and in the vitrified samples in poly(methyl methacrylate). The trends seen upon variation of m in N*m*N in solution are similar to those reported previously[8], namely the observation of the maximum I_D/I_M at $m=3$, the tendency for an odd–even effect for m of 2–5, and the loss of the odd–even effect at $m=5, 6$ in solvent of low η. Each N*m*N has the smallest value of I_D/I_M in glassy poly(methyl methacrylate). N3N is the bichromophoric model compound that shows the most excimer emission in poly(methyl methacrylate).

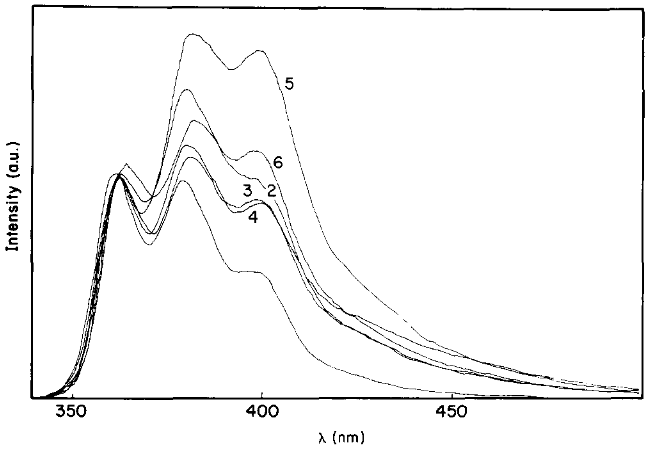

Figure 4 Normalized (at 362 nm) emission spectra for DMN and for P*m* ($m=2$–6) in 1,1,2,2-tetrachloroethane at 25°C, using excitation at 296 nm

Figure 3 depicts the normalized emission spectra for DMN and P*m* ($m=2$–6). Emission from intramolecular excimers is apparent in all of the polymers. In methanol there appear to be two excimer bands, located at ~400 and 450 nm. The ability to resolve two excimer bands is solvent dependent. In 1,1,2,2-tetrachloroethane there is a single excimer band, at 400 nm, as shown in *Figure 4*. The values of I_D/I_M are collected in *Table 1*. They were obtained from the spectra using equation (3) and values of I_{norm} in the range 357–367 nm. The largest values of I_D/I_M occur at P5 in four of the media, and at P3 in the other two media. Comparison of the results for the N*m*N and P*m* in poly(methyl methacrylate) reveals an interesting difference between the bichromophoric model compounds and the polymers. The bichromophoric model compounds always have values of I_D/I_M in poly(methyl methacrylate) that are much smaller than those observed in methyl methacrylate. In contrast, the polymers have values of I_D/I_M in poly(methyl methacrylate) that are much closer to those observed in methyl methacrylate. In the case of the smallest spacer, the value of I_D/I_M for P2 is actually larger in poly(methyl methacrylate) than in methyl methacrylate. The values of I_D/I_M in poly(methyl methacrylate) are of the same size for P2 and P3, and then decrease as *m* increases from P3 to P6.

Anisotropy of the fluorescence

The anisotropy of the fluorescence is very small when the samples are measured as dilute solutions in methyl methacrylate at ambient temperature. The values of *r* for 2MN, N*m*N, DMN and P*m* were all in the range 0.00–0.01. Substantially larger values of *r* are obtained when the molecules are placed in glassy poly(methyl methacrylate), as shown in *Tables 2* and *3*. The compounds with a single chromophore, 2MN and DMN, have values of *r* in the range 0.31–0.40, which are close to the value of 0.40 expected for a frozen isotropic array of isolated chromophores that have parallel transition moments for excitation and emission. Smaller values of *r*, in the range 0.20–0.28, are found for the bichromophoric compounds, and still smaller values, in the range 0.10–0.18, are observed for the polymers. The decrease in *r* upon proceeding from molecules with one chromophore (2MN and DMN) to the bichromophoric compounds (N*m*N) and then on to the polymers (P*m*) shows that intramolecular energy migration occurs in the molecules that contain more than one chromophore. The results for P2–P5 suggest that energy migration becomes less efficient as the size of the spacer decreases in the polymer, because *r* increases slowly with *m*, as shown in *Figure 5*.

Table 2 Anisotropies for 2-methyl naphthoate and the bichromophoric model compounds in poly(methyl methacrylate)

Compound	355/320[a]	375/336
2MN	0.359	0.396
N2N	0.199	0.244
N3N	0.200	0.246
N4N	0.214	0.261
N5N	0.216	0.275
N6N	0.224	0.279

[a] Wavelength (in nm) of emission (numerator) and excitation (denominator)

Table 3 Anisotropies for the dimethyl ester and the polyesters in poly(methyl methacrylate)

Polymer	359/336[a]	375/336
DMN	0.393	0.313
P2	0.123	0.096
P3	0.140	0.126
P4	0.161	0.151
P5	0.180	0.155
P6	0.163	0.145

[a] Wavelength (in nm) of emission (numerator) and excitation (denominator)

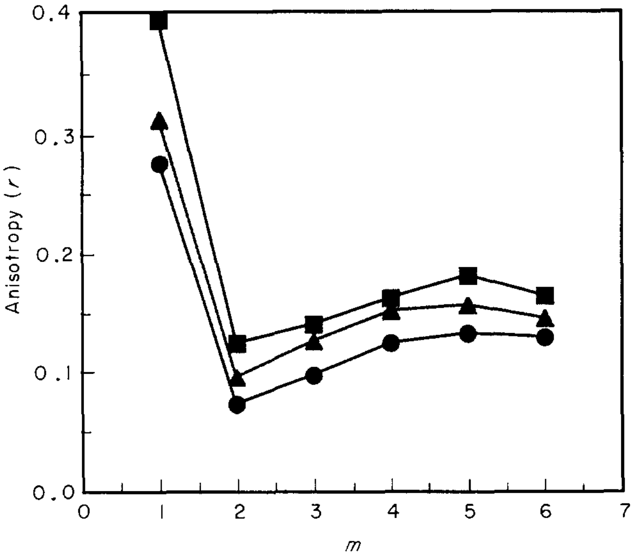

Figure 5 Anisotropy, *r*, measured at 359 (■), 375 (▲) and 400 nm (●), upon excitation at 336 nm, for P*m* in glassy poly(methyl methacrylate). The *r* values for DMN are plotted at *m* = 1

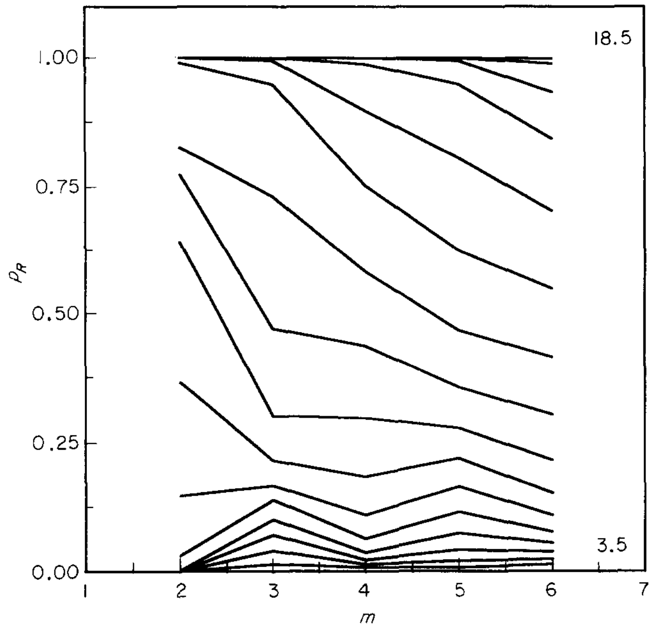

Figure 6 Dependence of p_R on *m* and *R* for *R* ranging from 3.5 to 18.5 Å, at intervals of 1 Å

The result for P6 is anomalous, because it does not continue the trend in *r* that was established by P2–P5.

Theoretical interpretation of the dependence of r *on* m *in the polyesters*

By a discrete enumeration of the conformations of the spacer, using *trans*, *gauche*$^+$ and *gauche*$^-$ states for each rotatable bond, the probability, p_R, was estimated for finding the centres of mass of the two naphthalene rings separated by a distance no larger than *R*. From its definition, p_R must approach 1 as *R* becomes large, and one expects the limiting value of 1 will be obtained at smaller *R* with the spacers of smaller *m*, due to the constraints placed on the separation of the two naphthalene rings by a short spacer. This expectation is realized, as shown in *Figure 6*. A value of *R* of 14.5 Å is sufficient to produce $p_R = 1$ if $m = 2$, but a value of 19.5 Å is required if $m = 6$. The values of p_R display an odd–even effect for

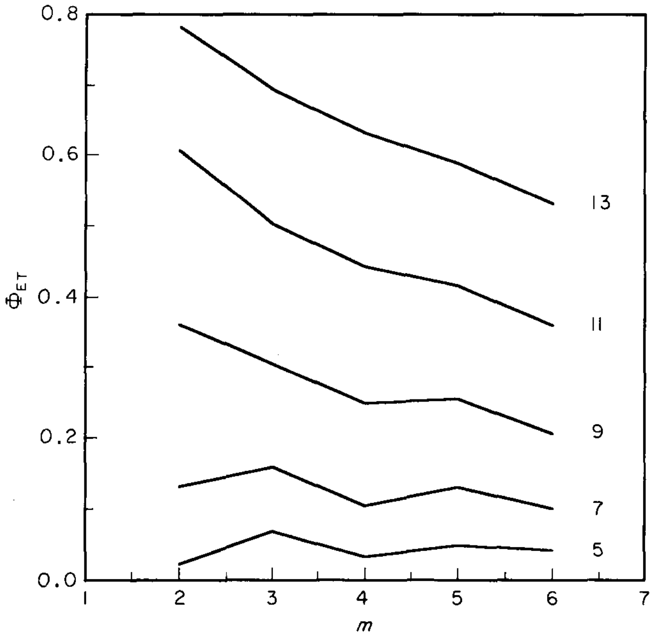

Figure 7 Estimates of the efficiency of Förster energy transfer, Φ_{ET}, with five different assumptions about the value of R_0 (5, 7, 9, 11 and 13 Å) for an isotropic ensemble of chromophores

$R < 8.5$ Å, and they exhibit a monotonic decrease as *m* increases for $\sim 11 < R(\text{Å}) < 14$ Å.

In order to provide a comparison with the observed value of the anisotropy in poly(methyl methacrylate), the efficiency of Förster transfer in a frozen system was calculated as:

$$\Phi_{ET} = \sum p(1 + R^6/R_0^6)^{-1} \tag{4}$$

where *p* denotes the probability of a conformation, *R* is the distance between the two naphthalene rings and R_0 is the Förster radius when the chromophores are distributed randomly. (The actual values of the orientation factor, κ^2, calculated by averaging over all conformations are 0.58, 0.62, 0.67, 0.65 and 0.66 for the N*m*N with $m = 2, 3, 4, 5$ and 6, respectively. Since these values are close to two-thirds, they support the assumption that the orientations are nearly random.) The result is depicted in *Figure 7* for five different assumptions about the value of R_0. An odd–even effect is predicted if R_0 were 7.35 Å, which is the value expected for transfer from naphthalene to naphthalene[14]. The monotonic decrease in Φ_{ET} with an increase in *m* from 2 to 5 does not occur until R_0 is as large as 11 Å. Comparison of this result from the calculation with the behaviour of *r* for the polyesters in poly(methyl methacrylate), which shows a monotonic trend for *m* from 2 to 5, suggests that the effective R_0 increases by ~50% when naphthalene is replaced by the naphthalene diester.

The ratios of the Förster radii for self-transfer by two molecules, X*→X and Y*→Y, in the same environment can be written as:

$$\frac{R_{0X}^6}{R_{0Y}^6} = \frac{\kappa_X^2 \phi_X \,\text{int}_X}{\kappa_Y^2 \phi_Y \,\text{int}_Y} \tag{5}$$

where ϕ denotes the quantum yield for fluorescence and int denotes the overlap integral for excitation and emission spectra, normalized to one. Measurements with naphthalene, 2MN and DMN in 1,2-dichloroethane at 25°C show that the most important term in the right-hand side is ϕ_X/ϕ_Y. The quantum yields are in the ratio 1:6.7:20.4 for naphthalene:2MN:DMN. The ratio of the overlap integrals makes a smaller contribution in the same direction. Combining the two effects, the ratio of the R_0 for naphthalene:2MN:DMN is 1:1.6:1.9. If R_0 for naphthalene is taken to be 7.35 Å, the values for 2MN and DMN are 12 and 14 Å, as expected from the theoretical analysis depicted in *Figure 7*[14].

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