

LUMINESCENCE STUDIES IN POLYMERS—XI*

ACENAPHTHYLENE POLYMERS AND COPOLYMERS WITH METHYLMETHACRYLATE: POLARIZATION, YIELD AND DECAY OF THE FLUORESCENCE AS A FUNCTION OF TEMPERATURE IN SOLUTION

C. DAVID, D. BAEYENS-VOLANT and M. PIENS

Faculté des Sciences, Université Libre de Bruxelles, Campus Plaine 206/1, 1050 Bruxelles, Belgium

(Received 16 July 1979; in revised form 4 October 1979)

Abstract—For polymers of acenaphthylene and copolymers with methymethacrylate measurement of the polarization of the fluorescence in glassy solution at 77K has been combined with analysis of the intensity and decay of excimer and monomer fluorescence over a large temperature range. Activation energies and frequency factors corresponding to several photophysical processes have been determined and compared with those reported previously for 1-vinylnaphthalene polymer and copolymers.

1. INTRODUCTION

Photophysical processes involving the first excited singlet state of poly-1-vinylnaphthalene and copolymers with methymethacrylate have been investigated recently in our laboratory [1–3]. The decay and relative intensity of monomer and excimer fluorescence in solution as a function of temperature [2] and the polarization of the fluorescence of glassy solutions [1] and films [3] were studied as a function of copolymer composition. This research was extended to copolymers of acenaphthylene and methymethacrylate, with results reported here. In acenaphthylene polymers and copolymers, the aromatic chromophore is rigidly held to the chain and excimer can only form between next-to-nearest neighbouring groups [4–6].

2. EXPERIMENTAL

Copolymers were synthesized by free radical reaction using AIBN as initiator in benzene solution at 60°C. They were purified by successive cycles of dissolution in benzene and precipitation in hexane. Their compositions were calculated from reactivity ratios (respectively 2.25 for AcN and 0.48 for MMA [7]) and feed composition using the usual copolymerization equation. Conversion was controlled by absorption spectroscopy at 400 nm and kept below 10%. The compositions of copolymers were determined by absorption spectroscopy and controlled by simulation of the polymerization of one chain on an IBM 360 computer (see Section 3.2). Excellent agreement was obtained (Table 1).

The polarized emission spectra were obtained with an Hitachi-Perkin-Elmer model MPF2A spectrofluorimeter as previously described [1]. The solutions (10^{-4} M in acenaphthene units) were carefully outgassed by the freeze-thawing technique at a pressure of 10^{-5} mm Hg and the cells sealed *in vacuo* before emission or decay-time measurements. The emission spectra as a function of temperature were recorded using a laboratory built device consisting of: an Osram HBO 200W High pressure Hg lamp, a

Bausch & Lomb high intensity monochromator equipped with a 200–400 nm grating (2700 grooves/mm) for selecting the excitation wavelength, a grating monochromator coming from a Hitachi-Perkin-Elmer mod. 139 UV-Vis. spectrophotometer for analysis of the emission spectrum and a Hamamatsu R106 photomultiplier. The decay times were measured using a TWR nanosecond decay time fluorimeter (Deuterium lamp) connected to a Tektronix 547 oscilloscope. The following combinations of filters were used:

(1) excimer fluorescence decay: u.v. D25 Hitachi-Perkin-Elmer filter (excitation) + 1 cm of a 72% NaNO₂ solution (analysis);

(2) normal fluorescence decay: 4 cm chlorine at a pressure of 510 Torr (excitation) + a Corning CS760 + 2 cm of a 15% KCr(SO₄)₂·12H₂O solution in H₂SO₄ 1 N (analysis).

3. RESULTS AND DISCUSSION

3.1. Polarization of the fluorescence in glassy solution at 77 K

The absorption spectra of the copolymers 3-97 and 41-59, polyacenaphthylene and acenaphthene are given in Fig. 1. The fluorescence of copolymer 3-97, polyacenaphthylene and acenaphthene in glassy 2MTHF is reported in Fig. 2. The absorption and emission spectra of all copolymers are similar but show a small bathochromic displacement when AcN content increases. They are however markedly different from those of PAcN and acenaphthene. The absorption polarization spectra based on the fluorescence (APF) are obtained by adjusting the analyser monochromator at the maximum of three different vibrational structures and varying the wavelength of the exciting light. They are given in Figs 3 and 4, for acenaphthene and the copolymer 3-97. The polarization is defined as:

$$p = \frac{I_{VV} - GI_{VH}}{I_{VV} + GI_{VH}}$$

where *V* and *H* (*V* = vertical, *H* = horizontal) indicate the orientation of the polarizer and analyser. The

* Part X: C. David, D. Baeyens-Volant, P. Macedo de Abreu and G. Geuskens, *Eur. Polym. J.* 13, 841 (1977).

Table 1. Photophysical parameters for acenaphthylene-methylmethacrylate copolymers

AcN-MMA experimental	Copolymer composition AcN-MMA simulated	E_{DM} ($\text{kcal}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$)		E_{IP} ($\text{kcal}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$)		$k_{FD} + k_{IP}^0$ (10^6 sec^{-1})		k'_{IP} (10^6 sec^{-1})		$(k_M + k_{DM}M)^*$ (10^7 sec^{-1})		$k_{FM} + k_{IM}^0$ (10^6 sec^{-1})		E_M ($\text{kcal}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$)		k'_{IM} (10^6 sec^{-1})	
		E_{DM} ($\text{kcal}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$)		E_{IP} ($\text{kcal}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$)		$k_{FD} + k_{IP}^0$ (10^6 sec^{-1})		k'_{IP} (10^6 sec^{-1})		$(k_M + k_{DM}M)^*$ (10^7 sec^{-1})		$k_{FM} + k_{IM}^0$ (10^6 sec^{-1})		E_M ($\text{kcal}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$)		k'_{IM} (10^6 sec^{-1})	
PAcN	PAcN	0.8 (3.3)		3.7 (15.5)		15.4		2.9		5.1		33.0		—		—	
70-30	69-31	1.4 (5.8)		4.7 (19.6)		13.5		8.4		4.8		25.0		—		—	
41-59	41-59	1.4 (5.8)		5.0 (20.9)		12.7		11.5		4.2		23.4		—		—	
25-75	23-77	1.4 (5.8)		5.7 (23.8)		12.1		25.9		3.5		21.0		—		—	
10-90	8-92	1.4 (5.8)		—		—		—		2.9		16.5		—		—	
3-97	3-97	—		—		—		—		2.3		15.8		1.6 (6.7)		1.1	

* At room temperature [18].

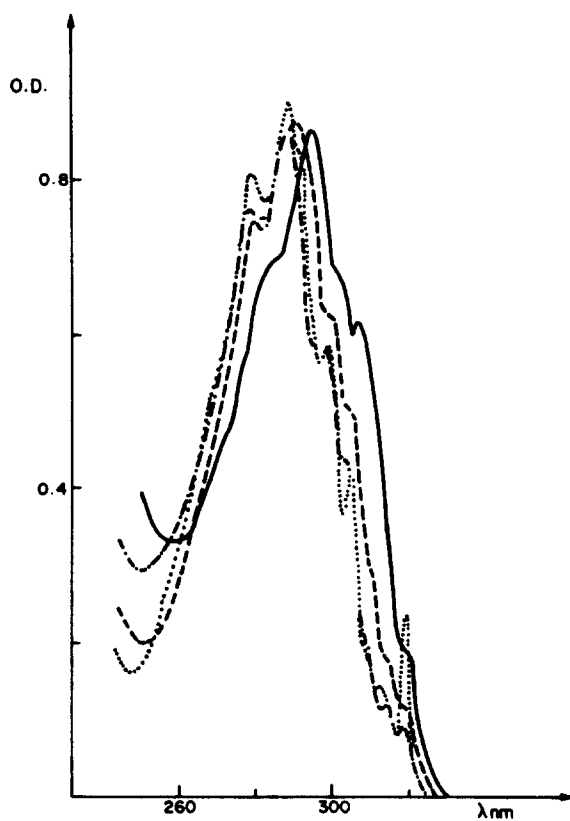


Fig. 1. Absorption spectra of acenaphthene chromophores ($C \approx 10^{-4}$ M in AcN units) — polyacenaphthylene; — — — copolymer acenaphthylene-methylmethacrylate 3-97; - - - copolymer AcN-MMA 41-59; ····· acenaphthene.

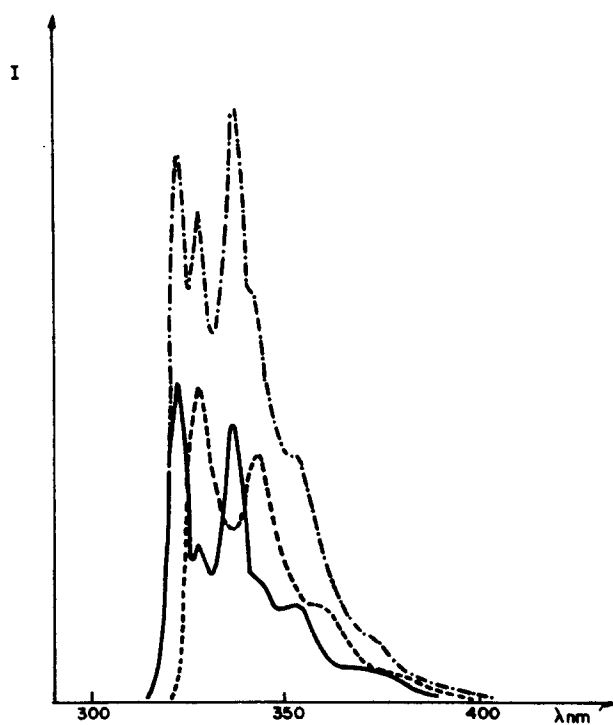


Fig. 2. Fluorescence in MTHF at 77 K of: — polyacenaphthylene, — — — acenaphthene, - - - copolymer acenaphthylene-methylmethacrylate 3-97. $\lambda_{exc} = 300$ nm; $C \approx 10^{-4}$ M in AcN units.

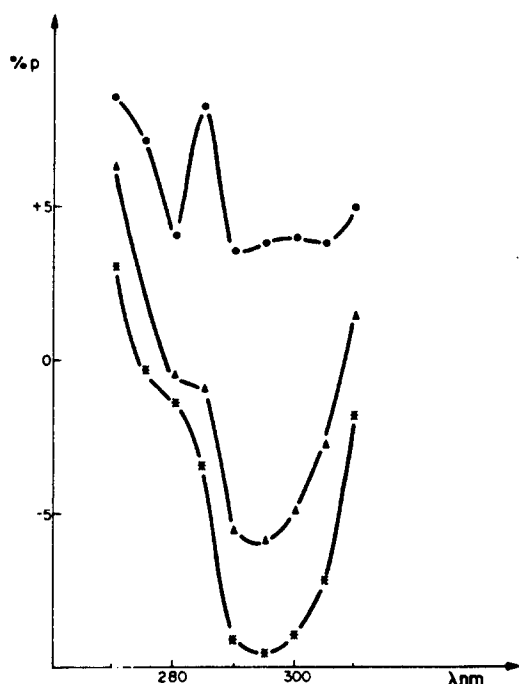


Fig. 3. Absorption polarization spectra based on the fluorescence (APF) for acenaphthene in MTHF at 77 K ($C \approx 10^{-4}$ M in AcN units). $\lambda_{\text{analysis}}$: ● 327 nm; ▲ 337 nm; * 322 nm.

factor $G = I_{HV}/I_{HH}$ is a correction for the anisotropy introduced by the optical system. It is reasonable to assume by comparison with naphthalene [8,9] that there are two series of vibrational levels polarized in opposite directions in acenaphthene. The vibrations at 322 and 337 nm belong to one series and the vibrations at 327 and 342 nm to the other. In the copolymer the relative importance of the second series increases and imposes its sign to the maximum at 337 nm. The emission spectrum of PAcN being completely depolarized, APF spectra could not be recorded. These results show that data of fluorescence polarization must be carefully analysed before introducing them in any correlation. In the present system, indeed, the polarization of copolymers cannot be compared with those of the homopolymer and of the model compound.

Quantitative correlation of the polarization p of the fluorescence as a function of copolymer composition has been discussed previously [1] in relation with different models of energy migration proposed by Jablonski, Förster, Ore and Weber for non-polymeric systems. In this last case, a linear relation between $1/p$ and the chromophore concentration has been proposed and verified if energy migration occurs between isolated immobile randomly distributed chromophores and induces depolarization. The assumption of random distribution of the chromophores in the coil is unlikely to hold for glassy solutions of polymers unless the mol fraction of fluorescent monomer is low. In that case, migration occurs through the coil and a linear relation is obtained between $1/p$ and the mol fraction of fluorescent monomer. When the mol fraction of aromatic chromophores is low, transfer may occur by exchange or dipole-dipole interactions to a

neighbouring unit but the contribution of this transfer to depolarization is weak if the transition moments do not deviate much from parallelism. When the length of the aromatic sequence increases, migration along the chain becomes more important; each step contributes to a loss of polarization since neighbouring chromophores have to respect the conformation of the chain. Depolarization thus occurs efficiently and a steep increase in the function $1/p = f(\text{mol fraction})$ is observed [1].

In agreement with these qualitative arguments, Soutar *et al.* [10] proposed and verified a linear relation between $1/p$ and the mean length of the sequence of aromatic chromophores for some copolymer systems.

The situation for PAcN and copolymers is however quite different: excimers cannot form between neighbouring units since the chromophores cannot attain a sandwich parallel conformation. The depolarization subsequent to migration between neighbouring units is thus much more efficient than in the previously cited copolymers. As a result, the residual polarization of a copolymer containing 10% AcN units is very weak. The value of $1/p$ as a function of mol fraction AcN is given in Fig. 5. Owing to the large error (± 0.01) on the polarization values any quantitative correlation seems meaningless.

3.2 Excimer fluorescence in solution at room temperature

The excimer and monomer fluorescence as a function of copolymer composition is given in Fig. 6. Fluorescence of intramolecular dimer could not be detected [19]. The relative intensities of monomer and

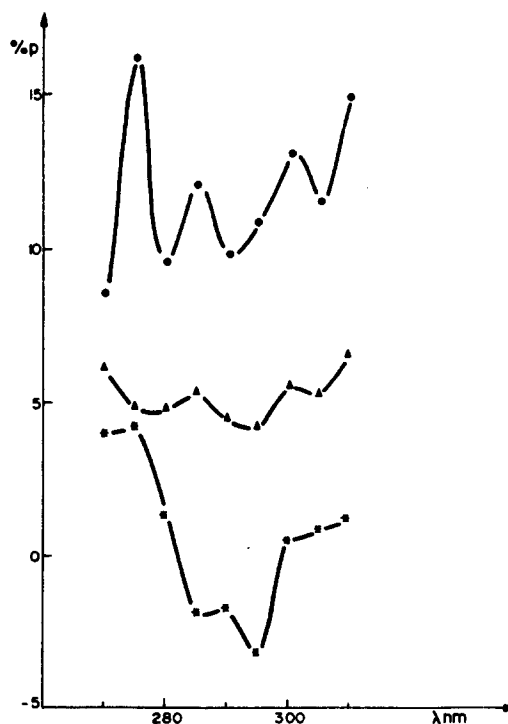


Fig. 4. Absorption polarization spectra based on the fluorescence (APF) for copolymer acenaphthylene-methylmethacrylate 3-97 in MTHF at 77 K. ($C \approx 10^{-4}$ M in AcN units). $\lambda_{\text{analysis}}$: ● 327 nm; ▲ 337 nm; * 322 nm.

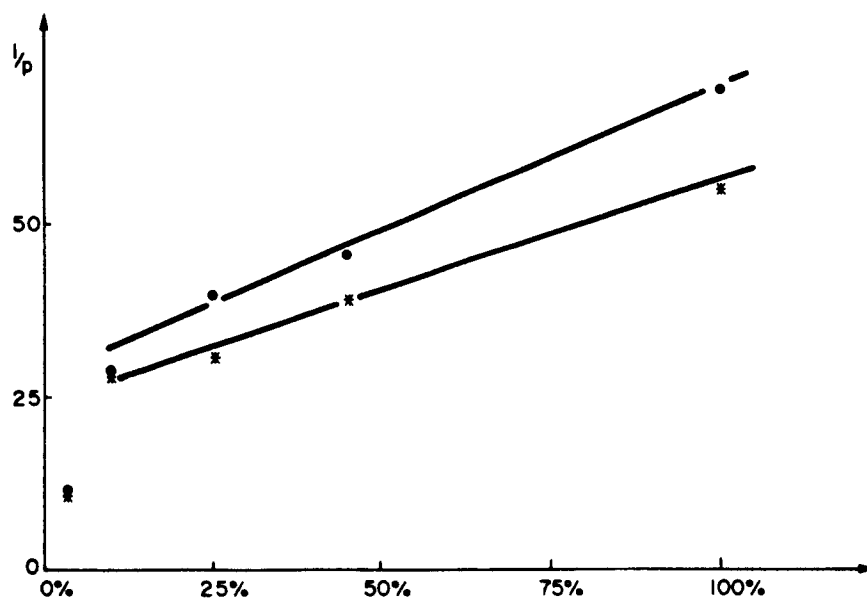


Fig. 5. $1/p$ as a function of copolymer composition for the fluorescence at 337 nm of acenaphthylene-methylmethacrylate copolymers in MTHF at 77 K. Excitation wavelength: ● 295 nm, * 305 nm. $C \approx 10^{-4}$ M in AcN units.

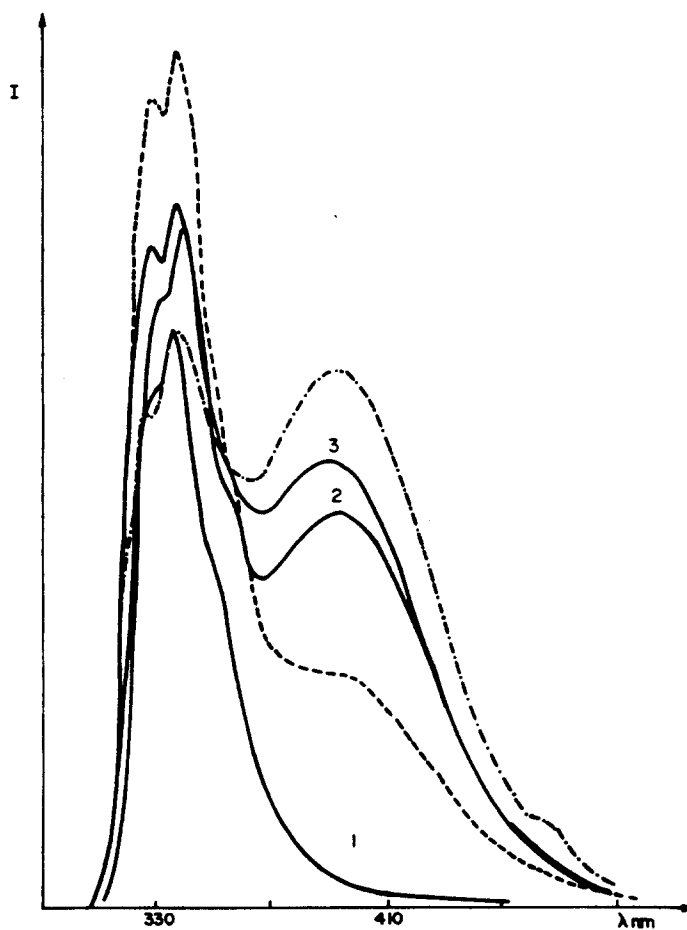


Fig. 6. Emission spectra at room temperature of polyacenaphthylene and copolymers with methylmethacrylate (1) 3-97, ---- 25-75, (2) 41-59, - · - · - 70-30 (3) polyacenaphthylene. Relative arbitrary units [17].

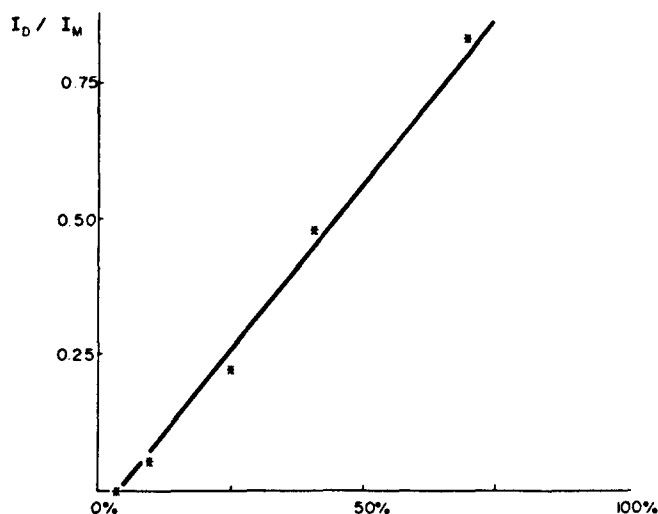


Fig. 7. Ratio of monomer to excimer fluorescence at room temperature as a function of copolymer composition (in mol % AcN units).

excimer fluorescence are the result of several different competitive steps as described by the usual kinetic scheme [2] but it is still more complicated than it appears there. Indeed, the rate constant for excimer formation k_{DM} in polymer systems includes for most authors the rate of energy migration to a pair and the rate of attaining a favourable conformation for excimer formation. Only Harrah [11] and Johnson [12] have separated the rate of migration and the rate of excimer sampling in their kinetic treatment of homopolymers. In any case, energy migration in copolymers can occur intramolecularly along the chain but can also occur by collisional or non-collisional exchange or dipole-dipole interaction between non-neighbouring units which are brought to a favourable distance by diffusional movements of chain segments in the coil. The relative importance of "along chain" and "diffusional" migration is expected to depend on the composition of copolymers but also on their nature. Indeed, the vibronic mechanism of Harrah [11] could be effective in copolymers if the vibrational movements are compatible. The efficiency of exchange or dipole-dipole interactions between two aromatic chromophores M depends on the nature of M, and on the statistical composition, conformation and microtacticity of the copolymer chain. The probability of excimer sampling is also very complex since it certainly depends on the number and configuration of neighbouring units of M* (triads AM*M or MM*M). Various models have been proposed to justify the relative contribution of excimer and monomer fluorescence in copolymers but their experimental verification over a large range of copolymer composition is difficult owing to the small contribution of I_M and I_D in copolymers of respectively low and high content of aromatic chromophores and hence to the large error on the ratio of these values. David *et al.* [13] proposed that energy transfer occurs to pairs at the site of which excimer sampling occurs. Reid and Soutar [10] verified a model according to which sequences of aromatic chromophores promote efficient migration to populate excimer sites. The ratio I_D/I_M is then proportional to $f_{MM}\bar{l}_M$, where f_{MM} is the

fraction of links between aromatic species and \bar{l}_M is the mean sequence length of aromatic species.

The case of PAcN is however quite different since excimers do not form between neighbouring units but between next-to-nearest neighbouring units. Linearity between I_D/I_M and f_{MM} is not verified and would be meaningless in this case. However linearity is obtained for I_D/I_M as a function of the mol fraction of M in the copolymers (Fig. 7). The problem was to find for this transfer a physical model the properties of which are directly related to the mol fraction of acenaphthylene chromophores in the chain. In the following discussion, AcN units will be represented by the symbol 1 and MMA units by the symbol 0. In a first model, the sum of the percentage of 1 and 0 units, respectively centres of triads 111 and 101 in which excimer can form, was calculated for the different copolymers using the run number R but this sum is not proportional to the mol fraction of 1. A better approximation is to take into account the probability of excimer formation by considering the position of 1 in a sequence. Indeed, in the absence of migration, the probability of excimer formation when a photon is absorbed in a sequence 0011100 is $\frac{2}{3}$ whereas it is one in a sequence 0010100. If the higher probability of photon absorption in the first sequence is introduced in the calculation, a function is obtained that is not linearly related to the composition.

Table 2. Number of possibilities for excimer formation

Sequences	Number of possibilities for excimer formation
-0011100-	2
-00111100-	4
-001111100-	6
-0010100-	2
-001010100-	4
-00111010100-	6
-001111010100-	8
⋮	⋮

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

[illegible]

```

0 0 1 1 1 0 0 1 0 0 0 0 1 0 1 0 0 0 0 0 0 0 0 1 1 0 1 0 0 1 0 0 0 1 0 0 0 0 1 1 0 0 1 0 0 0 0 1 0 0
1 0 0 0 1 0 1 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 1 0 0 1 0 0 0 0 0 0 0 0 1 0 1 1 0 0 0 1
0 0 1 0 0 0 0 0 1 1 1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 0 0 0 0
0 1 0 0 1 0 0 0 0 0 1 0 1 0 1 1 0 0 0 0 0 0 0 0 1 1 1 0 1 0 0 0 0 0 0 0 0 1 0 0 0 1 0 0 1 0 1 1 0 1 1
0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 0 0 0 0 1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 1 1 1 0 1 0

```

0011100100001011000001011110101110010110010001101
10011010001011010000000110100100101010000010101001
001011001111101100000000000010100000000100001011
010010011010101101000001101110010101001001010101
010101000101001000100001000010000100000001001111001

1 1 1 1 1 0 0 1 1 0 0 1 1 1 1 1 0 0 1 0 1 1 0 1 1 1 1 1 0 1 1 1 1 1 0 1 1 1 1 1 0 0 0 1 1 1 1
1 0 1 1 1 1 1 1 1 0 1 1 1 1 1 1 0 1 0 1 0 1 1 1 1 1 1 1 1 0 1 0 1 1 1 0 1 0 0 0 1 1 1 1 1 0 1 1
0 0 1 1 1 1 1 1 1 1 1 1 1 0 1 1 0 0 0 1 1 0 1 0 1 0 1 0 1 0 1 1 1 1 0 0 0 0 1 0 0 0 1 1 0 1 1 1
0 1 1 0 1 0 0 1 1 1 1 1 1 1 0 1 1 0 1 1 0 1 1 0 1 1 1 1 1 1 1 1 0 0 1 1 1 1 0 1 1 1 0 1 1 1
0 1 1 1 0 1 0 1 0 1 1 1 1 1 1 1 0 0 0 1 1 1 1 0 1 0 1 1 1 1 1 1 1 1 0 0 1 0 1 1 1 1 0 1 1 1 1 1 0 0

E.P.J. 16/5—D

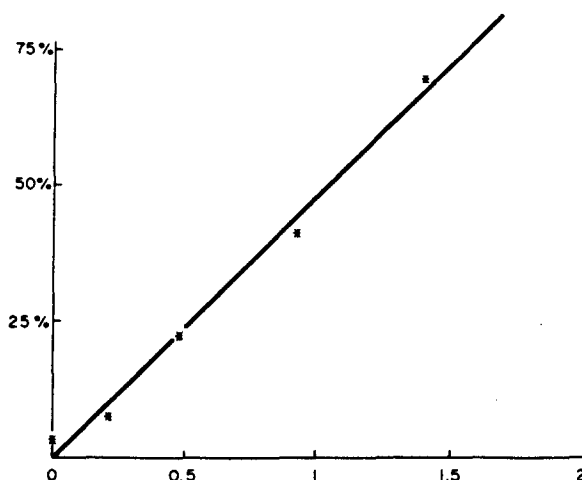


Fig. 9. Composition of the copolymers (in mol % AcN) as a function of the ratio between the number of possibilities to form excimers (D^*) and the number of AcN units.

different initial value would result in a different image of the copolymer. The different images obtained by simulation using different series of pseudo-random numbers correspond to the different macromolecules synthesized in the laboratory but all of them have the same average composition. Since the images of Fig. 8 have been built using the same initial value for IX, they can be compared. We have counted for the different sequences the number of possibilities of excimer formation for each copolymer according to the models given in Table 2 for some characteristic sequences. In Fig. 9, the composition of the simulated copolymers is plotted as a function of the ratio between the number of possibilities for the formation of D^* and the total number of absorbing chromophores. Linearity is obtained. In terms of energy migration, this means that migration over sequences equal to or larger than two 0 units is negligible compared with monomer deactivation of excimer formation.

3.3. Fluorescence intensity and decay as a function of temperature

The ratio I_M/I_D as a function of $1/T$ is given in Fig. 10. The minimum of the curves corresponds to $T \approx 308\text{K}$ whereas it is observed at $T \approx 276\text{K}$ for VN-MMA copolymers [2]. An iso-emissive point is observed for each copolymer in the following low temperature ranges: 140–246K for the copolymer 25-75, 129–258K for the copolymer 41-59, 132–227K for the copolymer 70-30.

The ratio I_M/I_D has been studied as a function of $1/T$ for many low molecular weight aromatic molecules [15]. A V-shaped curve is usually obtained. In the high temperature portion of the curve, I_M/I_D increases with decreasing $1/T$ owing to the dissociation of the excimer and subsequent increase of I_M ($k_{MD} > k_D$). In the low temperature region, the reverse condition ($k_D > k_{MD}$) prevails. PVN and copolymers were studied previously [2]. Since neither increase of I_M nor single exponential decay for I_M and I_D were observed in the high temperature portion of the V-shaped curve, another interpretation of the

results was proposed. It is also valid for PAcN and copolymers. In these systems, the condition $k_{MD} < k_D$ is compatible with the experimental results over the whole temperature region if k_D is of the form

$$k_D = k_{FD} + k_{ID} = k_D^0 + k'_{ID} \exp(-E_{ID}/RT)$$

where $k_D^0 = k_{FD} + k_{ID}^0$ as usually reported for low molecular weight aromatic compounds. Complementary conditions are:

Condition 1: $k_D^0 < k'_{ID} \exp(-E_{ID}/RT)$ in the high temperature range.

Condition 2: $k_D^0 > k'_{ID} \exp(-E_{ID}/RT)$ in the low temperature range.

It was demonstrated that, if dissociation of the excimer is negligible, a V-shaped curve is obtained for $\log I_M/I_D$ as a function of $1/T$ providing $E_{ID} > E_{DM}$. The minimum is then observed either in the high temperature range where $k'_{ID} \exp(-E_{ID}/RT)$ is $> k_D^0$ or in the intermediate range where the parameters are of the same order of magnitude. The value of E_{DM} can thus be obtained from the slope of the linear portion of the curve in the low temperature region since $k_{MD} < k_D$ and condition 2 can be introduced in the general equation [18]

$$\frac{I_M}{I_D} = \frac{k_{FM}}{k_{FD}} \left(\frac{k_D + k_{MD}}{k_{DM} M} \right).$$

The values obtained for PAcN are given in Table 1. E_{ID} could not be obtained in the high temperature region as it was for PVN and copolymers. Indeed the position of the minimum is situated at higher temperature for PAcN and the high temperature region is too restricted. The intensity of the normal fluorescence of copolymer 3-97 as a function of $1/T$ is given in Fig. 11. The value of E_{IM} can be obtained from the linear portion of the curve as discussed previously [2]. A value of $1.6 \text{ kcal} \cdot \text{mol}^{-1}$ ($6.7 \text{ kJ} \cdot \text{mol}^{-1}$) is found.

Other photophysical parameters could be obtained from the decay curves. If excimer dissociation is negligible, the term $k_{MD}D^*$ can be suppressed in the expression of dM^*/dt and dD^*/dt obtained from scheme

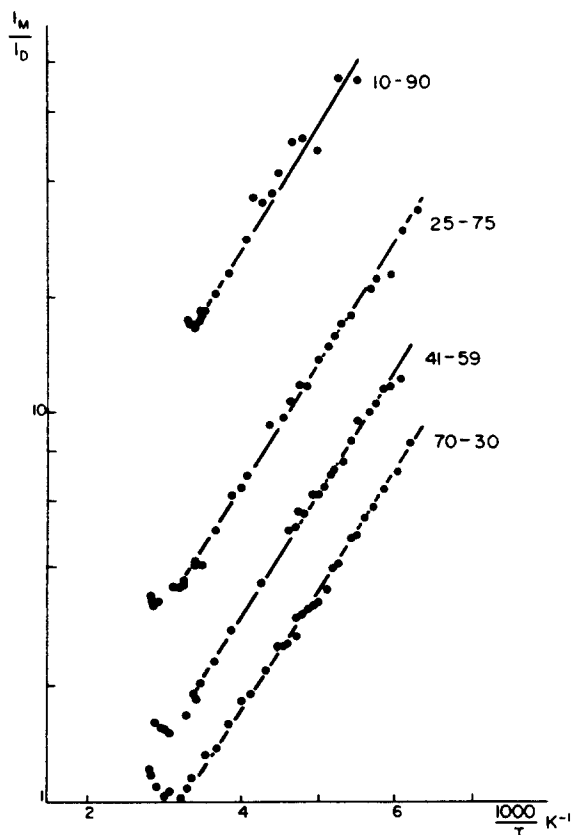


Fig. 10. Ratio of monomer to excimer fluorescence intensity as a function of $1000/T$.

1 of Ref [2]. After integration, this gives

$$i_M(t) = k_{FM} \exp[-(k_M + k_{DM}M)t] \quad (1)$$

$$i_D(t) = \frac{k_{FD}k_{DM}M}{k_D - (k_M + k_{DM}M)} \times \{\exp[-(k_M + k_{DM}M)t] - \exp(-k_D t)\} \quad (2)$$

This is only valid as a first approximation as will be shown later. This simplified treatment however allows useful correlation of the experimental data in PAcN copolymers and allows comparison with the results obtained for PVN copolymers.

Decay of I_D . The decay of I_D is exponential at sufficiently long time. The value of $\log k_D$ as a function of $1/T$ is given in Fig. 12. At low temperature, k_D is independent of temperature and reduces to $k_{FD} + k_{ID}^0$. If $\log(k_D - k_{FD} - k_{ID}^0)$ is plotted as a function of $1/T$, E_{ID} and k'_{ID} are obtained. The values are given in Table 1.

Decay of I_M . For the copolymer 3-97,

$$i_M(t) = I_0 \exp(-t/\tau_M)$$

with

$$\frac{1}{\tau_M} = k_{FM} + k_{IM}^0 + k'_{IM} \exp(-E_{IM}/RT) = k_M.$$

The values of k_M and $k_M - (k_{FM} + k_{IM}^0)$ as a function of $1/T$ are given in Fig. 11. Values of $15.8 \cdot 10^6 \text{ sec}^{-1}$, $1.6 \text{ kcal} \cdot \text{mol}^{-1}$ ($6.7 \text{ kJ} \cdot \text{mol}^{-1}$) and $1.1 \cdot 10^8 \text{ sec}^{-1}$ are obtained respectively for $k_{FM} + k_{IM}^0$, E_{IM} and k'_{IM} . Values of $i_M(t)$ for PAcN and copolymers 25-75, 41-59 and 70-30 are given by Eqn. (1). While k_D is measured

on the excimer emission at sufficiently long time, $(k_M + k_{DM}M)$ can be obtained from the decay of the normal fluorescence for the whole time scale. The values of $(k_M + k_{DM}M)$ measured at room temperature are given in Table 1. At 77 K, $k_{FM} + k_{IM}^0$ is obtained. In fluid medium, the decay constant of I_M increases with the AcN contents of the copolymer owing to the term $k_{DM}M$. Separation of the parameters k_M and $k_{DM}M$ has however not been performed since a plot of $\log I_M$ as a function of t shows a small departure from linearity at long times. This means that k_{MD} is not sufficiently smaller than k_D to verify Eqn (1) exactly. This effect is larger for the homopolymer than for the copolymer.

4. CONCLUSION

Photophysical parameters have been obtained for PAcN and copolymers AcN-MMA assuming that (1) excimer dissociation is less important than the other paths of excimer deactivation and (2) k_{ID} is the sum of two processes, one being temperature dependent and the other temperature independent. The validity of these assumptions is proved by the consistency of the results. Indeed fluorescence intensities and decay curves obtained respectively by steady and transient illumination could be interpreted. Furthermore the minimum of the curves relating $\log I_M/I_D$ to $1/T$ (Fig. 10) can be calculated exactly by introducing photophysical parameters obtained by photo-stationary and transient methods in the relation [2]

$$(E_{ID} - E_{DM})k_D = E_{ID}k_D^0$$

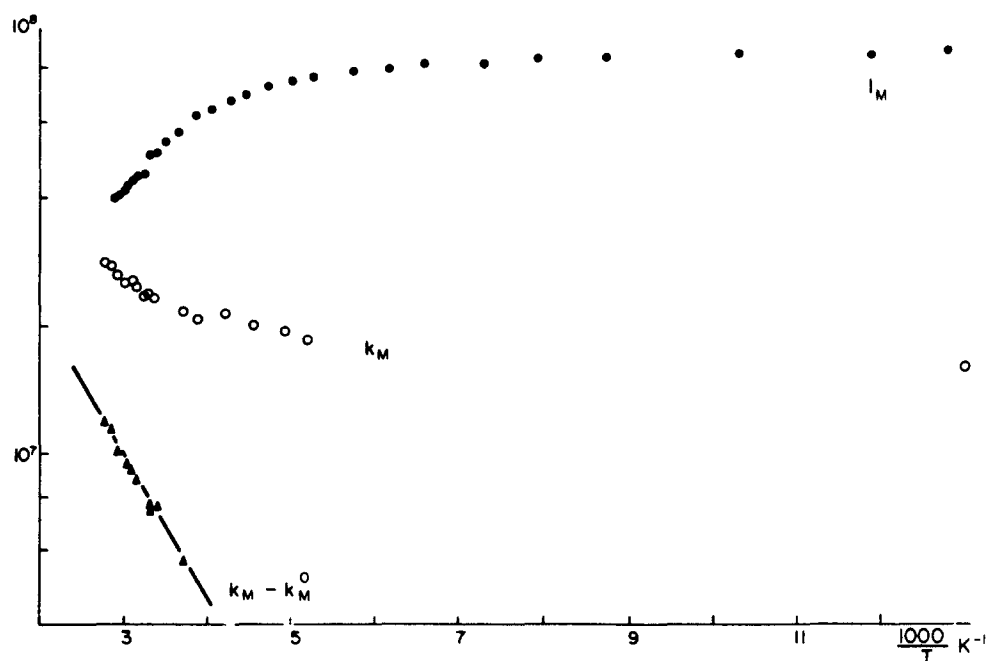


Fig. 11. Copolymer AcN-MMA. (●) monomer fluorescence intensity in arbitrary units; (○) k_M ; (▲) $k_M - k_M^0$ as functions of $1000/T$ with $k_M^0 = k_{FM} + k_{IM}$.

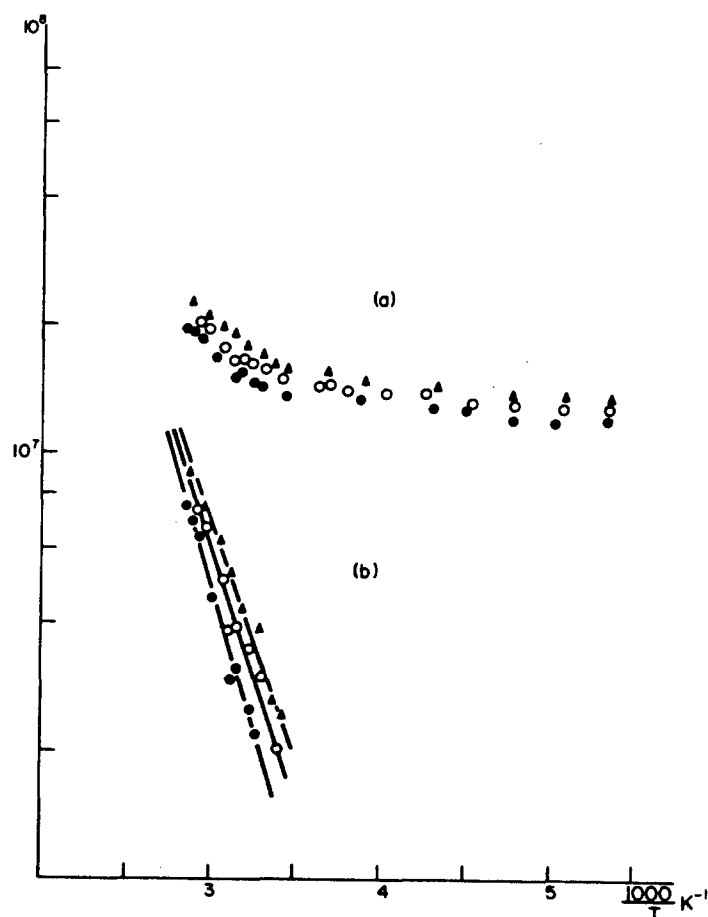


Fig. 12. (a) k_D ; (b) $k_D - k_D^0$ as functions of $1000/T$ for the copolymers AcN-MMA. ● 25-75; ○ 41-59; ▲ 70-30.

These parameters can be compared with those obtained previously for PVN. Except for k'_{ID} , the obtained values do not differ by more than a factor of two.

E_{DM} is lower for PAcN ($0.8 \text{ kcal} \cdot \text{mol}^{-1}$ or $3.3 \text{ kJ} \cdot \text{mol}^{-1}$) than for copolymers ($1.4 \text{ kcal} \cdot \text{mol}^{-1}$ or $5.8 \text{ kJ} \cdot \text{mol}^{-1}$) and PVN ($2.7 \text{ kcal} \cdot \text{mol}^{-1}$ or $11.3 \text{ kJ} \cdot \text{mol}^{-1}$). It can be proposed that the relative importance of excimer formation by excimer sampling and by migration to preformed excimer sites decreases as the rigidity of the chain increases. As a consequence, when excimer sampling is the dominant process, E_{DM} is related to conformational changes and to the microviscosity of the solvent. E_{DM} decreases by increasing the number of AcN units in the chain.

The assignment of the temperature independent (k_{ID}^0) and the temperature dependent ($k'_{ID} e^{-E_{ID}/RT}$) non-radiative deactivation processes to internal conversion or to intersystem crossing is difficult. Three mechanisms are possible for the temperature dependent term: 1. thermally activated intersystem crossing; 2. conversion to a higher non-fluorescent excimer state; 3. thermally activated internal conversion to a non-sandwich excimer configuration due to molecular motion subject to viscous constraint as proposed for pyrene [16]. Since E_{ID} is very different from E_{DM} in PAcN and PVN systems, it seems improbable that both are related to a viscosity dependent process. Further E_{ID} is larger than the temperature coefficient of the viscosity of the solvent. One of the first two hypotheses seems thus to be the more probable explanation.

The parameter k'_{ID} varies as E_{DM} in PAcN, PVN and copolymers and could thus be related to the rigidity of the chain.

An important difference between the AcN and the VN copolymers is observed for the minimum of the $\log I_M/I_D$ vs $1/T$ curve. A 30–40°C shift to higher temperature is indeed observed for AcN copolymers. This displacement results mainly from the difference in k'_{ID} with a minor contribution from the difference in E_{ID} and k_D^0 .

A physical model for excimer formation has been proposed using an image of the copolymer chains obtained by computer simulation of the free-radical copolymerization.

REFERENCES

1. C. David, D. Baeyens-Volant and G. Geuskens, *Eur. Polym. J.* **12**, 71 (1976).
2. C. David, M. Piens and G. Geuskens, *Eur. Polym. J.* **12**, 621 (1976).
3. C. David, N. Putman-de Lavareille and G. Geuskens, *Eur. Polym. J.* **13**, 15 (1977).
4. C. David, M. Lempereur and G. Geuskens, *Eur. Polym. J.* **8**, 417 (1972).
5. F. Schneider and J. Springer, *Makromolek. Chem.* **146**, 181 (1971).
6. Y. C. Wang and H. Morawetz, *Makromolek. Chem. Suppl.* **1**, 283 (1975).
7. K. Noma, M. Niwa and H. Norisada, *Doshida Daigaku Rikogaku Kenkyo Hokoku* **10**, 349 (1970). [From *Polymer Handbook* (Edited by J. Brandrup and E. H. Immergut). Wiley, New York (1975).]
8. H. Zimmermann and N. Joop, *Z. Elektrochem.* **65**, 61 (1961).
9. F. Dörr, In *Creation and Detection of the Excited State*, (Edited by A. A. Lamola), Vol. I, p. 53. Marcel Dekker, New York (1979).
10. R. F. Reid and I. Soutar, *J. Polym. Sci. Polym. Phys. Ed.* **15**, 873 (1977), and ref. cited.
11. C. W. Frank and L. A. Harrah, *J. chem. Phys.* **61**, 1526 (1974).
12. G. E. Johnson, *J. chem. Phys.* **62**, 4697 (1975).
13. C. David, M. Lempereur and G. Geuskens, *Eur. Polym. J.* **9**, 1315 (1973).
14. R. Robyn, J. Janssen, Centre de Recherche pour la Défense. Private communication.
15. J. B. Birks, *Photophysics of Aromatic Molecules*. Wiley, New York (1970).
16. J. B. Birks (editor) In *Organic Molecular Photophysics*, Vol. 2, p. 505. Wiley, New York (1975).
17. Obtained by cationic polymerization.
18. In the product $k_{DM}M$, M is not the molar concentration in aromatic groups since excimers are formed intramolecularly. It is a parameter related to the statistical composition of copolymers [1, 2].
19. The fluorescence of an intramolecular dimer has been observed by Hayashi and coworkers in 1-PVN and 2-PVN in cyclohexane and methylene chloride solutions [*J. phys. Chem.* **81**, 1571 (1977)]. Such an emission could not be detected either in the acenaphthylene polymer and copolymers used in this work or in the 1-vinylnaphthalene polymer and copolymers used in Ref. [2] even in cyclohexane. Most probably, the existence of intramolecular dimer is strongly dependent on the microtacticity of the chain.

Résumé—La polarisation de fluorescence de solutions vitreuses a été déterminée à 77 K. Les intensités de fluorescence d'excimère et de monomère ont été mesurées et les courbes de décroissance correspondantes analysées dans un large domaine de température. Les énergies d'activation et facteurs de fréquence correspondant à plusieurs processus photophysiques ont ainsi été obtenus et comparés avec ceux publiés précédemment pour le poly-1-vinylnaphtalène.