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LUMINESCENCE STUDIES IN POLYMERS—VIII*

POLY-1-VINYLNAPHTHALENE AND ITS COPOLYMERS WITH METHYLMETHACRYLATE: FLUORESCENCE YIELD AND LIFE-TIME AS A FUNCTION OF TEMPERATURE IN SOLUTION

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Abstract—Combining the measurement of fluorescence yield and decay-time as a function of temperature, the activation energies and frequency factors corresponding to several photophysical processes have been determined for solutions of poly-1-vinylnaphthalene and its copolymers with methylmethacrylate. The results are discussed in relation to copolymer composition and compared with those reported in the literature for model compounds. Excimer dissociation is found to be unimportant in the polymeric systems. This is tentatively assigned to a lower value of the frequency factor corresponding to excimer dissociation.

INTRODUCTION

Photophysical processes in polymer systems have been widely studied recently [1–10]. Most of them are based on analysis of the emission spectra and on measurement of fluorescence and phosphorescence intensities under different conditions. Life-time measurements have been seldom performed.

In the present work, measurement of fluorescence intensity as a function of temperature during steady illumination has been combined with determination of the rate of decay of the emission under flash condition for poly-1-vinylnaphthalene (PVN) and three copolymers of different composition of 1-vinylnaphthalene and methylmethacrylate in solution between 363 and 77°K. Several elementary rate constants, activation energies and frequency factors have been determined and compared with those reported for 1-methylnaphthalene [11, 12] and α,α'-dinaphthylpropane [13].

EXPERIMENTAL

Three copolymers were prepared by free radical reaction at 60°C using AIBN as initiator and limiting the conversion to less than 10%. Their molar compositions (% vinylnaphthalene/% methylmethacrylate) were 5/95, 40/60 and 65/35, as determined by u.v. absorption spectroscopy assuming that the molar extinction coefficient of naphthalene units in the copolymers is the same as in the homopolymer.

PVN was obtained by spontaneous polymerization of the purified monomer in the refrigerator. The polymer and copolymers were carefully purified by successive dissolutions and precipitations.

Methyltetrahydrofurane (Fluka) was purified through alumina columns and distilled under nitrogen on LiH_4Al. Its purity was tested by absorption spectroscopy and by fluophosphorimetry at 77°K.

The solutions (10^{-3} M in naphthalene units) were carefully outgassed by the freeze–thawing technique at a pressure of 10^{-5} mm Hg and the cells sealed under vacuo before emission or decay time measurements. The emission spectra as a function of temperature were recorded using a laboratory built device previously described [9]. The decay times were measured using a TWR nanosecond decay time fluorometer (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% $NaNO_2$ solution (analysis);

(2) normal fluorescence decay: 4 cm chlorine at a pressure of 510 torr (excitation) + a Corning CS760 + 2 cm of a 15% $KCr(SO_4)_2 \cdot 12\,H_2O$ solution in H_2SO_4 1 N (analysis).

RESULTS AND DISCUSSION

1. *Fluorescence intensity as a function of temperature*

The fluorescence spectrum of PVN and the copolymers 65/35 and 40/60 consists of normal and excimer fluorescence at room temperature. The ratio of their intensities strongly depends on temperature and, at a given temperature, I_M/I_D increases with decreasing vinylnaphthalene content. The values of log I_M, log I_D and log I_M/I_D as a function of $1/T$ are given in Fig. 1 for the copolymers. They have been published previously for the homopolymer [14]. An isoemissive point is observed for each copolymer in the temperature ranges: 176–120°K for PVN, 155–121°K for copolymer 65/35 and 211–117°K for copolymer 40/60.

The emission spectrum of copolymer 5/95 does not show any component of excimer fluorescence. The value of log I_M as a function of $1/T$ is given in Fig. 2. The envelope of the spectrum is independent of temperature.

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* Part VII. C. David, N. Putman-de Lavareille and G. Geuskens. *Europ. Polym. J.* **12**, 365 (1976).

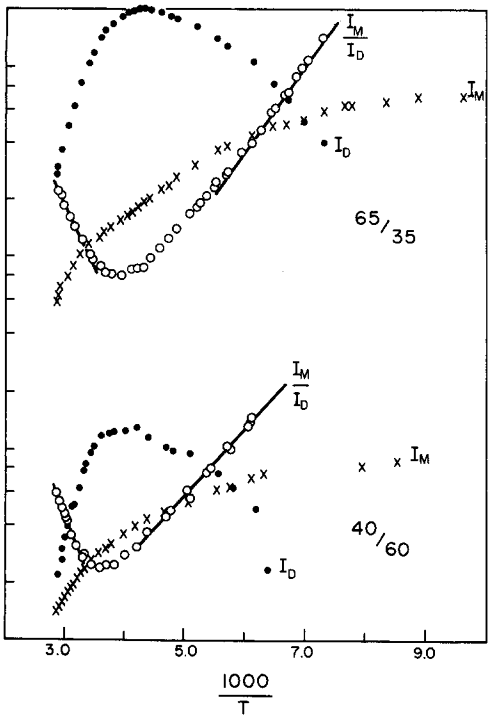

Fig. 1. Fluorescence intensity as a function of 1000/T

$I_M(\times)$ $I_D(\bullet)$ $\frac{I_M}{I_D}(\text{O})$.

relative arbitrary units – C = 10^{-3} M in naphthalene units–solvent: MTHF.

The usual sequence of photophysical processes is given in Scheme 1.

$^1M + h\nu \rightarrow {}^1M^*$	energy absorption	I_a	
$^1M^* \rightarrow {}^1M + h\nu_M$	fluorescence	k_{FM}	k_M
$^1M^* \rightarrow {}^1M$	internal conversion	k_{IM}	
$^1M^* \rightarrow {}^3M^*$	intersystem crossing		
$^3M^* \rightarrow {}^1M + h\nu_P$	phosphorescence	k_{PT}	k_T
$^3M^* \rightarrow {}^1M$	intersystem crossing	k_{GT}	
$^1M^* + {}^1M \rightleftarrows {}^1M + {}^1M^*$	singlet migration	k_{MM}	
$^1M^* + {}^1M \rightarrow {}^1D^* + {}^1M$	singlet excimer formation	k_{DM}	
$^1D^* \rightarrow {}^1M^* + {}^1M$	excimer dissociation	k_{MD}	
$^1D^* \rightarrow {}^1M + {}^1M + h\nu_D$	excimer fluorescence	k_{FD}	k_D
$^1D^* \rightarrow {}^3D^*$	intersystem crossing		
$^1D^* \rightarrow {}^1M + {}^1M$	dissociative internal conversion	k_{ID}	

Assuming stationary state conditions for the excited states

$$\frac{I_M}{I_D} = \frac{k_{FM}}{k_{FD}} \frac{(k_D + k_{MD})}{k_{DM}M} \tag{1}$$

$$I_M = k_{FM} \frac{I_a(k_D + k_{MD})}{(k_M + k_{DM}M)k_D + k_{MD}k_M} \tag{2}$$

$$I_D = k_{FD} \frac{I_a k_{DM} M}{(k_M + k_{DM}M)k_D + k_{MD}k_M} \tag{3}$$

In the expression of the rate of excimer formation, $k_{DM}MM^*$, 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 [15, 16].

The experimental results can be interpreted according to these equations. Figure 1 shows that a linear relation with a negative slope separated by a minimum from a linear relation with a positive slope is observed for log I_M/I_D as a function of increasing $1/T$.

For low molecular weight compounds, curves similar to those given in Fig. 1 have often been observed for log I_M/I_D as a function of $1/T$ [17]. In these cases, it was demonstrated that linearity is observed in the low temperature range because the condition $k_D > k_{MD}$ prevails. In the high temperature region, the reverse condition $k_D < k_{MD}$ is usually verified and dynamic equilibrium is attained: the excimer dissociates and this is accompanied by an increase of I_M and the appearance of an isoemissive point.

In the case of 1-vinylnaphthalene homopolymer and its copolymers with methylmethacrylate, such an increase of I_M in the high temperature region is not observed. A discontinuity in the decrease of I_M with T has however been reported [14] and previously assigned to excimer dissociation. This leads us to assume that the condition $k_D < k_{MD}$ is verified. The rate of normal and excimer fluorescence decay reported here however shows that dynamic equilibrium is not obeyed in the high temperature range (see 2 below).

We shall now demonstrate that for PVN and the copolymer, the reverse condition $k_{MD} < k_D$ is compatible with the experimental results over the whole temperature range investigated if k_D is of the form

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

where $k_D^\circ = k_{FD} + k_{ID}^\circ$ as usually reported for low molecular weight aromatic compounds [17]. Complementary conditions are:

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

Condition 2. $k_D^\circ > k'_{ID} \exp(-E_{ID}/RT)$ in the low temperature range. Derivation of Eqn. (1) gives:

$$\frac{\delta}{\delta[1/T]}\left(\ln \frac{I_M}{I_D}\right) = \frac{1}{R} \times \left\{ \frac{-E_{ID} \cdot k'_{ID} \exp(-E_{ID}/RT) - E_{MD}k_{MD}}{k_D^\circ + k'_{ID} \exp(-E_{ID}/RT) + k_{MD}} + E_{DM} \right\} \tag{4}$$

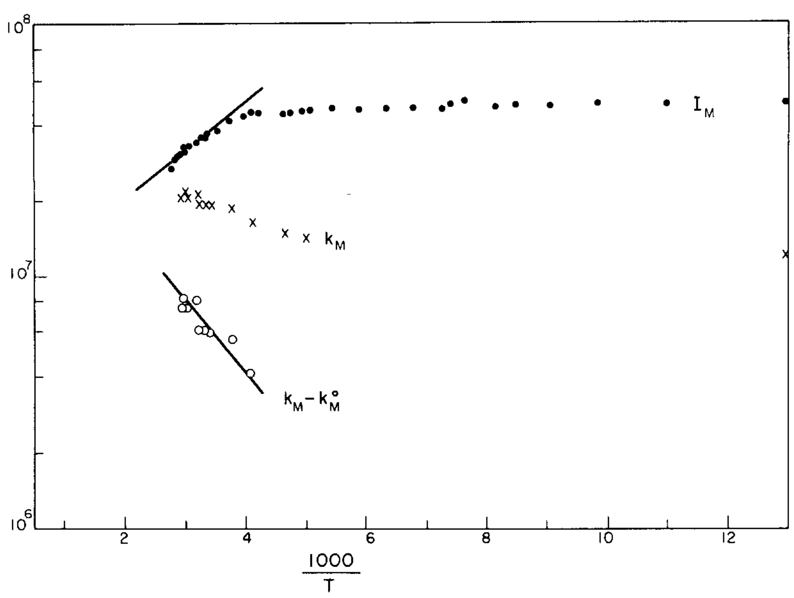

Fig. 2. Copolymer VN–MMA 5/95. (●): normal fluorescence intensity in relative arbitrary units. (×): k_M. (O): $k_M - k_M^\circ$.

At the minimum of ln I_M/I_D as a function of $1/T$, (4) is zero and:

$$(E_{MD} - E_{DM})\,k_{MD} = (E_{DM} - E_{ID})\,k_D + E_{ID}k_D^\circ \quad (5)$$

In a previous paper [18] the term $E_{ID}k_D^\circ$ was omitted by mistake. If excimer dissociation is negligible, (5) reduces to:

$$(E_{ID} - E_{DM})\,k_D = E_{ID}\,k_D^\circ \quad (6)$$

Considering (5), $E_{MD} - E_{DM}$ is always > 0. As a consequence, the right-side member of that equation obeys the same condition:

$$(E_{DM} - E_{ID})\,k_D + E_{ID}\,k_D^\circ > 0$$

which rearranges to

$$E_{DM} > E_{ID}\left(1 - \frac{k_D^\circ}{k_D}\right). \quad (7)$$

Taking into account conditions (1) and (2), (7) is verified:

—in the low temperature range, if $E_{DM} > 0$ since k_D°/k_D tends to 1. This is always the case.

—in the high temperature range, if $E_{DM} > E_{ID}$ since there k_D°/k_D tends to zero.

—in the intermediate temperature range providing Eqn. (7) is fulfilled as a whole, independently of the relative values of E_{ID} and E_{DM}.

If dissociation is negligible and conditions (1) and (2) are taken into account, (6) is verified in the high temperature range providing $E_{ID} = E_{DM}$. It is never obeyed in the low temperature range where $k_D = k_D^\circ$. In the intermediate range, E_{ID}–$E_{DM} > 0$ is compulsory since $E_{ID}k_D^\circ$ is positive.

This shows that if dissociation of the excimer is negligible, a U-shaped curve is observed for log I_M/I_D as a function of $1/T$ providing $E_{ID} = E_{DM}$. The minimum is then observed either in high temperature range where $k'_{ID}\exp(-E_D/RT)$ is larger than k_D°, or in the intermediate range where the parameters are of the same order of magnitude. This will be demonstrated to be the case for PVN and copolymers combining intensity and decay rate measurements as a function of temperature.

By simplification of Eqn. (1) ($k_{MD} < k_D$ and conditions 1 or 2 and derivation of log (I_M/I_D) as a function of $(1/T)$, E_{DM} can be obtained from the positive

Table 1. Photophysical parameters for 1-PVN copolymers with methylmethacrylate and 1-methylnaphthalene

	E_{DM}^{a}	E_{ID}^{ab}	E_{ID}^{ac}	$k'_{ID}\cdot 10^{-10}$ sec^{-1}	$(k_{FD} + k_{ID}^\circ)\cdot 10^{-6}$ sec^{-1}	E_{IM}	$(k_{FM} + k_{IM}^\circ)\cdot 10^{-6}$ sec^{-1}	$k'_{IM}\cdot 10^{-8}$ sec^{-1}
PVN	2.7	6.3	6.0	57.7	10.9	—	12.2	—
Cop. 65/35	2.2	5.3	5.3	8.2	9.3	—	12.6	—
Cop. 40/60	1.6	5.2	4.8	2.8	8.7	—	11.5	—
Cop. 5/95	—	—	—	—	—	1.4^{c}–0.9^{b}	12.0	0.6
1 MeN [12]	3.0^{f}	4.0		0.25	—	0.79	—	0.83
1 MeN [11]	—	6.7	—	32	5^{e}	—	—	—

a kcal·mole^{-1}
b intensity measurement
c decay measurement
e value for k_{ID}°
f E_{MD} = 7.7 kcal·mole^{-1}

slope in the low temperature range in the vicinity of the isoemissive point while E_{ID} can be obtained in the high temperature range where the negative slope gives E_{ID}–E_{DM}. The results are given in Table 1 for PVN and copolymers 65/35 and 40/60.

The intensity of the normal fluorescence of copolymer 5/95 varies as a function of temperature according to:

$$I_{\mathrm{M}} = k_{\mathrm{FM}} \frac{I_a}{k_{\mathrm{FM}} + k_{\mathrm{IM}}^{\circ} + k'_{\mathrm{IM}} \exp(-E_{\mathrm{IM}}/RT)} \tag{8}$$

If $k_{\mathrm{FM}} + k_{\mathrm{IM}}^{\circ} < k'_{\mathrm{IM}} \exp(-E_{\mathrm{IM}}/RT)$ at sufficiently high temperature, then a linear relation with slope E_{IM}/R is calculated for log I_{M} as a function of $1/T$. A value of 0.9 kcal·mole^{-1} is obtained for $1000/T \leqslant 4$ (Fig. 3).

2. *Measurements of emission decay*

The decays of normal and excimer fluorescences are given by (17):

$$i_{\mathrm{M}}(t) = k_{\mathrm{FM}} \frac{(\lambda_2 - X)}{(\lambda_2 - \lambda_1)} \{\exp(-\lambda_1 t) + A \exp(-\lambda_2 t)\} \tag{9}$$

$$i_{\mathrm{D}}(t) = k_{\mathrm{FD}} \frac{k_{\mathrm{DM}} M}{(\lambda_2 - \lambda_1)} \{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \tag{10}$$

where:

$$\lambda_{1,2} = \tfrac{1}{2}[X + Y \mp \{(Y - X)^2 + 4k_{\mathrm{MD}} k_{\mathrm{DM}} M\}^{1/2}] \tag{11}$$

$$A = \frac{(X - \lambda_1)}{(\lambda_2 - X)}$$

$$X = k_{\mathrm{M}} + k_{\mathrm{DM}} M \quad Y = k_{\mathrm{D}} + k_{\mathrm{MD}}.$$

Since, according to (11), the condition $\lambda_1 < \lambda_2$ is always satisfied, the term $\exp(-\lambda_2 t)$ is much smaller than $\exp(-\lambda_1 t)$ at sufficiently long time. The decay of I_{D} is then exponential and the measured parameter is λ_1.

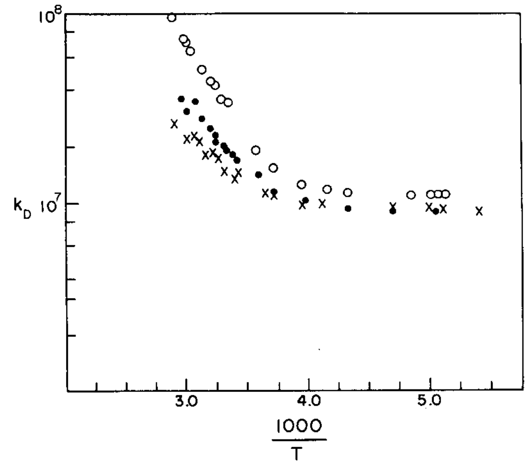

Fig. 3. k_{D} as a function of $1000/T$ for PVN (○); copolymer VN–MMA 65/35 (●); copolymer VN–MMA 40/60 (×).

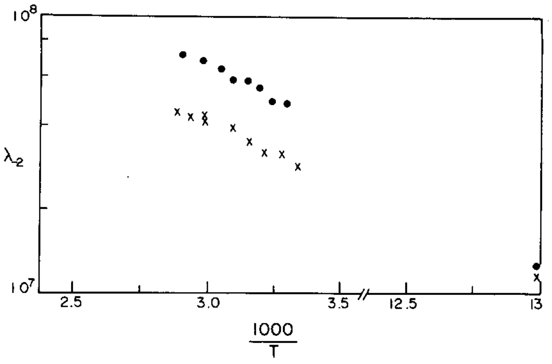

Fig. 4. $\lambda_2 (k_{\mathrm{M}} + k_{\mathrm{DM}} M)$ as a function of $1000/T$ for copolymer VN–MMA 65/35 (●) and copolymer VN–MMA 40/60 (×).

If excimer dissociation is negligible, the term $k_{\mathrm{MD}} D^*$ can be suppressed in the expression of $\mathrm{d}M^*/\mathrm{d}t$ and $\mathrm{d}D^*/\mathrm{d}t$ obtained from scheme 1. After integration, this gives:

$$i_{\mathrm{M}}(t) = k_{\mathrm{FM}} \exp[-(k_{\mathrm{M}} + k_{\mathrm{DM}} M)t] \tag{12}$$

$$i_{\mathrm{D}}(t) = \frac{k_{\mathrm{DM}} M}{[k_{\mathrm{D}} - (k_{\mathrm{M}} + k_{\mathrm{DM}} M)]} \{\exp[-(k_{\mathrm{M}} + k_{\mathrm{DM}} M)t] - \exp(-k_{\mathrm{D}} t)\} \tag{13}$$

At high temperature, the conditions k_{MD}, $k_{\mathrm{DM}} M \gg k_{\mathrm{M}}$, k_{D} is verified if dynamic equilibrium is attained. Putting these conditions in (11) gives:

$$\lambda_2 = k_{\mathrm{MD}} + k_{\mathrm{DM}}[M]$$

and $\exp(-\lambda_2 t)$ is negligible except at small t. Then $i_{\mathrm{M}}(t)$ and $i_{\mathrm{D}}(t)$ decay with a common life time:

$$i_{\mathrm{M}}(t) = \frac{k_{\mathrm{FM}} k_{\mathrm{MD}}}{k_{\mathrm{MD}} + k_{\mathrm{DM}}[M]} \exp(-\lambda t) \tag{14}$$

$$i_{\mathrm{D}}(t) \doteq \frac{k_{\mathrm{FD}} k_{\mathrm{DM}} M}{k_{\mathrm{MD}} + k_{\mathrm{DM}} M} \exp(-\lambda t) \tag{15}$$

where

$$\lambda = \frac{k_{\mathrm{M}} + \dfrac{k_{\mathrm{D}} k_{\mathrm{DM}} M}{k_{\mathrm{MD}}}}{1 + \dfrac{k_{\mathrm{DM}} M}{k_{\mathrm{MD}}}}.$$

The decay time of I_{M} and I_{D} being different over the whole temperature range for PVN and copolymers, Eqns. (14) and (15) are thus not verified and (12), (13) can be assumed to be valid in this case. The decay of I_{M} gives $(k_{\mathrm{M}} + k_{\mathrm{DM}} M)$ if exponential. The decay of I_{D} gives k_{D} at long times. These parameters have been measured as a function of temperature for the series of copolymers and the homopolymer.

2.1 *Decay of* I$_{\mathrm{D}}$. 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. 4. At low temperature k_{D} is independent of temperature and reduces to $k_{\mathrm{FD}} + k_{\mathrm{D}}^{\circ}$. If log $(k_{\mathrm{D}} - k_{\mathrm{FD}} - k_{\mathrm{D}}^{\circ})$ is plotted as a function of log $1/T$, E_{ID} and k'_{ID} are obtained. The values are given in Table 1. The agreement between the values of E_{ID} obtained from fluorescence yield and from emission decay is quite good.

2.2 *Decay of* I_M. For the copolymer 5/95, $I_M(t) = I_0 \exp(-t/\tau_M)$ with

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

The values of k_M and $k_M - (k_{FM} + k_{IM}^{\circ})$ as a function of $1/T$ are given in Fig. 2. Values of $12 \cdot 10^6$ sec^{-1}, 1.4 kcal·mole^{-1} and $0.6 \cdot 10^8$ sec^{-1} are obtained respectively for $k_{FM} + k_{IM}^{\circ}$, E_{IM} and k'_{IM}. The discrepancy between the values of E_M obtained by intensity measurement and by fluorescence decay may be due to the fact that in the first case $k_{FM} + k_{IM}^{\circ}$ is supposed to be much smaller than $k'_{IM} \exp(-E_{IM}/RT)$. This is not the case, as shown by Fig. 2. $I_M(t)$ for PVN and copolymers 65/35 and 40/60 are given by (12). When excimer dissociation is negligible, $\lambda_1 = k_D$ and $\lambda_2 = k_M + k_{DM}M$. While λ_1 is measured on the excimer emission at sufficiently long time, λ_2 corresponds to the decay of the normal fluorescence for the whole time scale. The values of λ_2 as a function of temperature are given in Fig. 4. When measured at 77°K, λ_2 is $k_{FM} + k_{IM}^{\circ}$. The obtained values are identical to those measured for the copolymer 5/95. In a fluid medium, λ_2 clearly increases with vinylnaphthalene content of the copolymer owing to the term $k_{DM}M$. This must be considered as a general trend of the dependence of λ_2 on composition. However, a quantitative evaluation of the kinetic parameters is difficult 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. (12) exactly. This effect is larger for the homopolymer than for the copolymers. It is also revealed by measurements of I_M as a function of T; a discontinuity of I_M has been previously reported for PVN [14] and a small discrepancy is observed for this polymer between the experimental value of the temperature corresponding to the minimum of log I_M/I_D as a function of $1/T$ and the value calculated using Eqn. (6).

3. *Comparison with photophysical parameters of model compounds*

Excimer formation of isolated chromophores is a diffusion limited process and E_{DM} is thus usually close to the temperature coefficient of the viscosity of the solvent [17]. In polymers, excimers are formed between nearest neighbours or next-to-nearest neighbours in the same chain and E_{DM} is related to internal rotation of the chromophores in a given solvent. This activation energy is thus expected to be different for polymers and for isolated model chromophores in the same solvent. Furthermore, in copolymers, it could be sensitive to interaction with the comonomer units. This is indeed observed in PVN and copolymers as shown by Table 1.

The parameters E_{IM}, $(k_{FM} + k_{IM}^{\circ})$ and $(k_{FD} + k_{ID}^{\circ})E_{ID}$ and k'_{ID} have the same order of magnitude for methylnaphthalene (values of Cundall and Pereira) and for the polymers, but the last two show some dependence on copolymer composition.

The most striking difference between models and polymers lies in the importance of excimer dissociation. For 1-methylnaphthalene, it is more important than the other modes of deactivation of the excimer at temperatures as low as 230°K (11); for the polymer, this condition is not realized even at 350°K. For the bichromophoric compound α,α′-dinaphthylpropane, a decrease of I_M and I_D similar to that observed in the present work has been reported to occur above 273°K. This difference between 1-methylnaphthalene and the polymer must be assigned to either k'_{MD} or E_{MD} since the other parameters are similar. For PVN, it can be calculated that E_{MD} should have the value of 9.9 kcal·mole^{-1} for k_{MD} to be of the same order of magnitude as k_D at 380°K, assuming that k'_{MD} has the value of 10^{14} sec^{-1} previously determined by Selinger for 1-methylnaphthalene [12]. This order of magnitude of k'_{MD} has been observed for other intermolecular excimers (17). The value of the binding energy of the excimer would then be $9.9 - 2.7 = 7.2$ kcal·mole^{-1} while it is 4.7 kcal·mole^{-1} for the 1-methylnaphthalene. A more probable explanation would be that k'_{MD} is smaller for the polymer than for the model. Assuming that B the binding energy of the excimer is 4.7 kcal·mole^{-1} for the polymer, E_{MD} would then be 7.4 kcal·mole^{-1}. In this case, k_{MD} would be of the same order of magnitude as k_D at 380°K if $k'_{MD} = 4 \cdot 10^{12}$ sec^{-1}. A value of k'_{MD} of $5 \cdot 10^{12}$ sec^{-1} has been reported for another intramolecular excimer (biscarbazolylpropane [20]), while this frequency factor is usually 10^{14} sec^{-1} or higher for intermolecular excimers [17]. Strong support for this low value of k'_{MD} for the polymer can be obtained by considering the frequency factors given in the literature for unimolecular reactions [19]. Dissociation of intra- and intermolecular excimers can be respectively compared to isomerizations ($A \rightarrow A'$) and dissociation ($A \rightarrow B + C$). Lower frequency factors are usually found for isomerizations. With this lower value of k'_{MD} would be associated a less negative value for the entropy of formation of the excimer. This is not unexpected since the loss in entropy associated with excimer formation between neighbouring groups in the same chain is lower than between independent molecules [17, 20].

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Résumé—Les énergies d'activation et les facteurs de fréquence correspondant à plusieurs processus photophysiques ont été mesurés pour des solutions de poly-1-vinylnaphtalène et des copolymères de 1-vinylnaphtalène et de méthacrylate de méthyle, en combinant les mesures de durée de vie et de rendement de fluorescence en fonction de la température. Ces résultats sont discutés en fonction de la composition du copolymère et comparés à ceux donnés dans la littérature pour les molécules modèles. La dissociation de l'excimère est peu importante dans les systèmes polymériques. Ceci est attribué à une plus faible valeur du facteur de fréquence correspondant à la dissociation de l'excimère.