European Polymer Journal, 1972, Vol. 8, pp. 1291–1297. Pergamon Press. Printed in England.

LUMINESCENCE STUDIES IN POLYMERS—II*

TEMPERATURE EFFECT ON POLYVINYLCARBAZOLE FLUORESCENCE

C. DAVID, M. PIENS and G. GEUSKENS

Faculté des Sciences, Université Libre de Bruxelles, 50, avenue F. D. Roosevelt, 1050 Brussels, Belgium

(*Received* 8 *May* 1972)

Abstract—Polyvinylcarbazole (PVCa) films and solutions emit normal and excimer fluorescence between 77 and 425 K. The absolute (I_M and I_D) and relative (I_M/I_D) intensities emitted strongly depend on temperature. The usual U-shaped curve is obtained for log I_M/I_D as a function of $1/T$ in the case of polymer films. In solution, two minima corresponding to two different excimers are observed. The formation and dissociation of PVCa excimers in films and solutions have been interpreted according to the usual kinetic scheme. The binding energies for the excimer in films and for the high temperature excimer in solutions are respectively 4 and 2·8 kcal mole^{-1}.

I. INTRODUCTION

THE INTENSITY of normal and excimer fluorescence strongly depends on temperature. A detailed study of this temperature effect has been undertaken recently for polyvinylnaphthalene and polyacenaphthylene films and solutions.[1] Excimer dissociation in films was shown to be negligible up to 425 K. The behaviour of solutions is quite different. Excimer dissociation occurs above 225 and 283 K respectively for polyvinylnaphthalene and polyacenaphthylene. The binding energy of excimers in solution is lower for the polymers than for the model compounds 1-methylnaphthalene and acenaphthene.

The present work concerns the analysis of the emission spectra of polyvinylcarbazole films and solutions between 77 and 425 K.

II. EXPERIMENTAL

Polyvinylcarbazole (LUVICAN M 150) was kindly supplied by BASF. It was purified by 7 dissolutions in benzene and precipitations in methanol to remove anthracene impurity. The purification of the solvents and the experimental device for recording the emission spectra have been previously described.[1,2] The excitation wavelength is 300 nm in all cases. The results have not been corrected for the response of the photomultiplier (Hamamatsu R 106).

III. RESULTS

PVCa films

The emission spectrum of PVCa films consists of normal and excimer fluorescence centred respectively at 370 and 403 nm. The spectra obtained at 77 and 300 K (Fig. 1) are similar to those reported by Offen[3] and Klöpffer.[4] The following equations have been used to separate the contribution of normal and excimer fluorescence at 370 and 403 nm:

$$I_{403} = I_D + 0{\cdot}21\ I_M$$
$$I_{370} = I_M + 0{\cdot}45\ I_D$$

where I_{403} and I_{370} are the total heights of the peak measured at 403 and 370 nm, I_D is the height corresponding to the excimer fluorescence intensity emitted at 403 nm and I_M is the height of the peak corresponding to the fluorescence intensity emitted at

* Part I—ref. (1).

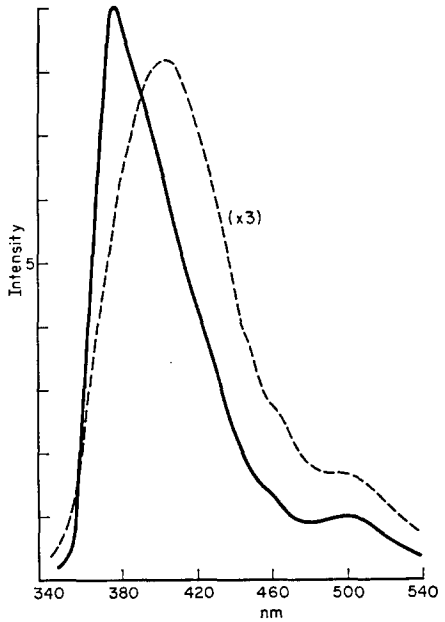

FIG. 1. Emission spectra of polyvinylcarbazole films; ——— at 77 K; - - - - at 298 K.

370 nm. The contribution of the normal fluorescence intensity at 403 nm has been determined from the spectrum of polyvinylcarbazole in a glass at 77 K where the excimer fluorescence is negligible. The contribution of the excimer fluorescence at 370 nm has been chosen in order to have a positive value for I_M in the temperature range studied. The binding energy measured for the excimer in solutions is insensitive to these corrections. An error of 0·5 kcal in the binding energy for excimer in films takes into account the potential inaccuracy.

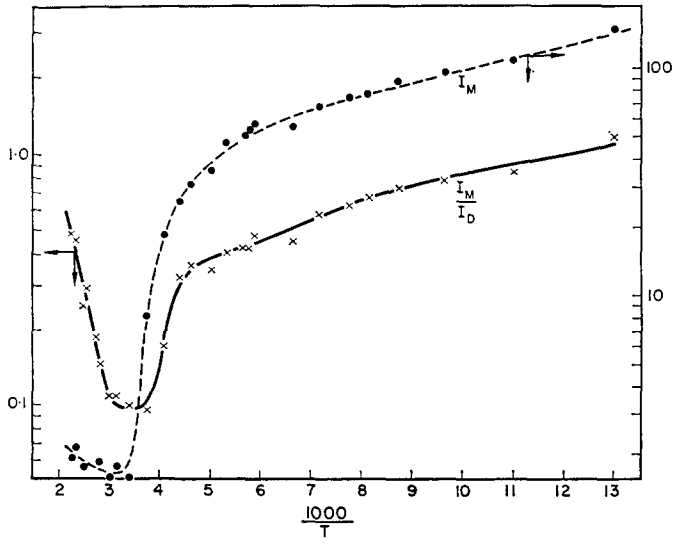

FIG. 2. Temperature dependence of the normal fluorescence intensity (●) and of I_M/I_D (×) for polyvinylcarbazole films.

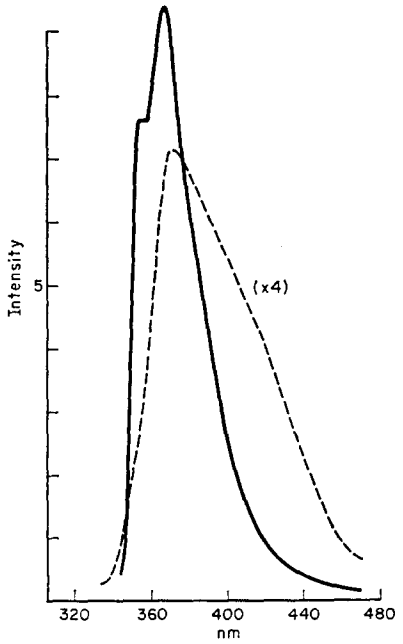

FIG. 3. Emission spectra of polyvinylcarbazole in MTHF: ——— at 77 K; - - - - at 298 K.

A U-shaped curve with a minimum corresponding to 294 K is observed for log I_M/I_D as a function of $1/T$ (Fig. 2). The variation of log I_M is shown on the same curve.

PVCa solutions

The emission spectra of PVCa solutions at 77 and 300 K are given in Fig. 3. Normal fluorescence and excimer fluorescence are emitted with λ_{max} at 370 and 403 nm. The

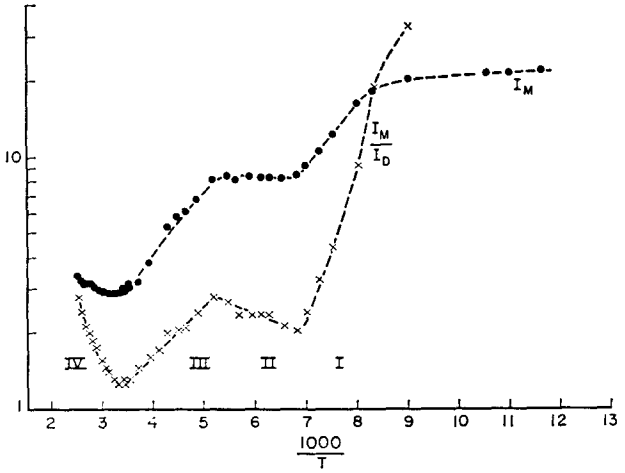

FIG. 4. Temperature dependence of the normal fluorescence intensity (●) and of I_M/I_D (×) for polyvinylcarbazole solutions in MTHF. ($C = 3 \times 10^{-4}$ M).

absolute and relative intensities of both emission I_M and I_M/I_D vary with temperature (Fig. 4). Corrections identical to those already described for films have been used to separate normal and excimer fluorescence. The values of the applied corrections do not significantly modify the shape of Fig. 4 nor the values of the measured activation energies. Instead of the U-shaped curve usually obtained for $\log I_M/I_D$ as a function of $1/T$, a curve with two minima is observed in MTHF solutions. In a binary mixture MTHF–THF 6:5, a minimum at $1/T = 3{\cdot}4 \times 10^{-3}$ is observed. This solvent mixture cannot be used in the temperature range corresponding to the other minimum: strong turbidity of the sample appears above the softening point of the glass and disturbs the emission measurements.

IV. DISCUSSION

The usual kinetic scheme applies to absorption and dissipation of energy in polymer systems in which excimer formation occurs and has been used with success in the case of polyvinylnaphthalene and polyacenaphthylene in solution.[1] The behaviour of many low molecular weight compounds is also adequately described by this model.[5]

If photostationarity is verified for the excited monomer M^* and dimer D^*:[1]

$$I_M = \frac{k_{FM}\, I_a(k_D + k_{MD})}{(k_M + k_{DM})\, k_D + k_{MD}\, k_M} \tag{1}$$

$$I_D = \frac{k_{FD}\, I_a\, k_{DM}}{(k_M + k_{DM})\, k_D + k_{MD}\, k_M} \tag{2}$$

$$\frac{I_M}{I_D} = \frac{k_{FM}}{k_{FD}} \cdot \frac{(k_{MD} + k_D)}{k_{DM}}. \tag{3}$$

Plotting $\log I_M/I_D$ as a function of $1/T$ usually gives a U-shaped curve, the minimum of which corresponds to the condition:

$$\frac{\delta \log \dfrac{I_M}{I_D}}{\delta \dfrac{1}{T}} = \frac{E_{DM}\, k_{DM}}{k_{DM}} - \frac{E_D\, k_D + E_{MD}\, k_{MD}}{k_D + k_{MD}} = 0. \tag{4}$$

(4) can be written

$$(E_{DM} - E_D)\, k_D = (E_{MD} - E_{DM})\, k_{MD}. \tag{5}$$

E_{DM} and E_{MD} are respectively the activation energies for excimer formation and dissociation.

$(E_{MD} - E_{DM})$ is equal to B, the binding energy of the excimer, which is always positive. Condition (5) thus implies that $(E_{DM} - E_D)$ also has a positive value.

The following conditions determine the shape of the curve.

1. In the low temperature region

$$\frac{\mathrm{d} \log \dfrac{I_M}{I_D}}{\mathrm{d} \dfrac{1}{T}} > 0. \tag{6}$$

Comparing (4) and (6):

$$(E_{DM} - E_D)\, k_D > (E_{MD} - E_{DM})\, k_{MD} \tag{7}$$

which also implies that $(E_{DM} - E_D)$ has a positive value. In the low temperature region, k_{MD} is smaller than k_D and a plot of log I_M/I_D as a function of $1/T$ gives $(E_D - E_{DM})$. If k_D and k_M are both independent of temperature (this condition is often satisfied at low temperature), an iso-emissive point is observed.

2. In the high temperature region

$$\frac{\mathrm{d} \log \dfrac{I_M}{I_D}}{\mathrm{d}\,\dfrac{1}{T}} < 0. \tag{8}$$

This implies that:

$$(E_{DM} - E_D)\, k_D < (E_{MD} - E_{DM})\, k_{MD}. \tag{9}$$

Equations (7) and (9) show that, going from the low to the high temperature region, k_{MD} increases faster than k_D in agreement with $E_{MD} > E_D$.

Equation (9) is valid even if $E_{DM} < E_D$; a steadily decreasing curve is then obtained instead of the usually observed U-shaped curve. It has been shown previously[5] that in the high temperature region k_D is negligible compared with k_{MD}. Since k_{FD} and k_{FM} are temperature independent, Eqn. (3) shows that, in this case, the slope of the linear portion of curve of Figs. 2 and 4 gives $E_{MD} - E_{DM} = \mathrm{B}$. If the set of conditions $k_{MD}, k_{DM} \gg k_M, k_D$ is satisfied, a photodynamic equilibrium is established[5] and an iso-emissive point is observed.

The emission spectrum of PVCa films is adequately described by the usual kinetic scheme. Normal and excimer fluorescence are observed over the whole temperature range. I_M and I_M/I_D vary with temperature, but there is no iso-emissive point. One minimum is observed for log I_M/I_D as a function of $1/T$. It corresponds to a temperature of about 293 K. In the low temperature range, excimers are formed and the slope of the linear portion of the curve gives $(E_D - E_{DM})$ since no isoemissive point is observed. Above 293 K, the excimer dissociates: I_M increases with temperature. The binding energy of the excimer is $4 \pm 0{\cdot}5$ kcal mole^{-1}. Values of the same order of magnitude have been reported in the literature for intermolecular excimer formation in low molecular weight compounds.[5] Comparison with the binding energy for excimer formation in bis-carbazolylpropane (which is the model compound of PVCa) is not possible since this compound has not been studied as a function of temperature.

As reported in the previous paper of this series,[1] the temperature dependence of the emission spectrum of PVN and PAcN films is quite different from that of PVCa. In the first two cases, normal fluorescence is never observed between 77 and 450 K.

The behaviour of PVCa solutions is rather exceptional: two minima are indeed observed (Fig. 4). The usual scheme[1] and Eqns. (4) and (5), which apply to systems in which one excimer is formed, cannot justify a curve with two minima, since equations (4) and (5) cannot be verified for three different values of $1/T$. If k_D and k_{MD} are both rate constant of the form $k = k_0 \mathrm{e}^{-E/RT}$, there is only one value of $1/T$ for which

the derivative (4) has a nul value. On the other hand, if k_D contains a temperature independent term as usually observed:[5]

$$k_D = k'_0 + k_0 \, e^{-E/RT}$$

the derivative can be zero at only two different temperatures. Neither of these possibilities agrees with the experimental results. These can be explained if one assumes that two different types of excimer can be formed.

The generalization of Eqn. (4) to the case of i excimers is:

$$\frac{\sum_i E_{DM}{}^i \, k_{DM}{}^i}{\sum_i k_{DM}{}^i} - \frac{\sum_i E_D{}^i \, k_D{}^i + \sum_i E_{DM}{}^i \, k_{DM}{}^i}{\sum_i k_D{}^i + \sum_i k_{MD}{}^i} = 0. \tag{8}$$

In the case of two excimers, Eqn. (8) can have a zero value for three different values of $1/T$ depending on the relative values of the various rate constants. If curve I_M/I_D (Fig. 4) is divided into four different temperature regions, the following hypotheses are reasonable. In region I at low temperature, only one excimer characterized by k_{MD}, k_{DM} and k_D is formed. The rate constants k'_{MD}, k'_{DM} and k'_D which characterizes the second excimer thus need not be considered. The usual condition $k_{MD} < k_D$ applies and, at the first minimum, Eqn. (5) is verified. In region II, dissociation of this first excimer is preponderant ($k_{MD} > k_D$) but k'_{DM} may eventually become appreciable. In regions III and IV, formation and dissociation of the second excimer respectively determine the shape of the curve.

These two successive excimers probably result from a change of conformation of the polymer chain. This conformational change would occur between 143 and 295 K. The binding energy of the second excimer (2·8 kcal mole^{-1}) can be deduced from Fig. 4. The linear portion of the curve in regions I, II and III cannot be interpreted in terms of activation energies owing to the complex kinetics prevailing in this temperature range. Such a conformational change with temperature is not unexpected for a rigid and bulky polymer chain and confirms an earlier suggestion that a low temperature transition occurs in stiff polymer chains.[6] The rigidity of the chain has been clearly demonstrated by the value of the steric factor σ. The steric factor σ is defined by

$$\sigma^2 = \frac{\overline{h_0^2}}{\overline{h_{0f}^2}}$$

where h_0 is the distance between chain-ends in the undisturbed state and (h_{0f}), the theoretical distance between chain-ends with completely free rotation around all C—C bonds.

σ was found to be 2·85 or 2·8 for PVCa[7,8] whereas it is 2·2 for polystyrene[9] and 1·6 for poly(ethylene).[9]

V. CONCLUSION

Normal and excimer fluorescence are both observed in PVCa films in the range 77–425 K while in the case of polyvinylnaphthalene and polyacenaphthylene, excimer fluorescence only is emitted.

In PVCa films, the usual U-shaped curve is obtained when log I_M/I_D is plotted against $1/T$. The binding energy of the excimer determined in the high temperature

region is 4 kcal mole^{-1}. The behaviour of PVCa solutions is quite different from that of polyvinylnaphthalene and polyacenaphthylene solutions. A curve with two minima corresponding to the formation and dissociation of two excimers is indeed observed for log I_M/I_D as a function of $1/T$. Each of those minima has been assigned to a different conformation of the rigid and bulky PVCa chain. This conformational change occurs between 143 and 295 K. The binding energy of the high temperature excimer has been determined above 295 K as 2·8 kcal mole^{-1}.

Acknowledgement—We are very grateful to the Fonds National de la Recherche Scientifique and to the Fonds de la Recherche Fondamentale Collective for financial support to the laboratory.

Thanks are also due to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture for a grant to one of us (M.P.).

REFERENCES

(1) C. David, M. Piens and G. Geuskens, *Europ. Polym. J.*, **8**, 1019 (1972).
(2) C. David, W. Demarteau and G. Geuskens, *Europ. Polym. J.* **6**, 537 (1970).
(3) P. C. Johnson and H. W. Offen, *J. chem. Phys.* **55**, 2945 (1971).
(4) W. Klöpffer. *J. chem. Phys.* **50**, 2337 (1969).
(5) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley (1969).
(6) J. Hughes and A. M. North, *Trans. Faraday Soc.* **62**, 1866 (1966).
(7) N. Kuwakara, S. Higashida, M. Nakata and M. Kaneko, *J. Polym. Sci.* **A2, 7**, 285 (1969).
(8) G. Sitaramajah and D. Jacobs, *Polymer* **11**, 165 (1970).
(9) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.* **3**, 196 (1963).

Résumé—Les solutions et les films de polyvinylcarbazole (PVCa) émettent de la fluorescence normale et de la fluorescence d'excimère entre 77 et 425 K. Les intensités absolues (I_M et I_D) et relatives (I_M/I_D), émises dépendent de la température. Une courbe en U est obtenue lorsque l'on porte en graphique log I_M/I_D en fonction de $1/T$ pour les films de polymère. En solution, deux minima correspondant à deux excimères différents sont observés. La formation et la dissociation des excimères du PVCa sous forme de films ou en solution ont été interprétées selon le schéma cinétique habituel. Les énergies de liaison de l'excimère, calculées dans le domaine des hautes températures, valent 4 et 2,8 kcal mole^{-1} respectivement dans les films et les solutions.

Sommario—Nel campo di temperatura tra 77 e 425 K, le soluzioni e pellicole di polivinilcarbazole (PVCa) emettono della fluorescenza normale e d'eccimero. Le intensità assolute (I_M e I_D) e relativa (I_M/I_D) dipendono fortemente dalla temperatura. Nel caso delle pellicole di polimero, mettendo log I_M/I_D in funzione di $1/T$, si ottiene la solita curva a forma di U. Nelle soluzioni, si osservono due minimi che corrispondono a due differenti eccimeri. La formazione e dissociazione di eccimeri di PVCa in pellicola e soluzione sono state interpretate secondo lo schema cinetico abituale. L'energie di legame per l'eccimero in pellicole e, alle alte temperature, per l'eccimero in soluzioni, sono rispettivamente di 4 e 2,8 kcal mole^{-1}.

Zusammenfassung—Filme und Lösungen von Polyvinylcarbazol (PVCa) emittieren zwischen 77 und 425 K normale und Excimer Fluoreszenz. Die emittierten absoluten (I_M und I_D) und relativen (I_M/I_D) Intensitäten sind stark temperaturabhängig. Im Fall von Polymerfilmen wird die übliche U-förmige Kurve für log I_M/I_D als Funktion von $1/T$ erhalten. In Lösung werden zwei Minima beobachtet, din zwei verschiedenen Excimeren entsprechen, Die Bildung und Dissoziation von PVCa Excimeren ie Filmen und Lösungen wurden nach dem gebräuchlichen kinetischen Schema gedeutet. Die Bindungsenergien für das Excimer in Filmen und für das Hochtemperatur-Excimer in Lösungen betragen jeweils 4 und 2,8 kcal Mol^{-1}.