Influence of polymeric media on the association of aromatic hydrocarbons

N. N. Barashkov*
Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75083-0688, USA

and T. V. Sakhno, R. N. Nurmukhametov and O. A. Khakhel
Karpov Institute of Physical Chemistry, Moscow 103064, Russia

Synchronous scanning over a range of excitation wavelengths and fluorescence measurements were used to study polystyrene, solid solutions of luminophores in poly(methyl methacrylate) (PMMA), and methyl methacrylate copolymers doped with pyrene, anthracene, and naphthalene. The complicated nature of the aggregation of aromatic hydrocarbons in solid polymers is revealed. The origin of their excimer-like fluorescence is also discussed.

(Keywords: fluorescence; synchronous scanning; excimer)

INTRODUCTION

The spectral properties of fluorescent polymers are important for many optical devices and instruments using such materials. Very often it is not the isolated molecules, but their associated species, that are responsible for the spectral-luminescence properties of coloured polymers. The so-called molecular excimers serve as such associates[1]. Excimers are dimers that are unstable in the ground state, with the complexes being formed only when the system is excited. Excimers dissociate to produce the molecular form upon their deactivation. The class of excimer-producing molecules is not strongly defined, but it comprises, in part, aromatic hydrocarbons with a flat molecular structure and some compounds containing heteroatoms.

Excimers are formed under various physico-chemical conditions in liquid solutions of monochromophoric molecules and in the gas and condensed phases, particularly in polymeric media[2]. The specific spectral manifestation of excimers is an emission band with an abnormally large Stokes shift (3000 to 5000 cm^{-1}). This arises with no qualitative changes in the absorption spectra of the systems being studied, which is evidence for the lack of aggregation in the ground state. Frequently, this pattern may be considered only as a first approximation. Some studies have already been carried out in which the excimer luminescence of a wide variety of systems (solutions, polymeric media, etc.) were studied. The results of these studies provide evidence of luminophore aggregation, i.e. the formation of complexes which are stable in their ground state and optically active in absorption[3]. As far as coloured polymeric systems are concerned, luminophore aggregation is of practical importance here. The use of organic glasses as

optically transparent media requires enhanced light transmission for materials of this class[4]. As we have demonstrated earlier for polymers of the excimer type (vinylpyrene copolymer with methyl methacrylate), the complexing of a luminescent additive may show up as a tail on the long-wavelength edge of the electronic absorption spectrum[5]. In order to extend the results of our studies to a wider variety of molecules we have now investigated the luminescent properties of polystyrene and polymeric systems containing pyrene, anthracene, and naphthalene.
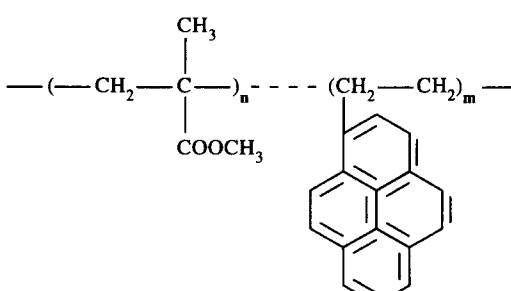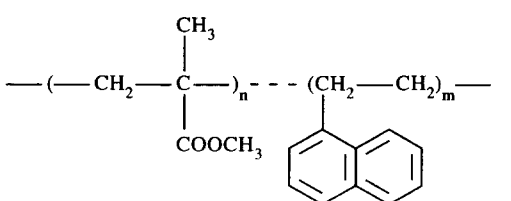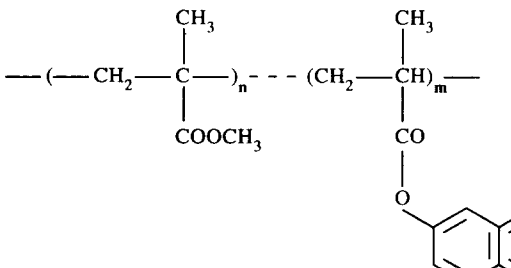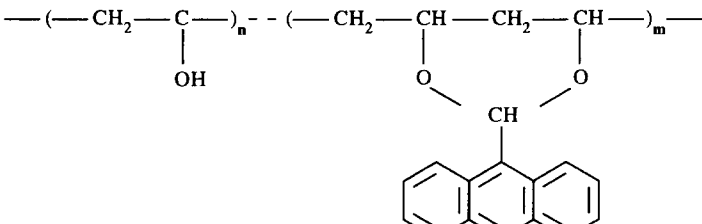
EXPERIMENTAL

The polymeric systems studied in this work are listed in *Table 1*. The luminophore was introduced into the polymeric matrix (samples 1–6), either at the synthesis stage according to the technique described in ref. 4, or by evaporating aqueous polymer–luminophore solutions (sample 7) at room temperature. The polystyrene films studied were prepared from optical-grade commercial polystyrene by evaporating the latter on to a quartz plate. Polymer 8 was prepared by the reaction of poly(vinyl alcohol) (PVA) with 9-anthraldehyde in a mixture (100 : 5 molar ratio) in N,N-dimethylacetamide in the presence of p-toluene sulfonic acid (5 wt% of PVA) at 100–140° C. Films (≈ 0.1 mm thick) obtained from aqueous solutions were dissolved in dichloroethane. Spectral-grade organic solvents were used without any additional purification. Polycrystalline pyrene was prepared from its saturated solution in benzene by slow evaporation for several days at room temperature.

Perkin-Elmer 554 and LOMO SDL-2 spectrometers were used to measure the spectra. For liquid solutions and powdered samples the spectra were taken in quartz cells (1–10 mm thick). Fluorescence was excited by

---
* To whom correspondence should be addressed

Table 1 Polymeric systems studied

#	System	
1	VPy-MMA copolymer	$-(-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_n---(CH_2-CH_2)_m-$
2	Py + PMMA solid solution	
3	Anthracene + PMMA solid solution	
4	Naphthalene + PMMA solid solution	
5	Vinyl naphthalene – MMA copolymer	$-(-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_n---(CH_2-CH_2)_m-$
6	NMA – MMA copolymer	$-(-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_n---(CH_2-\underset{\underset{CO}{|}}{\overset{\overset{CH_3}{|}}{CH}})_m-$
7	PySO$_3$H + PVA solid solution	
8	Anthracene – containing PVA	$-(-CH_2-\underset{\underset{OH}{|}}{C}-)_n--(-CH_2-CH-CH_2-CH-)_m-$
9	Polystyrene	

radiation incident at 90° with respect to the direction of recording. The surfaces of the flat cells and polymer samples were oriented at an angle of 60° between the excitation direction and directions normal to this. Measurements at 77 K were performed in a contact quartz Dewar vessel. The synchronously scanned spectra were taken either for coinciding wavelengths of excitation and fluorescence ($\lambda_{ex} = \lambda_{fl}$) or with monochromators adjusted at constant wavelength intervals of 10 nm ($\lambda_{fl} = \lambda_{ex} + 10$ nm). This was performed by recording the fluorescence signal while simultaneously scanning both λ_{ex} and λ_{fl}. The resulting intensity of the synchronously scanned spectra is a function of the intensity of a compound's excitation and fluorescence spectra and the extent to which these features overlap. By selecting a wavelength interval which approximately corresponds to the compound's Stoke's shift, spectral reduction to a single narrow band can be achieved[6,7]. The spectral wavelengths are indicated on the recording scale. To additionally reduce the intensity of scattered light in some cases when recording excitation and luminescence with synchronous scanning we installed normally oriented polariods in both channels.

RESULTS

Pyrene

The absorption and fluorescence spectra of solid solutions of pyrene in PMMA and of the vinylpyrene–methyl methacrylate copolymers are shown in *Figures 1* and *2*,
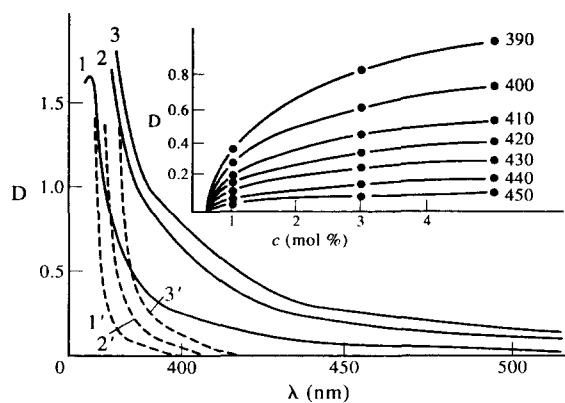
Figure 1 Absorption spectra of MMA–vinylpyrene copolymers (1, 2, 3) and solid solutions of pyrene in PMMA (1', 2', 3') with luminophore concentrations of 1.0 (1, 1'), 3.0 (2, 2'), and 5.0 (3, 3') mol% (all of the samples are in the form of 1 mm thick glassy films). The inset shows the concentration dependence of the optical density of the copolymer glasses at various wavelengths (indicated on the curves in nm)

resemblance of the absorption spectra of the above coloured glasses, there are some distinctions between them. In particular, the absorption spectra of the copolymers exhibit a weak band which is shifted toward lower energies with respect to the monomer absorption band. The optical density at these wavelengths for the copolymers as a function of the luminophore concentration is non-linear and is satisfactorily described by a square-root dependence, which is shown in the inset in *Figure 1*. Additional evidence in favour of the insignificant contribution of admixtures to this absorption is its sensitivity to such factors as orientation of the samples, which is manifested, in particular, by the disappearance of some of the fluorescence bands during stretching or dissolution of the films.

In our opinion, the most detailed information in these studies can be provided by measurements of the spectra when synchronously scanned over the excitation and fluorescence wavelengths (*Figure 2b*). As can be seen, the long-wavelength tail in the absorption of the copolymers shows several spectral centres, among which we can distinguish most clearly those with maxima at 470 and 500 nm. According to the commonly recognized terminology, the pyrene complexes fluorescing at 470 nm should be referred to as normal excimers, and the aggregates with the other luminescence maxima called

respectively. The identity of the vibrational structure of the molecular emission-spectrum component for these samples and the lack of any manifestation of unreacted vinylpyrene in either absorption or emission of the copolymer may indicate that the luminophore is incorporated in the polymer chain. Despite the close
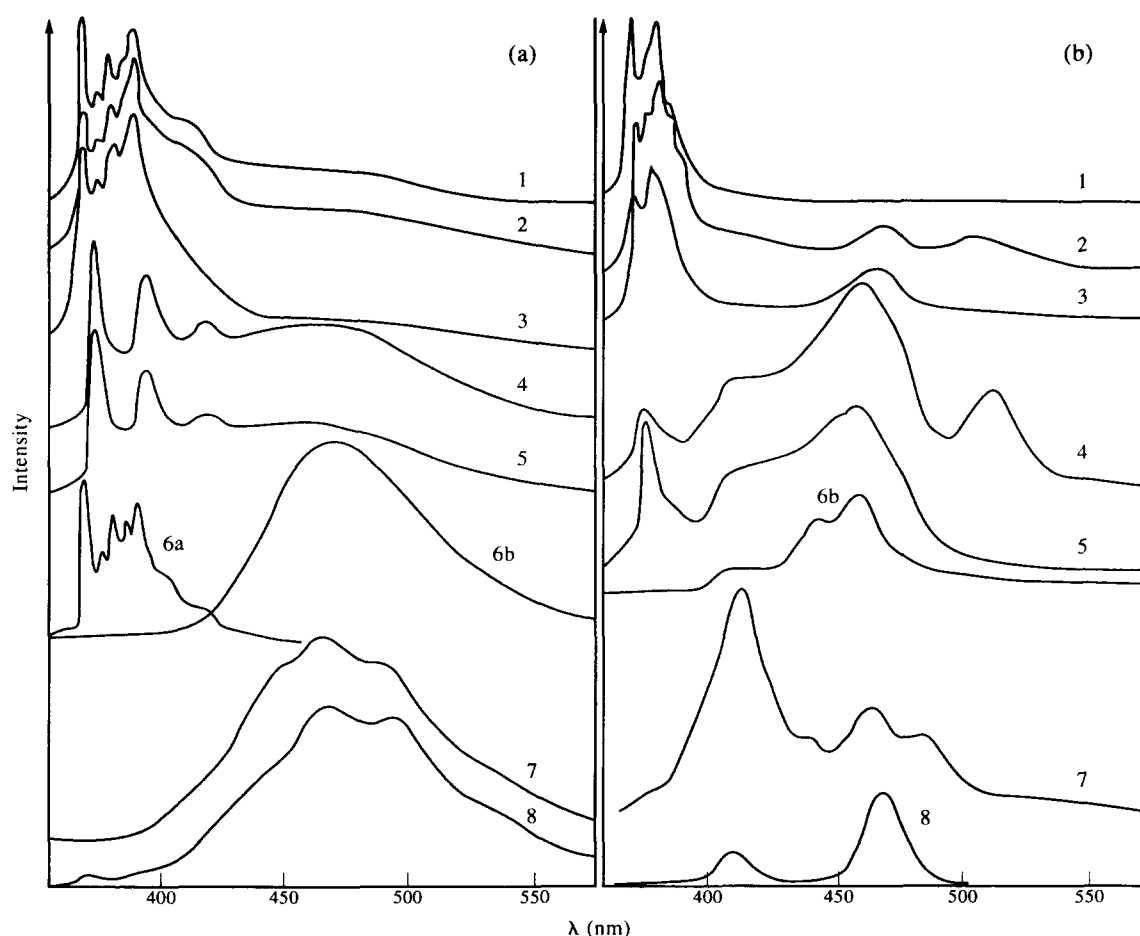
Figure 2 Fluorescence spectra at an excitation of 337 nm (a) and of synchronous scanning (b): (1) solid solution of pyrene in PMMA (5 mol%); (2) vinylpyrene (3 mol%)–MMA copolymer; (3) vinylpyrene (3 mol%)–MMA copolymer sample oriented by three- or four-fold stretching; (4) solid solution of 1-pyrene sulfonic acid in PVA (5×10^{-3} mol l^{-1}) dried in the dark; (6a) dilute (10^{-5} mol l^{-1}) and (6b) saturated solutions of pyrene in benzene; (7) original pyrene powder; (8) pyrene crystallized from a benzene solution (polycrystalline sample). All of the synchronous scanning spectra are taken with monochromators adjusted at wavelengths 10 nm apart, with spectra 6b, 7, and 8 being recorded in polarized light

secondary or dimer like excimers[3]. Spectrum 3 in *Figure 2b* relates to an experiment with oriented three- or four-fold stretching of the copolymer 1 sample. The lack in this spectrum of the band belonging to the centres responsible for the largest long-wavelength absorption is associated with their destruction and points to their aggregation nature. Dissolution of the copolymers with subsequent casting of the films leads to qualitatively similar results, and therefore we do not show their spectra here.

Fluorescence of the secondary excimers manifests itself in 'ordinary' copolymer spectra, although these are less clearly presented than in experiments with synchronous scanning. The undulation at $\sim 500\,nm$ (*Figure 2a*) is noteworthy. Generally, information about such phenomena can be inferred from an examination of the literature data, but as far as we know, the reasons for their existence have not been discussed as yet. Two similar components of the excimer band can be observed, e.g. in the emission spectra of the pyrene solution in cyclohexane [8]. These are most frequently cited in the literature as an example of excimer fluorescence; however, almost always these spectra are incorrectly presented.

Figure 3 presents a clearer pattern of the fluorescence spectra obtained for various aggregate states. The long-wavelength emission spectrum component is a super-position of several bands, which is demonstrated by specific undulations of the signal.

Figures 2 and *3* also display the spectra of pyrene power samples, benzene solutions of pyrene and 1-pyrene

sulfonic acid incorporated into PVA. Investigation of these systems enables us to follow the pyrene complexation under various conditions.

The spectra 7 in *Figure 2* were taken for the original pyrene powder. Along with the structured fluorescence pertaining to luminophore emission from the free-exciton state of pyrene single crystals (0–0 transition, $376\,nm^9$), in the long-wavelength part of the spectra we observed a pattern which is qualitatively similar to that recorded for the copolymer systems. Subsequent dissolution of the sample eliminates the excimer components, both in the fluorescence and synchronous scanning spectra (curve 6a in *Figure 2a*). However, we should suspect the absence of stable aggregates only in highly diluted samples. In concentrated benzene solutions association of pyrene in the ground state is clearly seen in the synchronous scanning spectra (curve 6b in *Figure 2b*).

In order to find the concentration limit for the detection of pyrene association by the synchronous scanning technique we studied solutions of this molecule in n-hexane at concentrations up to $10^{-2}\,mol\,l^{-1}$ (*Figure 4*). As can be seen, the spectra of highly diluted solutions (to $5 \times 10^{-3}\,mol\,l^{-1}$) exhibit molecular emission alone, although the normal fluorescence spectra contain the excimer band. In synchronous scanning spectra of more concentrated solutions the excimer component arises at 400–500 nm, which then is enhanced. Freezing the dilute solutions eliminates the excimer emission. However, in more concentrated matrices the excimer component persists (*Figure 4c*), and the component pertaining to the associates in the synchronous scanning spectrum becomes relatively more intense.

A similar aggregation pattern is also observed in solid
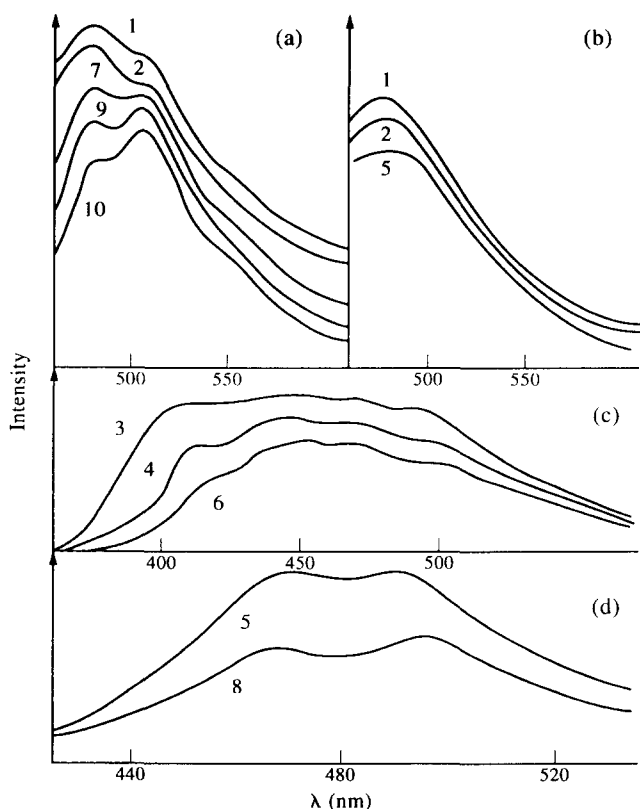
Figure 3 Fluorescence spectra of vinylpyrene (5 mol%)–MMA copolymers (a, b) and of saturated pyrene solutions in benzene (c, d) for excitation at various wavelengths: (1) 330; (2) 360; (3) 382; (4) 388; (5) 390; (6) 395; (7) 400; (8) 410; (9) 430; (10) 450 nm

Figure 4 Synchronous scanning spectra (1) and fluorescence spectra for an excitation at 337 nm (2) and for pyrene in n-hexane: (a) and (b) liquid solutions with concentrations of 10^{-4} and $10^{-2}\,mol\,l^{-1}$, respectively; (c) a frozen solution with a concentration of $10^{-2}\,mol\,l^{-1}$ at liquid nitrogen temperature

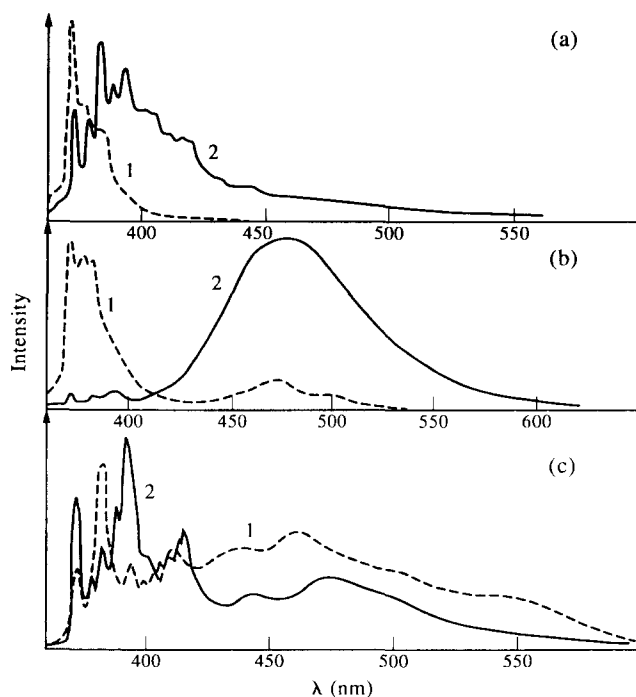solutions of 1-pyrene sulfonic acid in PVA (*Figure 2*). Complexation also depends on the luminophore concentration, e.g. PVA samples with a luminophore content below $5 \times 10^{-3}\,\text{mol}\,\text{l}^{-1}$ did not show detectable fluorescence in the synchronous scanning spectra within the 400–550 nm range. It is noteworthy that u.v. irradiation at the luminophore absorption band wavelength produces less energetic complexes; the component in spectrum 4 of *Figure 2b* with a maximum at 510 nm disappeared upon a repeat polymer dissolution.

Anthracene

Excimer emission of liquid solutions (a broad structureless band) is virtually undetectable in the ordinary spectra. The probability of formation of fluorescent complexes is low, and they are detected only in special experiments[10]. One of the reasons for this is the high chemical activity of the molecules: when the sandwich configuration of excited anthracene dimers is formed, anthracene was photodimerized to produce covalent bonds at the 9, 9', 10 and 10' positions[10]. Blocking of these positions with bulky substituents inhibits the photochemical processes, so that the data already available on excimers for various substituted anthracene derivatives are quite sufficient.

The fluorescence spectrum of an anthracene solid solution in PMMA is shown in *Figure 5a*. It features a well resolved vibrational structure inherent in isolated molecules; however, as the anthracene concentration in the matrix increases, the ratios of the vibrational band intensities change slightly with enhancement of the long-wavelength maxima. Two bands are recorded in the synchronous scanning spectra which have identical concentration dependences of their intensities; this may be an indication of associated species formation. The fluorescence spectra of the associates are shown in *Figure 5a* (curve 3).

We can distinguish a few more types of fluorescent associated species in the emission spectra of anthracene solid solutions (curve 4 in *Figure 2a*). These associates are weakly manifested in the synchronous scanning spectra. Formation of these centres in appreciable amounts is possible under different conditions of sample preparation, with the hydrophobicity of aromatic hydrocarbons being an effective factor here. For this reason, the experiments were conducted with the water-soluble copolymer 8, which is the product of interaction between PVA and 9-anthraldehyde. This latter compound does not fluoresce in polar solvents[4]: however, the anthracene nuclei emit intensively after the reaction with PVA, the long-wavelength part of the luminescence can be ascribed to the excimers. The luminescence and synchronous scanning spectra are displayed in *Figure 5b*. Along with the monomeric component, the scanning spectrum exhibits a broad band which is ascribed to the anthracene associates; complexes with maxima at 480 and 500 nm can be clearly distinguished in the spectrum. Generally, the nature of the bond between anthracene and the basic chain of the copolymer being considered rules out the possibility of any complexing of the neighbouring luminophore molecules in the chain. It is most likely that remote parts of the macromolecules or luminophores belonging to different chains form the aggregates. Thus, only the molecular-type luminescence centres are recorded when a polymer film is dissolved in water.
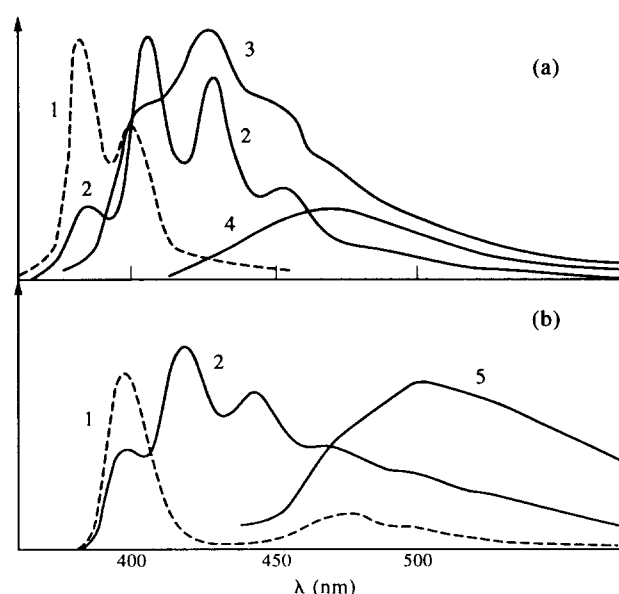

Figure 5 Synchronous scanning (1) and fluorescence (2–5) spectra of solid solutions of anthracene (2.0 mol%) in PMMA (a) and copolymer 8(b). The fluorescence spectra were excited at (2) 360, (3) 395, (4) 420, and (5) 430 nm, while the synchronous scanning spectra were recorded at $\lambda_{\text{rec}} = \lambda_{\text{excit}}$ (a) and $\lambda_{\text{rec}} = \lambda_{\text{excit}} + 10\,\text{nm}$ (b)

Naphthalene

Studies of naphthalene-containing polymers also demonstrate a complicated pattern of luminophore aggregation in the matrix. The spectra of samples 4 to 6 are displayed in *Figure 6*. The normal excimer fluorescence of naphthalene features a maximum at 390 nm[11]. This luminescence in the above spectra is less prominent than the fluorescence of the secondary excimers at ~ 350 nm. Emission of these aggregates is also clearly seen in the synchronous scanning spectra.

The spectra of copolymer 6 differ drastically from the other spectra (*Figure 6c*). Luminescence of these samples shows an intense band of the excimer type which is abnormally shifted to the red. The synchronous scanning (curve 1) reveals that this band is generated by three spectral centres with maxima at 415, 470 and 530 nm. The absorption spectrum of the copolymers is quite regular in this range and is represented by a weak, tail-type band. As far as we are aware, the position of the excimer fluorescence maximum in the luminescence spectrum of these glasses is the highest yet recorded naphthalene.

Polystyrene

The factors attenuating the u.v. and visible emission of polystyrene are diverse and have been analysed repeatedly in the literature[12,13]. However, association of chromophore groups in the polymer bulk has not been studied at all, and virtually no information is available on the optical activity of such aggregates in polystyrene. By analogy with other excimer-producing systems, one could expect a manifestation of the association at the long-wavelength edge of the polymer absorption spectrum. As can be seen in *Figure 7*, the associated species are responsible for the absorption band in the polystyrene spectrum up to 350 nm. The full set of spectral data provides evidence of several different types of associates. The different associates are identified more
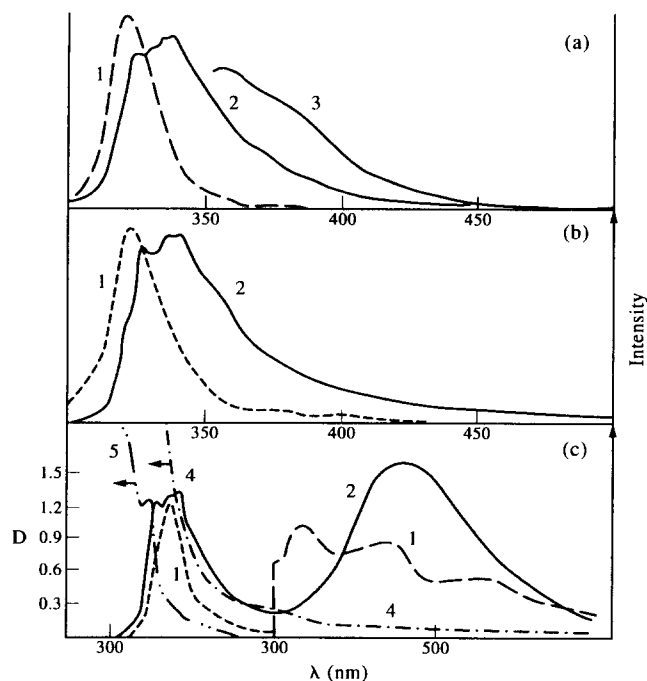
Figure 6 Synchronous scanning (1) and fluorescence (2, 3) spectra of a naphthalene solid solutions (2.0 mol%) in PMMA (a), 1-vinylnaphthalene (8.0 mol%)–MMA copolymer (b), and 2-naphthylmethyl methacrylate (20 mol%)–MMA copolymer (c). The fluorescence spectra were excited by light at (2) 254 and (3) 340 nm. Curves (4) and (5) relate to the absorption spectra of sample 6: (4) 1 mm glass plate; (5) its liquid solution. The synchronous scanning spectra in (a) and (b) are taken at $\lambda_{rec} = \lambda_{excit}$ and in (c) at $\lambda_{rec} = \lambda_{excit} + 10$ nm

clearly when the samples are scanned in polarized light with the monochromators adjusted at different wavelengths (see curve 4), which is apparently indicative of a substantial difference in the structure of the spectral centres.

DISCUSSION

Assignment of the long-wavelength absorption of systems with excimer-like luminescence to association of the molecules is, in our opinion, well substantiated by our experiments. In particular, this interpretation follows from the common spectral properties inherent
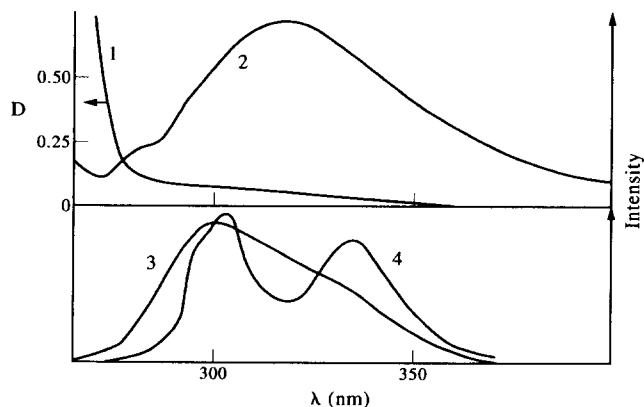

Figure 7 Absorption (1) and fluorescence (2) spectra of a polystyrene film excited at 254 nm. Curves (3) and (4) are the synchronous scanning spectra taken at identical wavelengths and with the monochromator wavelengths differing by 10 nm, respectively

in various systems containing different luminophore groups. It is unlikely that more than two molecules are involved in aggregate formation. This is inferred from the characteristic emission spectra which have the shape and fluorescence frequency intervals almost identical with those traditionally ascribed to excimers. Moreover, in systems with polymer chains the probability of formation of configurations consisting of three or more adjacent molecules is negligibly small compared to that of the formation of dimeric centres.

In spite of some common properties, the systems discussed above exhibit their own individual features. Note that the spectral peculiarities depend primarily on the conditions of preparation of the samples studied[2]. Our samples of anthracene solid solutions demonstrate the formation of associates of the physical-dimer type. The 0–0 transition (402 nm) band of these dimers is close to that of the sandwich dimers studied in ref. 14; however, fluorescence of the sandwich dimers better resembles that of spectrum 4 in *Figure 5a*. As should be expected, the excited sandwich dimers relax to the excimer geometry, which accounts for the significant bathochromic shift of its fluorescence. In our polymers, the anthracene excimer configuration in the excited state is not the most stable one because of the lack of the intense long-wavelength luminescence. Anthracene solid solutions in PMMA do not undergo photodimerization either, because irradiation of the samples with a mercury lamp for 6 h changes insignificantly the ratio of the intensity maxima for dimers and monomers in the synchronous scanning spectra.

The major discrepancy between anthracene solid solutions and pyrene solid solutions in PMMA is that the prominent long-wavelength band inherent in the excimers is absent in the emission spectra of the former. We emphasize this fact because the other features of the spectra are similar. The lower excited state of anthracene is represented by the intense ^1La_a transition, and this is associated with the manifestation of dimerization at the long-wavelength edge of the absorption spectrum of the molecules. The transition from the lower state is forbidden for pyrene, and therefore the synchronous scanning spectra do not show any intermolecular interactions, which are evidently insignificant. The pyrene solid solutions in PMMA (similar to the anthracene solutions) form weakly bound associates capable of relaxing to the excimer geometry. The concentration of dimers with a higher interaction energy is very low in solid solutions of both pyrene and anthracene in PMMA, and this is why the long-wavelength absorption component is missing in the spectra.

The chemical bond between pyrene and polymer apparently favours the formation of "tight" complexes upon hydrocarbon chain looping. It is known[15] that the number of contact sites in a macromolecule grows proportionally to N, where N is the number of segments in the chain. The concentration dependence of the optical density of copolymer glasses (see inset in *Figure 1*) conforms to this relationship. Therefore, we may infer that associates of any type start forming at a luminophore concentration of ~ 0.6 mol%. This apparently reflects the fact that the luminophore additive is statistically distributed in macromolecules when its concentration is below the above indicated value, which drastically reduces the dimerization efficiency.

Until recently, many authors have believed that excimer-producing molecules do not form aggregates in liquid organic solvents. It should be noted, however, that some fairly recent publications doubt this assertion[16]. We can draw from our studies more definite conclusions concerning the dimerization processes taking place under these conditions.

As is seen from spectrum 7 in *Figure 2b*, synchronous scanning of the original pyrene powder reveals aggregates, among which those complexes with their maximum at ~ 500 nm feature in the long-wavelength absorption. These complexes dissociate in benzene solutions and are absent in polycrystalline pyrene samples prepared by deposition from benzene solution. At the same time, the composition of the stable centres in the ground state, even at the lowest pyrene concentrations in n-hexane, at which the synchronous scanning spectra still exhibit the long-wavelength component, corresponds to that of the powder before dissolution. The structure of the aggregates formed obviously depends on the nature of the solvent. At the same time, the excimer components in the luminescence spectra of pyrene solutions in benzene and n-hexane which have been excited by radiation in the molecular-absorption-wavelength range have almost identical maximum positions and band half-widths, i.e. all of the conceivable structures of the excited state are equilibrated. Curiously, the band at 525 nm in the spectra of solid pyrene, as well as that of the copolymer samples, is evidence of an additional form of excimer centres (whose structure, stable in the ground state, is detected in frozen n-hexane solutions (*Figure 4c*)). As can be seen, the spectra indicate the presence of several more types of associated centres in the matrix near the 0–0 transition band of the isolated molecules (380–420 nm). Luminescence of these aggregates is characterized by prominent vibrational maxima. Investigations of pyrene in Shpol'skii's matrices[17] revealed up to ten such centre types (according to the data on the 0–0 band position), depending on the luminophore concentration and cooling conditions.

Thus, in liquid pyrene solutions, both molecular diffusion and direct excitation of stable molecular aggregates are responsible for the excimer fluorescence. The synchronous scanning technique enables us to detect intermolecular complexes possessing a high interaction energy in the ground state that is almost in resonance with the pumping radiation. Bearing in mind that in solutions the major fraction of dimers absorbing light at 400 or 450 nm (the lower level) relax to form low-energy states, we may assume that the efficiency of excimer formation by the latter mechanism is higher than it has been commonly believed. Quantitative estimations for various solvents may be a subject of special investigations.

The positions of the band maximum in the fluorescence spectrum of normal pyrene excimers, both in its solutions and in other systems, can be assigned to particular structures recorded in the synchronous scanning spectra. This is, to a lesser extent, true for polystyrene, because the maximum of its excimer component is a result of the superposition of several bands. However, the position of the luminescence maximum in this case is traditional. We did not observe such a bathochromic shift of the excimer-band maximum for naphthalene in the luminescence spectrum of

copolymer. Investigations of 1-naphthylmethyl methacrylate carried out in refs 18–20 show that the structure with the luminescence intensity maximum at 400 nm (or at shorter wavelengths) is the best equilibrated in the excited state. Another surprising peculiarity of the samples tested in this work is that even in spectra of the condensed naphthalene phase, i.e. crystals deformed by pressure[21], the fluorescence of the normal excimer is dominating. In principle, the abnormal shift of the excimer luminescence band observed for copolymer 6 can be accounted for in two different ways. The first mechanism is effective migration of the electronic excitation energy to rare aggregates possessing the lowest energy, and the second is relaxation of the more abundant excimer-producing centres to the geometry of the low-energy aggregates, which does not preclude energy transfer from the monomer to them. Which of these alternative mechanism is realized remains unclear, however, the specificity of interactions between the luminophore and matrix is responsible for formation of associates of the types revealed in the spectra, both in the ground and, particularly, in the excited state. An analysis of the literature data demonstrates that these complexes are also formed in other polymer systems. Thus, luminescence of the low-energy aggregates shows up as a band at 465 nm in the fluorescence spectra of polyvinyl naphthalene solutions in methyltetrahydrofuran[22]; this has not been discussed, however, by the authors of the paper.

The problems associated with the formation of diverse excimeric species have arisen during the past 10 to 15 years, and have still not yet been solved properly. The structure of excimers comprising various molecules has been discussed, invoking predominantly two sterically different aggregates[23–25], whereas the studies performed in this work (more comprehensive for pyrene) suggest the existence of at least six types of pyrene associates that exhibit excimer properties in the spectra. Interestingly, the frequency ranges, within which the associated forms are recorded, are almost independent of the medium, although, depending on the experimental conditions, the particular aggregates (stable in the ground and/or excited states) may show up in the spectra or disappear completely. The external factor mostly governs the composition of the spectral centres. In other words, any excimer-producing system can be considered as an ensemble of certain dimeric states with population of the levels governed by the environment medium. The spectral parameters (band maxima and half-widths, fluorescence lifetimes at each wavelength, etc.) are defined by the equilibrium composition attained in the system.

REFERENCES

1 Gordon, M. and Ware, W. R. (Eds) 'The Exciplex', Academic, New York, 1975
2 Guillet, J. 'Polymer Photophysics and Photochemistry', Cambridge University Press, Cambridge, 1985
3 Barashkov, N. N., Sakhno, T.V., Khakhel, O. A. and Nurmukhametov, R. N. *Russ. Chem. Rev.* (*Engl. Transl.*) 1993, **62**, 579
4 Barashkov, N. N. and Gunder, O. A. 'Fluorescent Polymers', Ellis Horwood, Chichester, 1994
5 Khakhel, O. A., Nurmukhametov, R. N., Nekrasov, V. V., Sakhno, T. V., Barashkov, N.N. and Muravjova, T. M. *Russ. J. Phys. Chem.* (*Engl. Trans.*) 1992, **66**, 1133

6   Tromberg, B. J., Burke, T. G., Doroshow, J. H. and Berns, M. W. *Proc. SPIE—Int. Soc. Opt. Eng.* 1989, **1054**, 152

7   Lloyd, J. B. F. and Evett, I. W. *Anal. Chem.* 1977, **49**, 1711

8   Birks, J. B. and Christophorou, L. S. *Spectrochim. Acta* 1963, **19**, 401

9   Matsui, A. and Hishimura, H. *J. Phys. Soc. Jpn* 1980, **49**, 659

10   Cherkasov, A. S. *Rep. State Opt. Inst.* 1983, **52**, 3 (in Russian)

11   Briks, J. B. and Christophorou, L. G. *Proc. Soc. London A.* 1963, **227**, 571

12   Kaino, T., Fujiki, N. and Jinguji, K. *Rev. Electrical Commun. Lab.* 1984, **32**, 478

13   Sakhno, T. V., Senchishin, V. G, and Barashkov, N. N. *J. Appl. Spectrosc.* 1991, **54**, 338

14   Candross, E. A. and Fergusson, J. *J. Chem. Phys.* 1966 **45**, 3554

15   Grosberg, A. Yu. and Khokhlov, A. R. 'Statistical Physics of Macromolecules', Nauka, Moskcow, 1989 (in Russian)

16   Andriessen, R., Ameloot, M., Boens, N. and De Schryver, F. C. *J. Phys. Chem.* 1992, **96**, 314

17   Klimova, L. P., Nersesova, G.I. and Glyadkovskii, V.I. *Izv. Akad. Nauk SSSR, Ser. Fiz.* 1975, **39**, 1910 (in Russian)

18   Holden, D. A., Wang, P. Y.-K. and Guillet, J. E. *Macromolecules* 1980, **13**, 295

19   Merle-Aubbry, L., Holden, D. A., Merle, Y. and Guillet, J. E. *Macromolecules* 1980, **13**, 1138

20   Guillet, J. E. and Rendall, W. A. *Macromolecules* 1986, **19**, 224

21   Jorther, J. *Pure Appl. Chem.* 1971, **27**, 289

22   David, S., Pients, M. and Geuskens, G. *Eur. Polym. J.* 1972, **8**, 1019

23   Zachariasse, K. A. and Duveneck, G. *J. Am. Chem. Soc.* 1987, **109**, 3790

24   Fox, M. A. and Brit, P. F. *Macromolecules* 1990, **23**, 4533

25   Lopez-Arbeloa, F., Van der Auraer, M. and De Schryver, F. C. *J. Photochem. Photobiol.* 1988, **A45**, 295