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Intramolecular Mobility and Intermolecular Interactions in Polymer Molecules Containing Photoactive Groups

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ABSTRACT: Solutions of polymers with side chains carrying anthracene residues exhibit excimer emission which becomes more pronounced with an increasing conformational mobility of the side chains as characterized by polarized luminescence. The dependence of the excimer luminescence on the dynamic flexibility of the side chains is much stronger when the conformational changes in the chain backbone are hindered by the formation of an interpolymer complex.

Introduction

As shown by Volkenstein in the 1970s,[1,2] a higher conformational mobility of functional groups attached to a macromolecule correlates with a higher reaction rate of these groups of the macromolecules in solution. This has been confirmed experimentally for reactions between the functional groups of natural or synthetic polymers and low molecular weight reagents,[3-5] for intermacromolecular reactions in the formation of protein–polymer conjugates,[6] and for the photodimerization of anthracene groups in molecules of anthracene-containing polymers.[7]

In several papers[3-7] the effect of intramolecular mobility of macromolecules in solution on the reaction of appended functional groups was discussed but the effect of the conformational lability of side chains bearing these functional groups has not been investigated. Recently, data were obtained showing the influence of the length of the chains to which the interacting groups are attached on electronic interactions in macromolecules.[8]

In the study of conformational-dynamic properties of polymer molecules in solutions excimer formation is widely used.[9] The present paper is concerned with excimer formation in solutions of anthracene-containing (photoactive groups PhG) polymers involving interactions between PhG located in side chains differing in their conformational labilities characterized quantitatively by polarized luminescence. This conformational lability may be studied when the mobility of the main polymer chain is hindered by inserting the polymer chain into an interpolymer complex formed by cooperative hydrogen bonding.[10,11]

Experimental Section

Polymers with covalently bonded anthracene-containing groups chosen for investigation are listed in Table 1. They were obtained either by the free-radical copolymerization of the main monomer with an anthracene-containing monomer or by the reaction of functional groups of (co)polymers with appropriate anthracene-containing reagents.

The following anthracene-containing monomers were used: *N*-(9-anthrylmethyl)methacrylamide[12] (Table 1, polymer III) and *N*-(9-anthrylmethyl)carbamate of 2-oxyethyl methacrylate[13] (Table 1, polymers V and VII).

To attach anthracene groups to amino- and hydroxyl- or carboxyl-containing (co)polymers, 9-anthrylmethyl isocyanate[13] (Table 1, polymers II and IV) and 9-anthryldiazomethane[10] (Table 1, polymer VI) were used. Polymer II was obtained by reacting the amino groups of vinylpyrrolidone–allylamine copolymer with 9-anthrylmethyl isocyanate.[13] Polymer I was obtained by reacting the amino groups of vinylpyrrolidone–allylamine copolymer with 9-anthraldehyde followed by reduction of the aldimine bonds formed with the aid of sodium borohydride.

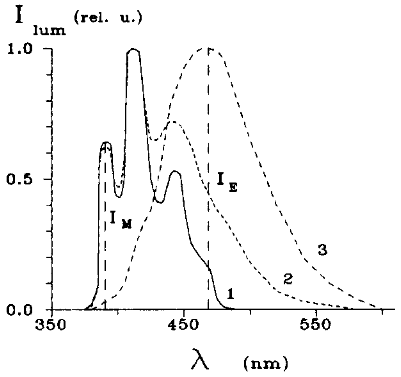

Figure 1. Luminescence spectra of aqueous (5% DMF) solutions of VAL–VA–PhG copolymers (Table 1, IV). N_{PhG} = 0.2 (1), 3 (2), and 19 (3). C_{pol} = 0.01%, 25 °C, λ_{ex} = 365 nm.

The molecular weights of the polymers were determined from intrinsic viscosity measurements in methanol (PMAA, 26 °C; PVP, 30 °C; PPMA, 25 °C), chloroform (PVAL–VA, 25 °C), and toluene (PMMA, 25 °C) using the Mark–Kuhn–Staudinger equations.[14]

The thermodynamic flexibility of PhG-bearing side chains was varied by increasing the length of the side chains and changing the chemical structure of the spacer between the anthracene group and the main polymer chain. It was characterized by the value of $1/P$ as a function of T/η (where P is the polarization of luminescence, T is the temperature, and η is the viscosity) extrapolated to $T/\eta = 0$ and designated by $1/P_0'$. The value of $1/P_0'$ is related to the amplitude of the high-frequency motion of the luminescent group PhG.[10,15]

To determine $1/P_0'$, polymers with a low PhG content were used (not more than 1 PhG per macromolecule).

The values P and $1/P_0'$ were also used to determine the value of the relaxation time τ_{IMM} characterizing the intramolecular mobility of the macromolecule in solution:[10,15]

$$\tau_{IMM} = 3\tau_f \frac{1/P_0' + 1/3}{1/P - 1/P_0'}$$

in which τ_f is the lifetime of the excited state measured by phase fluorimetry.[10]

Luminescence spectra were recorded on a spectrofluorimeter[10] using an excitation wavelength of 365 nm.

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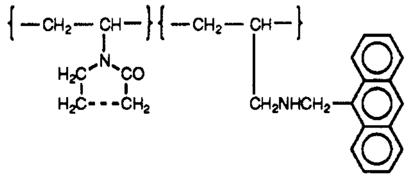
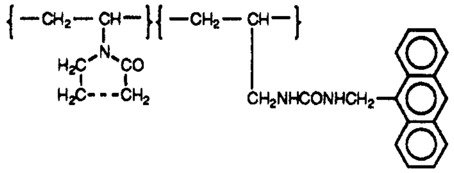
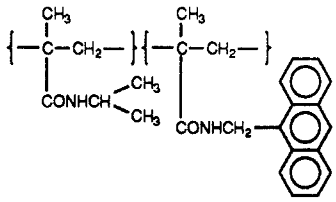
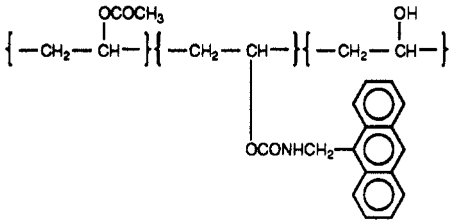
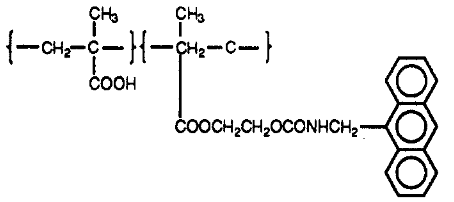
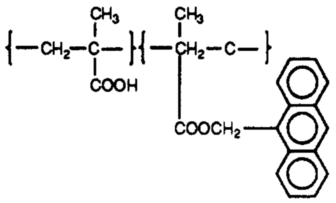
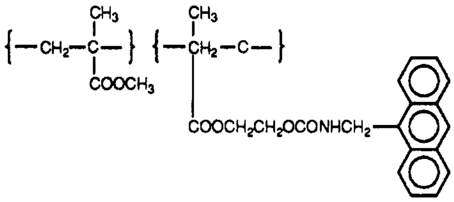
Table 1. Chemical Structures of PhG-Containing Polymers

polymer		structure of main polymer unit and unit with anthracene-containing photoactive group (PhG)	N_{PhG}[a]	n_{PhG}[b]
poly(vinylpyrrolidone) PVP-PhG $\mathrm{MW}_\eta = 25000$	I		6	2.4
	II		6	2.4
polyisopropylmethacrylamide PPMA-PhG $\mathrm{MW}_\eta = 50000$	III		6	1.6
copolymer of vinyl alcohol and vinyl acetate P(VAl-VA)-PhG (85-15) mol % $\mathrm{MW}_\eta = 10000$	IV		0.2 3 19	0.1 1.4 8.3
poly(methacrylic acid) PMAA-PhG $\mathrm{MW}_\eta = 10000$	V		5 9	4 7.7
	VI		9	7.7
poly(methyl methacrylate) PMMA-PhG $\mathrm{MW}_\eta = 20000$	VII		15	7.7

[a] N_{PhG} = number of PhG units per macromolecule. [b] n_{PhG} = number of PhG units per 100 monomer units (mol %).

The fraction of excimer emission of PhG, θ_{E}, was evaluated from changes in the luminescence spectra by

$$\theta_{\mathrm{E}} = \frac{(I_{\mathrm{E}}/I_{\mathrm{M}}) - (I_{\mathrm{E}}/I_{\mathrm{M}})_0}{(I_{\mathrm{E}}/I_{\mathrm{M}})_{\mathrm{E}} - (I_{\mathrm{E}}/I_{\mathrm{M}})_0}$$

where I_{E} and I_{M} are the intensities of the luminescence at the maximum of the excimer band (λ_{E} = 460-470 nm) and at the emission maximum of anthracene (λ_{M} = 390 nm). $(I_{\mathrm{E}}/I_{\mathrm{M}})_0$, $(I_{\mathrm{E}}/I_{\mathrm{M}})_{\mathrm{E}}$, and $(I_{\mathrm{E}}/I_{\mathrm{M}})$ are the ratios of these intensities in the luminescence spectra of polymer solutions in the absence of excimer emission, with pure excimer emission, and in the luminescence spectrum of the solution of the polymer investigated, respectively (Figure 1).

Excimer formation was studied for various PhG contents in the molecule, $N_{\mathrm{PhG}} \simeq$ 5-15, or for various PhG contents per 100 monomeric units, $n_{\mathrm{PhG}} \simeq$ 1-8. The PhG content has been evaluated by measuring UV spectra of polymer organic solutions (DMF or methanol) at λ = 386 nm, assuming a characteristic molar absorption coefficient for anthracene residues equal to $\epsilon = 10^4$ L·mol^{-1}·cm^{-1}.

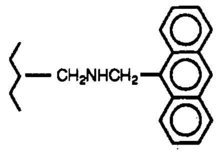
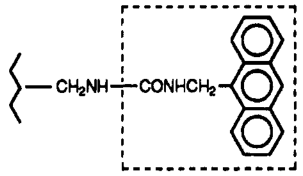
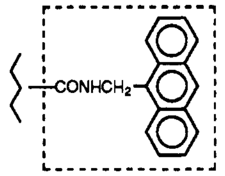
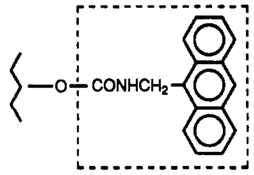
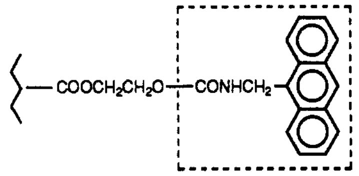
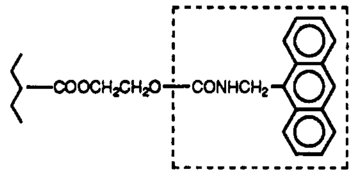
To prepare aqueous solutions, PhG-containing polymers were first dissolved in an organic solvent (methanol or DMF). Water was added to a small amount of polymer solution in an organic solvent. The concentration of organic solvent in the final solution

Table 2. Chemical Structures of the Polymers, Molecular Weights M_η and Compositions of the Polymer Mixtures in Solution Used for Interpolymer Complexes [(Polymer I–PhG) – Polymer II] Preparation[a]

	polymer I[b]	$M_\eta \times 10^{-3}$	polymer II	$M_\eta \times 10^{-3}$	β	solvent
I	PVP–PhG	25	PMAA	40–360	1	H_2O (5% DMF)
II	PVP–PhG	25	PMAA	40–360	1	H_2O (5% DMF)
III	PPMA–PhG	50	PMAA	40–360	1	H_2O (5% DMF)
IV	P(VAl–VA)–PhG	10	PMAA	40–360	1	H_2O (5% DMF)
V-1	PMAA–PhG	10	PVC[c]	20	5	CH_3OH
V-2	PMAA–PhG	10	PEG[d]	40	2	H_2O (2% CH_3OH)

[a] C_{pol} = 0.01%, 25 °C. β = [polymer II]/[polymer I–PhG] (in mol of monomer residues). [b] Polymer structure is given in Table 1. [c] PVC = poly(vinylcaprolactam). [d] PEG = poly(ethylene glycol).

Table 3. Structure of PhG-Bearing Side Chains in the Molecules of PhG-Containing Polymers, Conformational-Dynamic Characteristics of the Macromolecules, and the Fraction of Excimer Emission of PhG (θ_E) in the Luminescence Spectra of Solutions of Free PhG-Containing Polymers (P) and the Same Polymers Included in Interpolymer Complexes (IPC)

			τ_{IMM} (ns)		$1/P_0'$		θ_E (%)	
IPC	structure of PhG-bearing side chain	N_{PhG}	P	IPC	P	IPC	P	IPC
I		6	17	700	9		0	0
II		6	17	700	11	8	0.5	3
III		6	23	500	8	7.5	0	0
IV		3	14	150	12	10	1.0	10
V-1		9	13	1000	15		3	19
V-2		5	90	300		12	15	23

was 5%. Investigations were carried out in dilute solutions at a polymer content in solution of 0.01%.

The excimer yield was measured for free PhG-containing polymers and for the same polymers included into interpolymer complexes formed by cooperative hydrogen bonding. The interpolymer complexes investigated are listed in Table 2.

Results and Discussion

In the analysis of luminescence spectra of solutions of PhG-containing polymers, the fraction of the excimer emission in the spectra, θ_E, was determined. It was found that increasing the thermodynamic flexibility of the PhG-bearing side chains (parameter $1/P_0'$) leads to a slightly higher excimer emission (Table 3, II, III and IV, V).

The difference in the fraction of excimer emission, θ_E, of polymers being compared (Table 3, II and III on the one hand and IV and V on the other) becomes more pronounced when these polymers are included into an interpolymer complex (IPC) formed by cooperative hydrogen bonding. The IPC formation was accompanied by a decrease in the mobility of the main chain, with the relaxation times, τ_{IMM}, increasing by 1 or 2 orders of magnitude.

It was found that under these conditions even a slight increase in the length of the PhG-bearing side chains (by insertion of a CH_2NH group) influences the fraction of excimer emission in the luminescence spectra of the PhG-

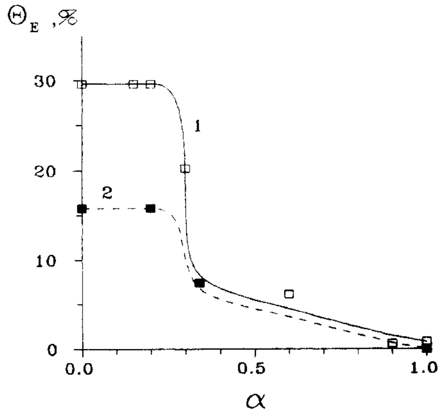


Figure 2. Fraction of excimer emission θ_E of aqueous (2% methanol) PMAA-PhG solutions for PhG in long side chains (Table 1, V; N_{PhG} = 9) (1) and for PhG in short side chains (Table 1, VI; N_{PhG} = 9) (2) vs α, the degree of PMAA neutralization. C_{PMAA} = 0.01%, 25 °C.

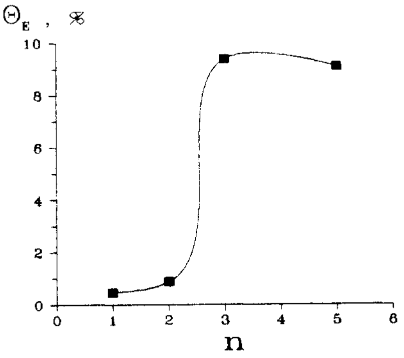


Figure 3. Change in the fraction of excimer emission θ_E of PMAA-PhG solutions (Table 1, V; N_{PhG} = 5) in $H(CH_2)_nOH$ solutions. C_{PMAA} = 0.01%, 25 °C.

containing polymer (see Table 3). The inclusion of macromolecules in an IPC with a tertiary structure (of the globular type) not only leads to the hindrance of motion of the main chain but also causes a contraction of the coil and a decrease in the inter-PhG distance.[16] However, a decreasing distance between PhG groups in short side chains ($1/P_0'$ = 8–9) does not lead to an increase in excimer emission (Table 3), whereas it provides favorable conditions for increasing θ_E for PhG in slightly longer side chains from 0–3% to 10% (cf. I, III, and IV, Table 3). A further increase in side chain length ($1/P_0'$ = 11–12) enhances the fraction of excimer emission, θ_E, to 19–23% (see Table 3).

These data show that excimer emission in polymers depends on the conformational lability of PhG-bearing side chains when the motions of the main chain were hindered. These results imply that the introduction of PhG into longer side chains with higher conformational lability should increase the sensitivity of excimer formation to conformational transformations of macromolecules in solution in which the distance between PhG-bearing side chains decreases.

To check this assumption, PhG-containing polymers V, VI, and VII (Table 1) were used. The changes in the luminescence spectra of an aqueous solution of polymers V and VI (PMAA) containing PhG in long and in short side chains were analyzed when the chain expanded during the ionization of the carboxyl groups[10] (Figure 2). These changes were also analyzed for polymer V (PMAA) solution in a series of alcohols (Figure 3) as a function of the solvent power of the medium characterized by the reduced viscosity (η_{sp}/C) of PMAA solutions, which changed from 1.6 dL/g in methanol to 0.5 dL/g in isopropyl alcohol. The fraction of excimer emission correlates with the reduced viscosity of the polymer solution. A good correlation was detected between θ_E and changes in the intramolecular structure of PMAA, which led to changes in intramolecular mobility (τ_{IMM})[10] and to changes in volume of the macromolecular coil as $\tau_{IMM} \simeq 1/[\eta]$.[10]

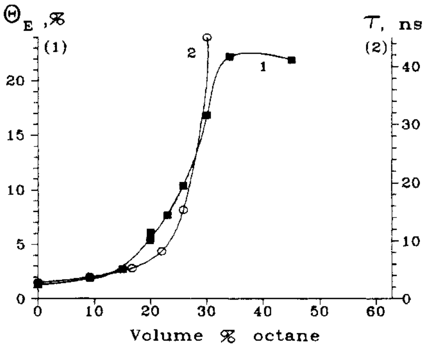


Figure 4. Fraction of the excimer emission θ_E of solutions of PhG-containing PMMA (Table 1, VII; N_{PhG} = 15) (1) and intramolecular relaxation times τ_{IMM} of macromolecules (2) in toluene–octane mixtures. C_{PMMA} = 0.01%, 25 °C. Curve 2 is from ref 10.

The hydrophobic attraction that can occur between aromatic groups in aqueous solutions[17-19] is absent in organic solvents. Nevertheless the electronic interactions between the photoactive anthrylmethyl carbamate oxyethyl methacrylate groups are conformation sensitive not only in aqueous polymer solutions but also in polymer solutions in organic solvents. This is indicated not only by the data obtained for PMAA in different alcohols (Figure 3) but also by those for PMMA in toluene–octane mixtures with different compositions (Figure 4). When octane, a precipitant, is added to toluene, the PMMA coil shrinks (τ_{IMM} increases[10]) and the fraction of excimer emission increases (Figure 4). A good correlation was observed between θ_E and changes in nanosecond relaxation processes or the changes in volume of the macromolecular coil as $\tau_{IMM} \simeq 1/[\eta]$.[10]

Conclusions

We show that with increasing conformational mobility of PhG-bearing side chains, the excimer emission becomes sensitive to conformational transformations of macromolecules and may be used to study structural changes in polymer molecules in solution. The conformational lability of side chains which bear functional photoactive groups plays just as an important a role in electronic interactions as the intramolecular mobility of the main chain in chemical reactions with the participation of reactive polymer groups.

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References and Notes

(1) Volkenstein, M. V. *Vestn. Akad. Nauk SSSR, Ser. Biol.* **1971**, *6*, 805.
(2) Volkenstein, M. V. *Vestn. Akad. Nauk SSSR* **1982**, *10*, 56.
(3) Krakovyak, M. G.; Anufrieva, E. V.; Ananieva, T. D.; Lushchik, V. B.; Shelekhov, N. S.; Skorokhodov, S. S. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1975**, *39*, 2354.
(4) Krakovyak, M. G.; Anufrieva, E. V.; Lushchik, V. B.; Gromova, R. A. *Vysokomol. Soedin., Ser. B* **1978**, *B20*, 131.
(5) Anufrieva, E. V.; Krakovyak, M. G.; Kuznetsova, N. P.; Goodkin, L. R.; Pautov, V. D. *Vysokomol. Soedin., Ser. B* **1978**, *B20*, 129.

(6) Anufrieva, E. V.; Pautov, V. D.; Krakovyak, M. G.; Ananieva, T. D.; Lushchik, V. B. *Vysokomol. Soedin., Ser. A* **1989**, *A31*, 100.
(7) Anufrieva, E. V.; Tcherkasskaya, O. V.; Lushchik, V. B.; Krakovyak, M. G. *Vysokomol. Soedin., Ser. A* **1992**, *A34*, 29.
(8) Morawetz, H. *Bull. Soc. Chim. Belg.* **1990**, *99, No. 11-12*, 869.
(9) Morawetz, H. *J. Fluores.* **1989**, *43*, 59.
(10) Anufrieva, E. V.; Gotlib, Yu. Ya *Adv. Polym. Sci.* **1981**, *40*, 1. Anufrieva, E. V.; Lushchik, V. B.; Nekrassova, T. N.; Pautov, V. D.; Sychova, E. A.; Tcherkasskaya, O. V.; Sheveleva, T. V. *J. Appl. Spectrosc.* **1987**, *46*, 931.
(11) Litmanovich, A. A.; Papisov, I. M.; Kabanov, V. A. *Eur. Polym. J.* **1981**, *17*, 981.
(12) Anufrieva, E. V.; Pautov, V. D.; Lushchik, V. B.; Mirzakhidov, H. A.; Musaev, U. N.; Krakovyak, M. G. *Vysokomol. Soedin., Ser. B* **1989**, *B31*, 772.
(13) Krakovyak, M. G.; Lushchik, V. B.; Sycheva, E. A.; Anufrieva, E. V. *Vysokomol. Soedin., Ser. B* **1986**, *B28*, 289.
(14) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; John Wiley and Sons: New York, 1975. Chantore, O.; Juaita, M.; Trossarelli, L. *Makromol. Chem.* **1979**, *180*, 969.
(15) Anufrieva, E. V. *Pure Appl. Chem.* **1982**, *54*, 533.
(16) Tcherkasskaya, O. V.; Anufrieva, E. V.; Krakovyak, M. G.; Ananieva, T. D.; Lushchik, V. B. *Vysokomol. Soedin., Ser. A* **1992**, *A34*, 90.
(17) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.
(18) Morishima, Y.; Tominaga, Y.; Nomura, Sh.; Kamachi, M.; Okada, T. *J. Phys. Chem.* **1992**, *96*, 1990.
(19) Duhamel, J.; Yekta, Ah.; Zhong, H. Y.; Winnik, M. A. *Macromolecules* **1992**, *25*, 7024.

Author-Supplied Registry No. PMAA, 25087-26-7; PMMA, 9011-14-7; P(VAL–VA), 25213-24-5; PVP, 9003-39-8; PEG, 25322-68-3; water, 7732-18-5; methanol, 67-56-1; DMF, 68-12-2.