Fluorescence of Solutions of Mixed Donor- and Acceptor-Labeled Polymers

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ABSTRACT: Solutions containing mixtures of carbazole- and anthracene-labeled methyl methacrylate–methacrylic acid copolymers were studied by viscosity and reflectance fluorescence. The ratio of anthracene and carbazole fluorescence intensities, I_A/I_C, increased with solution concentration in the same manner in different solvents and for unneutralized and neutralized polymers. Identical results were also obtained for solutions in which the chromophores were not attached to polymers. These and other experimental data as well as theoretical considerations suggest that *radiative* rather than *nonradiative* energy transfer is dominant and that the use of fluorescence measurements on solutions of donor- and acceptor-labeled polymers for the estimation of the critical concentration for chain overlap may not be reliable.

Introduction

The viscometric behavior of ionomers in solvents of low polarity has been interpreted[2] as indicating that the mutual attraction of ion-pairs appended to the polymer chains is intramolecular in dilute solutions, leading to a chain contraction, but becomes intermolecular at higher ionomer concentrations, producing the strikingly high viscosity of such systems. Previous work in this laboratory[3] showed that the association between anionic and cationic polymers labeled with donor and acceptor fluorophores may be followed by an increase in nonradiative energy transfer (NET),[4] and this suggested to us that the transition from intramolecular to intermolecular ion-pair association might also be reflected in an increase of NET in a solution containing donor- and acceptor-labeled ionomers.

Although our study was initially designed to demonstrate a behavior characteristic of ionomer solutions, the results had a much broader significance. We found that the fluorescence behavior of solutions containing polymers labeled with donor and acceptor fluorophores at label concentrations similar to those used in a previous study[5] is identical with that of solutions in which these labels are unattached to polymers. Thus, the fluorescence data do not reflect polymer chain overlap.

Results and Discussion

The viscometric behavior of solutions containing unneutralized or neutralized mixtures of equal weights of two methyl methacrylate terpolymers, one with 3.4 mol % methacrylic acid and 0.13 mol % *N*-carbazolylethyl methacrylate (CEM), the other with 3.1 mol % methacrylic acid and 0.13 mol % 9-anthrylmethyl methacrylate (AMM), is represented in Figure 1. In dioxane solution, neutralization of the terpolymer leads to the behavior first reported by Lundberg and Phillips,[2] i.e., a reduction in the viscosity at low solution concentrations, due to an intramolecular association of ion pairs, and a rapid viscosity increase in the concentration range where intermolecular ion-pair association becomes important. In ethylene glycol monoethyl ether ("ethylcellosolve", EC), a poor solvent for the unneutralized polymer,[6] the solution viscosity for the unneutralized terpolymer is much lower; when the terpolymer is neutralized, hydroxyls of CE solvate the ion pairs, and there is no evidence for a strong intermolecular interaction at higher solution concentrations. At high dilution, the reduced viscosity is seen to increase due to the mutual repulsion of the anionic groups, as is typical of polyelectrolytes.[2]

The fluorescence data, characterized by I_A/I_C, the ratio of the emission intensities of the anthracene at 413 nm and the carbazole at 360 nm, are plotted in Figure 2. They reveal no significant difference in the I_A/I_C between the unneutralized terpolymer in dioxane and in EC and no change in this ratio in dioxane solution when the donor- and acceptor-labeled terpolymers are neutralized. More significant still, the same result is obtained for a solution containing the free monomers, CEM and AMM, in place of the labeled polymers. This result shows that I_A/I_C in the solutions containing the labeled polymers is the same as in a solution where the fluorophores are distributed at random, and we interpret this finding as indicating that I_A/I_C is determined by radiative energy transfer (RET) rather than by NET. It is then not surprising that I_A/I_C for the mixed donor- and acceptor-labeled ionomers in dioxane shows no evidence for the transition from the intramolecular to the intermolecular ion-pair association.

The conclusion that I_A/I_C reflects radiative rather than nonradiative energy transfer is supported by two additional observations. (a) When the CEM and AMM monomers or the fluorophore-labeled terpolymers were incorporated into a poly(methyl methacrylate) film, the I_A/I_C increased much less than when the reflectance fluorescence was measured in solutions of the same fluorophore concentration (Figure 3). This is the expected behavior of RET, which depends on the pathlength of the emitted beam in the sample, whereas NET is independent of this factor. (b) The excited lifetime of CEM in dioxane solutions containing equal concentrations of CEM and AMM was measured[7] as 9.7, 10.3, and 9.8 ns for 0.4×10^{-4}, 1.5×10^{-4}, and 3×10^{-4} M concentrations of each chromophore; the absence of a shortening of the excited lifetime of the donor accompanying its reduced emission intensity is an unambiguous test of RET.

Theoretical considerations also support this conclusion. The efficiency of NET for randomly distributed donors and acceptors is given by[8]

$$\text{Eff.} = \pi^{1/2} \exp(x^2)[1 - \text{erf}\,(x)] \qquad x = (R_0/7.66)^3 c \qquad (1)$$

where R_0 is the characteristic distance (in Å) for Eff. = 0.5,[4] and c is the acceptor molarity. For the CEM–AMM donor–acceptor pair, R_0 = 28 Å,[9] so that at a solution concentration of 0.015 g/mL at which the viscosity of the ionomer solution in dioxane indicates incipient overlap of the polymer coils, the efficiency of NET would be less than 1%, well below the detection limit.

The present results call for a reexamination of some earlier reports in which the effect of RET was not considered. It is now clear that RET must have contributed significantly to the fluorescence behavior of solutions containing a naphthalene-labeled polycation and an anthracene-labeled polyanion studied by Nagata and Morawetz.[3] Yet, that study was concerned with polymer complex formation below the critical chain overlap con-

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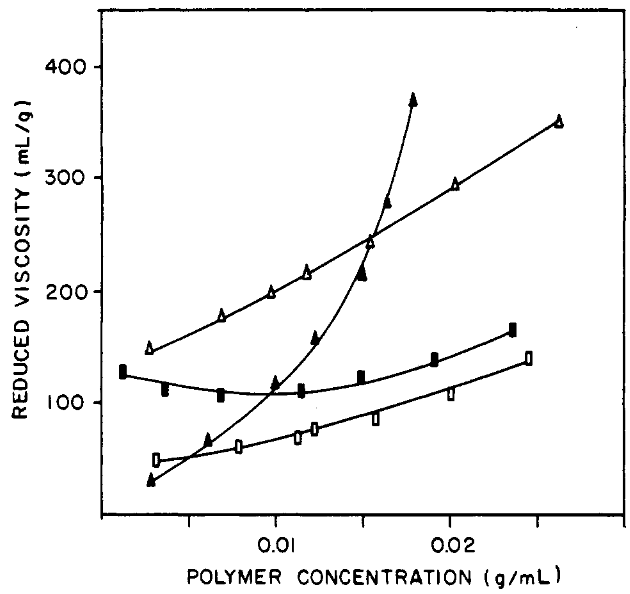

Figure 1. Solution viscosity of mixed terpolymers. Unneutralized in dioxane (△); neutralized in dioxane (▲); unneutralized in EC (□); neutralized in EC (■).

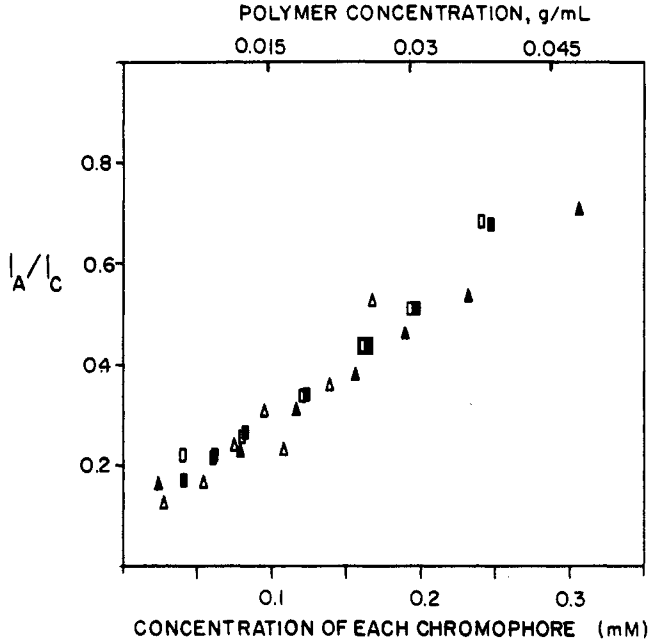

Figure 2. Fluorescence intensity ratio I_A/I_C of mixed terpolymers, unneutralized in dioxane (■), neutralized in dioxane (△), and unneutralized in EC (□). Values of I_A/I_C for mixtures of CEM and AMM in dioxane (▲).

centration, c^*,[10] and complexation of donor- and acceptor-labeled polymers was undoubtedly accompanied by an increase in NET, as evidenced by the decrease in energy transfer on addition of simple electrolytes, which would lead to a dissociation of the polycation–polyanion complex.

A more serious question is raised concerning the use of I_A/I_C by Torkelson and Gilbert[5] in solutions of a mixture of anthracene- and carbazole-labeled polystyrene to estimate c^*. Their label concentrations were even lower than ours, and both our experimental data and the theoretical argument given above suggest that their emission spectra reflected RET, which would not be sensitive to chain overlap. The relation given in eq 1 shows that with the use of the carbazole–anthracene donor–acceptor pair much higher fluorescent label concentrations would have to be used to obtain significant (e.g., 10%) NET at polymer concentrations corresponding to incipient chain overlap.

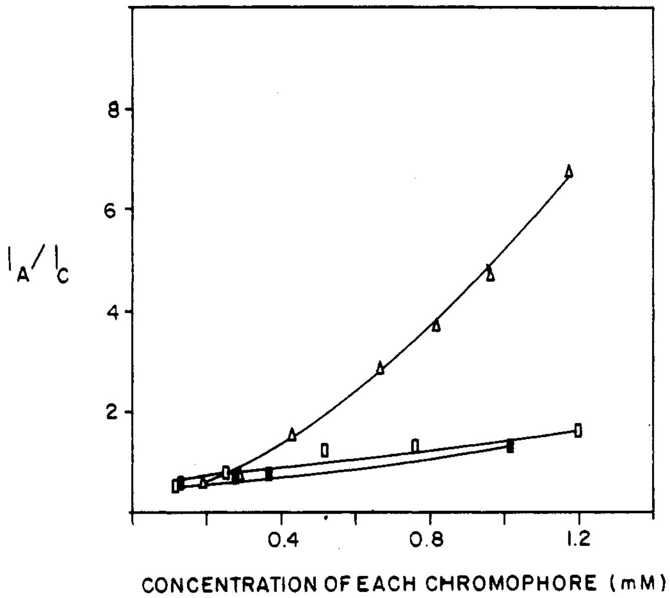

Figure 3. Fluorescence intensity ratio I_A/I_C for CEM and AMM mixtures in dioxane solution (△) and in a poly(methyl methacrylate) (PMM) film (□). Values of I_A/I_C for the mixed terpolymers in PMM film (■).

It should be noted that the transition from an intramolecular to an intermolecular ion-pair association, which we have failed to demonstrate by energy transfer, has recently been beautifully confirmed by another fluorescence phenomenon: Granville et al.[11] quaternized α,ω-bis(dimethylamino)polystyrene either with 3-(1-pyrenyl)-1-bromopropane or with 1-bromoethane. In dilute solutions containing only polystyrene with ion-pair end groups containing pyrene residues, intramolecular ion-pair association led to strong pyrene excimer emission. However, on addition of polystyrene whose ion-pair end groups did not contain pyrene, intermolecular ion-pair association reduced the pyrene excimer emission intensity.

Finally, we should consider the implication of the present results on the characterization of polymer chain overlap in solid blends of donor- and acceptor-labeled polymers.[8,12-16] In such systems, although RET may not be negligible, NET makes undoubtedly an important contribution to energy transfer. This is proved by three types of previous experiments: (a) Freeze-dried solutions of donor- and acceptor-labeled polymer blends have emission spectra depending on the nature of the original solvent and the concentration of the solution from which they were derived.[14] (b) The unfolding of collapsed polymer molecules, doubly labeled with donors and acceptors, into an unlabeled polymer matrix, may be followed by a change in the emission spectrum.[15] (c) Films cast from a blend of donor- and acceptor-labeled polymers have emission spectra reflecting the dependence of the polymer compatibility on the casting solvent.[16] On the other hand, if the contribution of RET to the energy transfer is not negligible, an interpretation of the relative donor and acceptor fluorescence intensity from labeled polymer blends in terms of the size of the phase domains[13] may not be justified.

Experimental Section

The fluorescent monomers CEM and AMM were prepared as previously described.[9] Terpolymers of methyl methacrylate, methacrylic acid, and CEM or AMM were prepared using ABIN initiator at 60 °C, keeping the conversion below 20%. They were precipitated from dioxane into methanol and from acetone into hexane and vacuum dried. The acid content was determined by titration with methanolic sodium methoxide using phenolphthalein as the end-point indicator. The CEM and AMM content was obtained by UV absorbence.[9] Intrinsic viscosities in acetone at 25 °C were 65 mL/g for the carbazole-labeled terpolymer and 66 mL/g for the anthracene-labeled terpolymer. The poly(methyl methacrylate) used for the casting of films containing CEM and AMM or the mixed labeled terpolymers had $[\eta] = 54$ mL/g.

The neutralization of the mixed CEM- and AMM-labeled terpolymers was carried out in a 1:5 mixture of dioxane and methanol, followed by precipitation into hexane and vacuum drying.

Films were cast from a 8% dioxane solution on glass plates. After 24-h evaporation, the films were vacuum dried for 24 h at room temperature and for 24 h at 45 °C. The film thickness ranged from 0.03 to 0.05 mm.

Solutions of monomers were prepared shortly before measurement. The dissolution of the neutralized terpolymers required several hours of stirring at 60 °C.

Emission spectra in the reflectance mode were recorded on a Perkin-Elmer MPF 44B fluorescence spectrometer. An excitation wavelength of 296 nm was used, and the emission intensities of the anthracene acceptor and carbazole donor were read at 413 and 360 nm, respectively.

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Registry No. PMM, 9011-14-7; (AMM)(methacrylic acid)(methyl methacrylate) (copolymer), 118400-65-0; (CEM)(methacrylic acid)(methyl methacrylate) (copolymer), 118400-66-1.

References and Notes

(1) On a leave of absence from the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.
(2) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *20*, 1143. Hara, M.; Lee, A. H.; Wu, J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1407.
(3) Nagata, I.; Morawetz, H. *Macromolecules* **1981**, *14*, 87.
(4) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(5) Torkelson, J. M.; Gilbert, S. R. *Macromolecules* **1987**, *20*, 1860.
(6) Horský, J.; Petrus, V.; Bohdanecký, M. *Polym. Bull.* **1987**, *17*, 551.
(7) C. Pham Van Cang, private communication.
(8) Berlman, I. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973; p 29.
(9) Amrani, F.; Hung, J.-M.; Morawetz, H. Macromolecules **1980**, *13*, 649.
(10) Daoud, M., et al. *Macromolecules* **1975**, *8*, 804.
(11) Granville, M.; Jérôme, R. J.; Teyssié, P. *Macromolecules* **1988**, *21*, 2894.
(12) Albert, B., et al. *Macromolecules* **1985**, *18*, 388; *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2577.
(13) Mikeš, F.; Morawetz, H.; Dennis, K. S. *Macromolecules* **1984**, *17*, 60.
(14) Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428.
(15) Liu, C. Y.; Morawetz, H. *Macromolecules* **1988**, *21*, 515.
(16) Morawetz, H. *Science* **1988**, *240*, 172.

Laser Desorption Mass Spectrometry of Polysilanes

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ABSTRACT: Laser ablation of a variety of polysilanes at 308 nm using fluences of 150–250 mJ/cm^2 per pulse, well above the photoablation threshold, is a photothermal process and yields products identical with those obtained in vacuum pyrolysis with a CO$_2$ laser. Unsaturated hydrocarbon products characteristic of the side chains have been identified unequivocally. Silicon-containing products have not been identified individually, and it is proposed that they are a mixture of cyclic carbosilanes, mostly containing no more than two or three silicon atoms linked to each other. A reaction mechanism for the ablation process is proposed and involves no previously unknown reaction steps. The results demonstrate that laser-desorption mass spectrometry is a good analytical tool for the identification of side chains in this class of polymers and suggest that laser-desorption gas chromatography or even simple pyrolysis gas chromatography will be useful. Due to the high volatility of the hydrocarbons, the presence of even quite long side chains on the polymer backbone need not be a source of much concern in practical applications of the photoablation process.

Introduction

High molecular weight polysilanes were probably first prepared over 60 years ago[1] but because of their insoluble and intractable nature elicited little scientific interest. The recent synthesis of soluble derivatives has changed the situation dramatically and led to several proposed applications.[2]

The discovery of rapid ablation of neat solid polysilanes with UV laser light suggested their potential utility as self-developing photoresists.[3] Further interest in this application[4-6] as well as others, such as the use of laser photoablation of polysilanes for optical storage and for their analytical characterization, has prompted the present study. We had two primary objectives:

(i) A probing of the mechanism of polysilane volatilization with 308-nm laser radiation, from the photoablation threshold to higher fluences. The main factor of interest presently is the chemical nature of the ablated materials. The interesting issue of the relative importance of photochemical and photothermal contributions to the process[7-9] will be treated separately.[10]

(ii) An assessment of the value of laser desorption mass spectrometry (LDMS), secondary ion mass spectrometry (SIMS), and fast atom bombardment mass spectrometry (FAB) for the structural characterization of polysilanes.

A brief report of an LDMS investigation of the copolymer of dimethylsilylene and cyclohexylmethylsilylene under conditions of low fluence at shorter wavelengths (248