# A Study of the Aggregation and Deaggregation in the Solution of Copolymer of 2-Vinylnaphthalene with Methyl Methacrylate by Intercoil Excimer Fluorescence

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ABSTRACT: The intermolecular excimer fluorescence was employed as a probe of the phase separation in the poly(2-vinylnaphthalene-*co*-MMA)/THF–MeOH system. The turbidity point has been located by the solvent dependence of $I_e/I_m$ and found to be independent of solution concentration in the dilute regime. The kinetic processes of deaggregation and aggregation of macromolecule coils as a function of solvent were followed by a stopped-flow apparatus and a diode array fluorescence spectrophotometer. It has been found that the excimer to monomer fluorescence ratio ($I_e/I_m$) is a function of polymer–polymer interaction. The experimental results show that the disappearance of the turbid phase in a good solvent has the character of first-order kinetics. The kinetic constant has been measured to be 0.37, 0.15, and 0.13 $s^{-1}$ for the final volume fraction of methanol in the final solvent mixture of 0.25, 0.42, and 0.47, respectively. The aggregation of coils in a poor solvent is a slower process that depends on coil diffusion. Stirring can speed up the phase separation efficiently.

## Introduction

It has been recognized for a number of years that the ratio of excimer to monomer fluorescence ($I_e/I_m$) in naphthalene-containing polymers is very dependent on solvent (and/or coil density).[1–4] The general observation is that a poor solvent enhances the excimer fluorescence at the expense of the monomer component. This observation is rationalized as follows: for a poor solvent, the coil density is increased such that naphthalene–naphthalene separations are decreased, which in turn leads to a higher density of excimer-forming sites. Furthermore, a high chromophore density may enhance electronic energy migration, with a concomitent increase in excimer fluorescence via trapping.

The results presented in this paper were obtained from our initial experiments using time-resolved (ca. 25 ms)[2] fluorescence spectroscopy of rapidly mixed polymer solutions. These experiments have the general objective of elucidating the time dependence of intra- and interpolymer interactions as a function of solvent-induced coil changes. The polymer system we have studied is a random copolymer of 2-vinylnaphthalene and methyl methacrylate. We find that (1) the rate at which $I_e/I_m$ changes in going from a poor solvent to a good solvent is not the same as the reverse process and (2) the changes of $I_e/I_m$ in going from a good solvent to a poor solvent have several distinct time scales, including a very slow step in which polymer aggregation is occurring. There exists older work that describes the nonequality of association and dissociation rates of macromolecular aggregation.[6,7]

We find very little literature that deals with these issues, especially using very sensitive fluorescence techniques. The only directly relevant report that we are aware of is the study of dansyl-labeled poly(methacrylic acid) by Bednar et al.[8] The dansyl probe is environmentally sensitive, and its fluorescence intensity was found to have a biphasic time dependence following a pH jump. Part of this time dependence was quite slow and is similar to the "intermediate" time range behavior of our polymer–solvent studies. Bednar et al. ascribed these changes to intracoil conformational changes that were surprisingly slow. These authors did not suggest that there was any interpolymer effect on their results, and based on the time dependence they report, this seems reasonable.

We believe that time-resolved spectroscopic techniques coupled with stopped-flow methods can provide a useful insight into a variety of polymer properties that are ordinarily studied only under equilibrium conditions. In the present case, it is clear that the $I_e/I_m$ ratio responds not only to isolated coil properties but also to aggregation. It would not be possible to make this distinction using standard steady-state fluorescence.

## Experimental Section

1. **Instruments and Fluorescence Measurement.** A SPEX FLUOROG 2 fluorescence spectrophotometer with a 150-W xenon lamp, a SPEX 1680 model 0.22-m spectrometer as excitation monochromator, a SPEX 1681 0.22-m spectrometer as the emission monochromator, and a diode array detector, Tracor Northern 6100 series, were employed to collect the steady-state and time-resolved spectra in the polymer system. Recording of the spectra and analysis of data were carried out on a Tracor Northern 6500 controller/analyzer which can be governed by an outside starting trigger. A homemade, hand-operated syringe stopped-flow apparatus (see Figure 1) was used to perform kinetic fluorescence measurements. It is composed of two solution syringes, three reservoir syringes, a Teflon mixer, a quartz cell with 2-mm diameter, and a photodiode trigger generator which produces a start trigger into the Tracor Northern 6500 at the beginning of a mixing injection. The mixing effect of it has been checked by mixing a dilute aqueous solution of fluorescein with water. It takes about 30 ms to approach uniform mixing after stopping the flow. Presumably this is a function of mixing jet design and the rate at which the syringes are emptied.

The steady-state and time-resolved emission spectra were measured in normal, square quartz cell at front face geometry and in the flow cell at right-angle geometry, respectively. An excitation wavelength of 278 nm was used for all emission spectra. The slit width was selected to be 2.5 and 0.5 mm for excitation and emission monochromator, respectively. An exposure time of 0.05 s was used, and background subtraction was automatically carried out in recording the emission spectrum. The final emission spectrum is the average of 4 or 20 scans. The wavelength of emission spectra was calibrated by a low-pressure mercury lamp. The integrated intensities from 422.4 to 474.6 nm and from 314.8 to 338.7 nm were taken as the excimer and monomer band fluorescence intensity in the polymer system, respectively.

2. **Polymer and Solvents.** The synthesis of the 2-vinyl random copolymer with methyl methacrylate (60% 2-vinylnaphthalene) has been published elsewhere.[9] The molecular weight was determined to be about $1.0 \times 10^4$ on a Waters HPLC with four $\mu$-Styragel columns ($10^2$, $10^3$, $10^4$, and $10^5$ Å) by using

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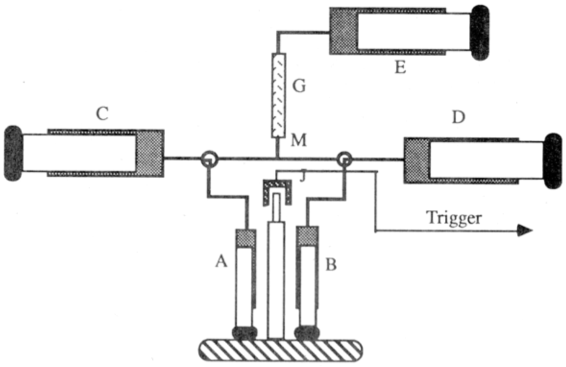

**Figure 1.** Schematic diagram of a homemade stopped-flow apparatus. A and B, injection syringes; C–E, reservoir syringes; G, round flow cell; H, syringe driver; J, photodiode trigger generator; M, Teflon mixer.

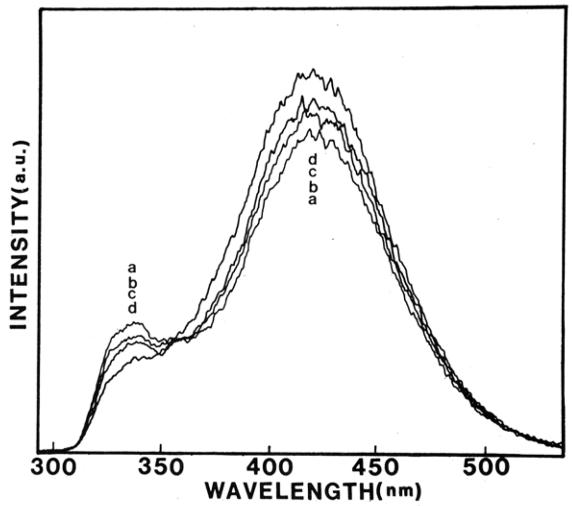

**Figure 2.** Emission spectra of poly(2-vinylnaphthalene-*co*-MMA) in mixing solvents containing (a) 0%, (b) 40%, (c) 50%, and (d) 60% methanol.

monodisperse polystyrene samples as standards.

THF of HPLC grade and methanol of spectrophotometric grade (both from Aldrich) were used as the good solvent and nonsolvent, respectively, and were mixed in different ratios to obtain a series of good-to-poor solvents for the polymer.

The homogeneous and turbid solutions of the polymer used in this work were prepared within 1–1.5 h of the measurement of the emission spectra.

## Results

**1. Intra- and Intercoil Excimer Interaction and the Determination of the Turbid Point in Poly(2VN-*co*-MMA)/THF–MeOH.** Figure 2 shows the emission spectra for the copolymer solution in a series of mixed solvents with a different ratio of methanol to THF. As is obvious from Figure 2, the emission intensity of monomer is decreasing and that of the excimer is increasing with the fraction of nonsolvent, methanol. The intensity ratio of excimer-to-monomer emission ($I_e/I_m$) changes systematically with solvent mixture (see Figure 3). This ratio changes slope drastically at the turbidity point. In the single-phase region, the solution is uniform and the $I_e/I_m$ ratio slowly increases with methanol fraction. Because the solution is so dilute, there is no interaction between different coils.[10] Thus, the change in the $I_e/I_m$ ratio can be understood as the result of the shrinkage of isolated coils and the concomitant increase in intracoil excimer interaction between nonadjacent chromophores. In the dual-phase region, phase separation occurs and the solution becomes turbid. The large increase in $I_e/I_m$ must be the result of the new concentrated phase and enhancement of intercoil excimer interaction. The volume fraction of methanol at the intersection of the straight lines corresponds to the turbidity point of the solution (47.3 vol %). It was found that the turbidity point is almost the same (within experiment error) for a polymer concentration of 0.05 and 0.275 mg/mL.

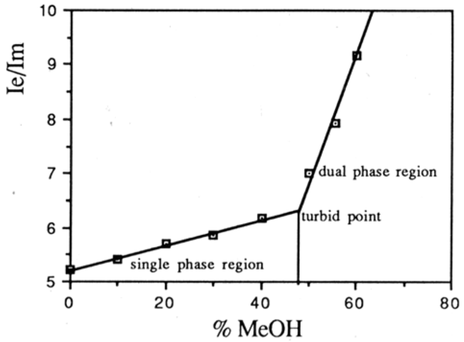

**Figure 3.** Solvent dependence of $I_e/I_m$ for poly(2-vinylnaphthalene-*co*-MMA)/THF–MeOH ($c$ = 0.055 g/L).

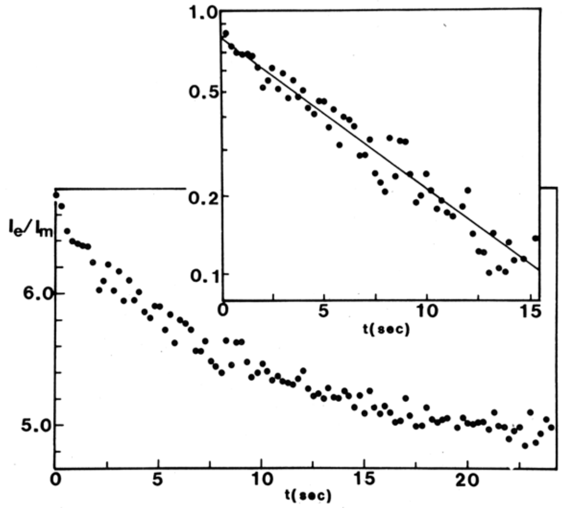

**Figure 4.** Change in $I_e/I_m$ with time after mixing of a fresh, turbid poly(2-vinylnaphthalene-*co*-MMA) solution (THF:MeOH = 1:1 V/V) with a mixed solvent (THF:MeOH = 5:4) (insert: semilog plot of $\{(I_e/I_m) - (I_e/I_m)_{eq}\}$ versus time).

**2. Kinetics for the Dissolution of the Precipitate in Turbid Solution.** After a fresh, turbid solution was mixed in which the ratio of THF to MeOH is 1:1 (V/V) with a better solvent (THF:MeOH = 5:4 V/V), the emission spectrum change with time was recorded. The decrease in $I_e/I_m$ with time (Figure 4) is due to the decrease in mole fraction of the concentrated phase and in the presumed intercoil excimer interaction. The plot of log $\{I_e/I_m - (I_e/I_m)_{eq}\}$ versus time follows first-order kinetics as shown in Figure 4. The rate at which the concentrated phase disappears depends on the mixed solvent. We have selected three solvent compositions to study this effect. The rate constant from plots like Figure 4 was measured to be 0.37, 0.15, and 0.13 s$^{-1}$ for the final volume fraction of MeOH in the solution of 0.25, 0.42, and 0.47, respectively.

**3. Aggregation of the Macromolecule Coils in a Poor Solvent.** When a solution of the polymer in a good solvent, THF, is mixed with methanol, the aggregation of coils in the solution can be observed in the flow cell. The time-resolved emission spectra have been recorded and are shown in Figure 5. The experimental results in Figure 6 indicate that there are three time regimes: (1) the iso-

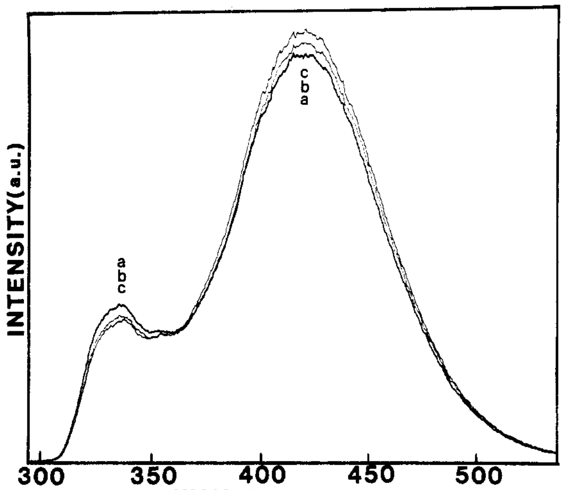

**Figure 5.** Time-resolved emission spectra for mixing of a solution of poly(2-vinylnaphthalene-*co*-MMA)/THF with MeOH recorded at (a) 39, (b) 216, and (c) 590 s.

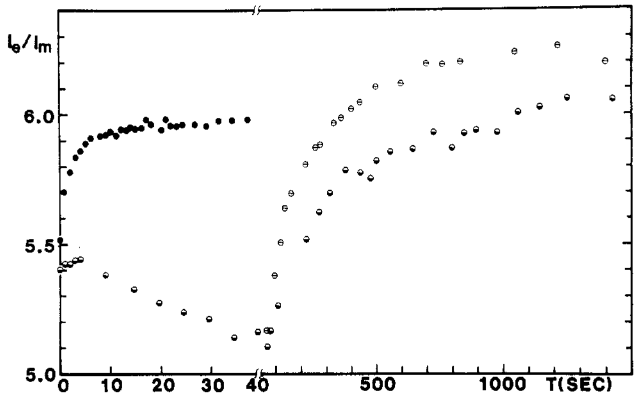

**Figure 6.** Change in $I_e/I_m$ with time for the mixing conditions of Figure 5. (a) ⊖ 0.05 g/L; (b) ⊖, 0.275 g/L; (c) ●, 0.106 g/L with stirring.

lated coil in the solution experiences a sudden change in environment and contracts with an increase in $I_e/I_m$ (this is too rapid to be followed by our instrument). (2) The $I_e/I_m$ ratio decreases gradually with time to ca. 40 s. This phenomenon is hard to understand. Possibly at the end of the first step the contracted coil has trapped extra molecules of THF which are then released as the equilibrium state is approached. We think of this as an "annealing" process. (3) After ca. 40 s, the $I_e/I_m$ increases slowly with time, which we attribute to the aggregation of coils. We have found that this process is more rapid in a more concentrated solution (cf. 0.275 g/L and 0.05 g/L in Figure 6). In order to verify that the kinetic processes are dominated by diffusion, we carried out the simple addition of MeOH to a rapidly stirred polymer–THF solution. While it is not possible to unambiguously determine the time equal zero point, one observes rapid changes in the continuously monitored fluorescence spectrum upon addition of MeOH. The $I_e/I_m$ ratio obtains the equilibrium value within 15–20 s of MeOH addition, approximately 20 times faster than the unstirred solution. Thus, it would seem that the changes we observe at longer times as the result of polymer diffusion with the possible exception of those that occur on a time scale shorter than ca. 50 ms.

## Discussion

While the use of $I_e/I_m$ ratios to monitor polymer conformational changes has been used for years, we are not aware of any experimental results that bear on the rate at which these changes occur. While we are not able to follow all the purely intracoil processes (which probably occur on a time scale on the order of the dead and mixing time of our apparatus), we clearly observe a intercoil process that contributes to the $I_e/I_m$ ratio. So far as we know, this intercoil contribution has not been clearly demonstrated previously. It is also interesting that the time dependence of dissolution depends on the solvent quality in a systematic way, although this observation has been known qualitatively to any polymer chemist.

The present work also demonstrates that stopped-flow spectroscopic techniques may be applied advantageously in polymer science to a variety of intra- and interpolymer processes.

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**Registry No.** (2VN)(MMA) (copolymer), 53640-71-4.

## References and Notes

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(5) It is important to emphasize that the time resolution in the present context is governed by the properties of the mixing system and the gated diode array detector, not the ultimate resolution of the fluorescence process itself (ca. 20 ns for naphthyl polymers).
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