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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

FLUORESCENCE TECHNIQUE TO STUDY FREE-RADICAL POLYMERIZATION OF 2-VINYLNAPHTHALENE

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Online publication date: 30 June 2001

To cite this Article Yilmaz, Yasar , Yagc, Yusuf and Pekcan, Önder(2001) 'FLUORESCENCE TECHNIQUE TO STUDY FREE-RADICAL POLYMERIZATION OF 2-VINYLNAPHTHALENE', *Journal of Macromolecular Science, Part A*, 38: 7, 741 – 749

To link to this Article: DOI: 10.1081/MA-100103877

URL: <http://dx.doi.org/10.1081/MA-100103877>

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NOTE

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ABSTRACT

A novel technique based on steady-state fluorescence measurements was introduced to study free-radical polymerization of 2-vinylnaphthalene (2VN). Both spectroscopic and kinetic studies of polymerization of 2VN in toluene solution have been carried out over the temperature range between 50 and 70°C. The effective radius of interaction of 2VN required for excimer formation was found to be around 3.5 nm. The product of reaction rate constant k_p and steady-state radical concentration $[M\bullet]$, $k_p[M\bullet]$ was calculated for 2-vinylnaphthalene (2VN) polymerization carried out at the temperatures 50, 60, 65, and 70°C. A sudden change in the value of $k_p[M\bullet]$ was observed above 60°C, indicating that polymerization proceeds effectively just at and above this temperature.

Key Words: Steady-state fluorescence technique; Free-radical polymerization; Ecimer formation.

INTRODUCTION

In 1954, Förster and Kasper discovered that when the concentration of the pyrene solutions was increased, a new structureless emission band appeared, red-shifted to the normal pyrene emission which decreased in intensity [1]. Since the

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absorption spectrum was found to be independent of concentration, the new emission was ascribed to a complex of an agitated and ground-state pyrene molecule. Similar phenomena were soon noted with other aromatic molecules. In the crystalline state, an emission characteristic of excited dimer ("excimer") was observed only when the molecules lay face-to-face at a distance of about 0.35 nm [2], and it was concluded that this is the geometry required for excimer formation.

Of particular interest was the finding that 1,3-diphenylpropane exhibits typical excimer emission independent of its concentration, so that excimer formation had to be intra molecular [3]. No other α,ω -diphenylalkane behaved in this way, so that it was first believed that intramolecular excimer formation is only possible if the two chromophores are linked by a three-atom bridge. Later it was found that such a restriction is not valid with all chromophores and that α,ω -dipyrenylalkanes, in particular, form intramolecular excimers even for derivatives of long paraffin hydrocarbons [4].

At present, we are concerned with the polymerization of 2VN. The free-radical polymerization of 2VN and the effective radius of interaction of 2VN monomers required for excimer formation were studied monitoring the fluorescence intensity of naphthalene molecules attached to the vinyl groups, in toluene as a function of reaction time.

EXPERIMENTAL

In this work, we monitored the free radical polymerization (FRP) of 2VN by using an *in situ* steady-state fluorescence technique. The FRP processes were performed separately at 50, 60, 65, and 70°C, and monitored against reaction time, *t*. The radical polymerization of 2VN was performed in toluene solutions in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The monomer, 2VN (Koch Light), was purified by multiple recrystallization. The initiator, AIBN (Merck), was recrystallized twice from methanol. The solvent, toluene (Merck), was distilled twice over sodium.

AIBN (0.38 mg/mL) and 2VN (0.9 mM) were dissolved in toluene and this stock solution was divided and transferred into round glass tubes. Four different samples were prepared for the fluorescence experiments. All samples were deoxygenated by bubbling nitrogen for 15 minutes, and radical polymerization of 2VN was performed in the fluorescence accessory of the spectrometer. Each of the samples was excited at 340 nm during *in situ* experiments, and the variation in fluorescence emission intensity was monitored with the time drive mode of the spectrometer, by staying at 360 nm peak of 2VN spectra. All measurements were made at the 90° position and slit widths were kept at 7.5 mm. No shift was observed in the wavelength of the maximum peak during the polymerization process.

Steady-state fluorescence measurements were carried out using a model LS-50 spectrometer of Perkin&Elmer, equipped with a temperature controller. All measurements were made at the 90° position and slit widths were kept at 7.5 nm.

Before steady-state polymerization experiments, we carried out some experiments at room temperature to find out the spectroscopic characteristics of 2VN-toluene solution.

RESULTS AND DISCUSSION

Figure 1 shows excitation and emission spectra of 2VN monomers dissolved in toluene (Merck). The excitation and emission maxima were recorded as 340 and 360 nm, respectively. Having defined these maxima, each of the samples of 2VN-toluene solution prepared in different concentrations was agitated at 340 nm light and emission intensity monitored in the range from 250 to 500 nm. Fluorescence emission intensity IM collected at 360 nm vs. 2VN concentration is plotted in Figure 2. As the concentration is increased, fluorescence emission intensity coming from the 2VN monomers decreases rapidly. When the concentration of 5 mM was reached, a second peak appeared. The second peak of which the maximum appeared at 460 nm was interpreted as the excimer fluorescence. The normalized emission and excimer fluorescence spectra are shown together in Figure 3. When the concentration of 5 mM was passed over, the excimer fluores-

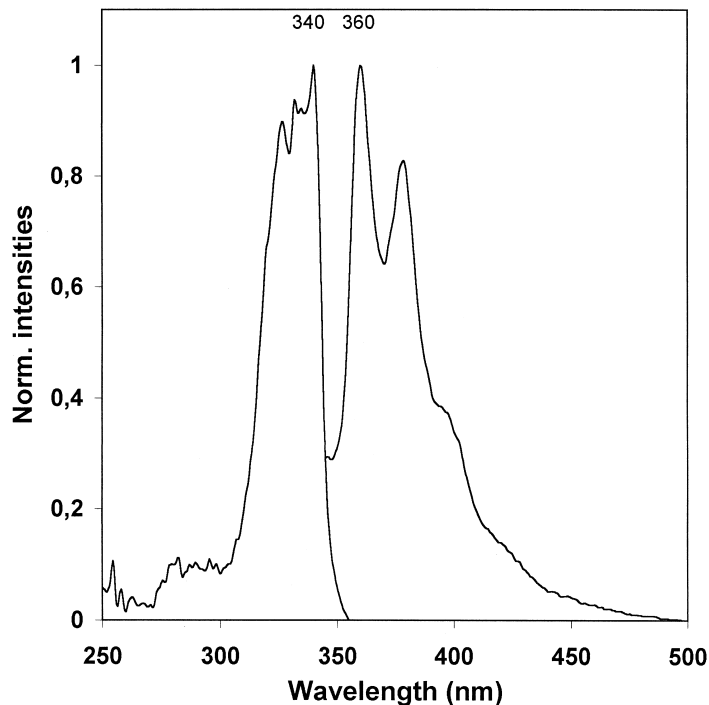


Figure 1. Normalized agitation (left) and emission (right) spectra from the 2VN-toluene solution, at the room temperature.

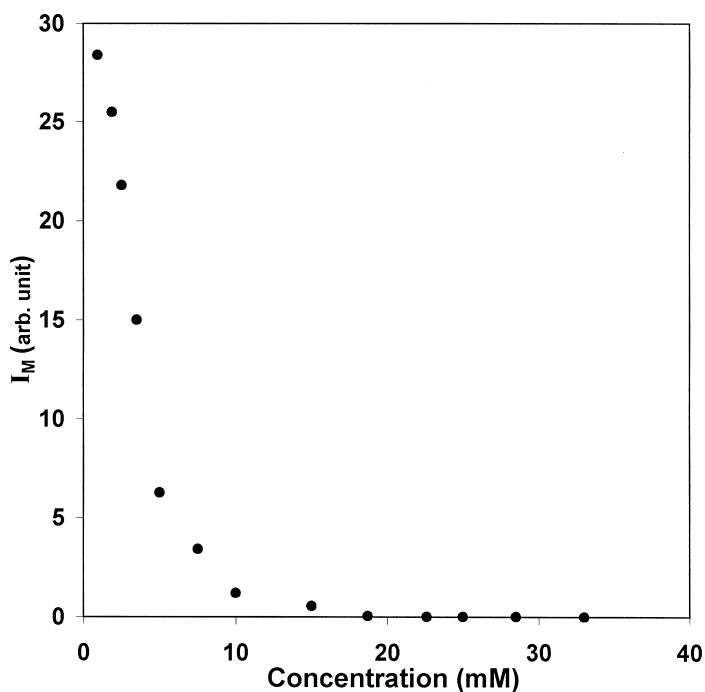


Figure 2. Dependence of the fluorescence emission intensity I_M to the concentration of 2VN monomer in toluene. There was no change in the shape and in the wavelength of the emission spectra for the entire concentration region.

cence intensity overcomes the monomer fluorescence intensity. Figure 4 presents the ratio of the excimer to the monomer fluorescence intensities I_E/I_M measured at the 460 and 360 nm respectively, as a function of the 2VN concentration. No shift at the maxima of the spectra was observed as the concentration was varied.

The following results can be concluded as the results of the above findings. Since the 2VN monomer are far away from each other in low concentrations, they do not have a chance to form excimer. At and above the concentration of 5 mM the 2VN monomers come to the close proximity, and have the chance to be able to form excimer. Above the concentration of 10 mM the ratio I_E/I_M increases almost linearly with 2VN monomer concentration.

We derived the following relation for the effective radius of interaction, R , of 2VN monomers dissolved in toluene solution, as a function of the concentration c , (Equation 1).

$$R = \frac{0.592}{c^{1/3}} \quad (1)$$

where the units of the concentration c and R are M and nm , respectively. This relation can be derived easily accepting that the monomers are dispersed homoge-

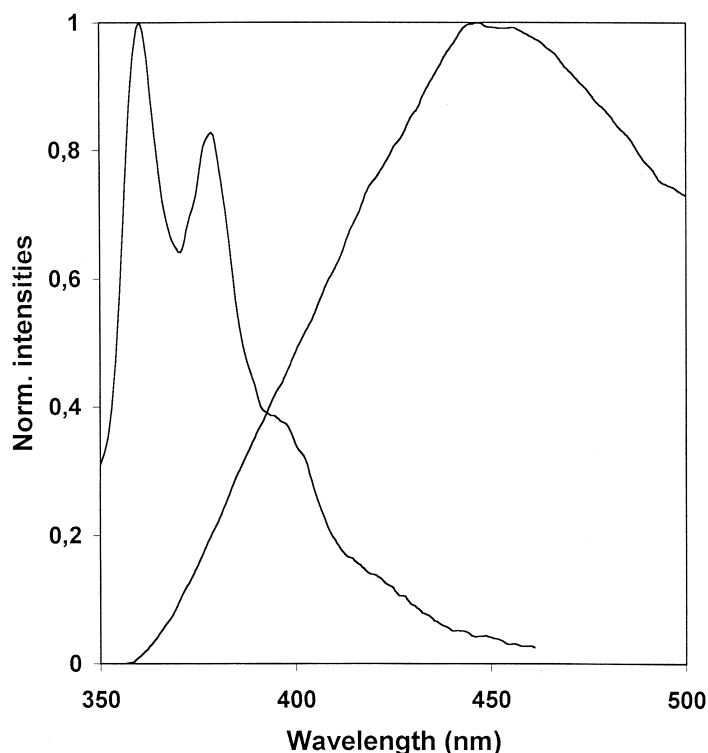


Figure 3. Normalized monomer (left) and excimer (right) emission spectra from the 2VN-toluene solution at the room temperature. The concentration of 2VN is about 5mM.

nously in toluene over all the sample cell, and each of them are present at the center of an imaginary sphere of radius R . For some critical value of R , as the 2VN monomers come close enough to each other, they have the chance to form excimer. When the critical concentration, 5 mM, at which excimer formation started to be observable, is substituted in relation (1), one can get the result 3.46 nm for the effective radius of interaction for excimer formation.

In the second part of our work, we monitored the free radical polymerization of 2VN in toluene solution in the presence of AIBN as an initiator. The free radical polymerization processes were performed separately at 50, 60, 65, and 70°C and monitored against time, as mentioned in the first paragraph of this section.

In Figure 5, we present a typical spectrum for the normalized 2VN emission intensity I_{MF} as a function of the reaction time performed at 60°C. It can be seen from the Figure, that the fluorescence intensity decrease exponentially with time. As the temperature is increased, the decrease in fluorescence intensity accelerates and the reaction time decreases.

The concentration of the 2VN was chosen as 0.9 mM, at which point we had not observed excimer formation (see Figure 4). The reason for the decrease in the fluorescence intensity with time can be explained by the onset of the polymeriza-

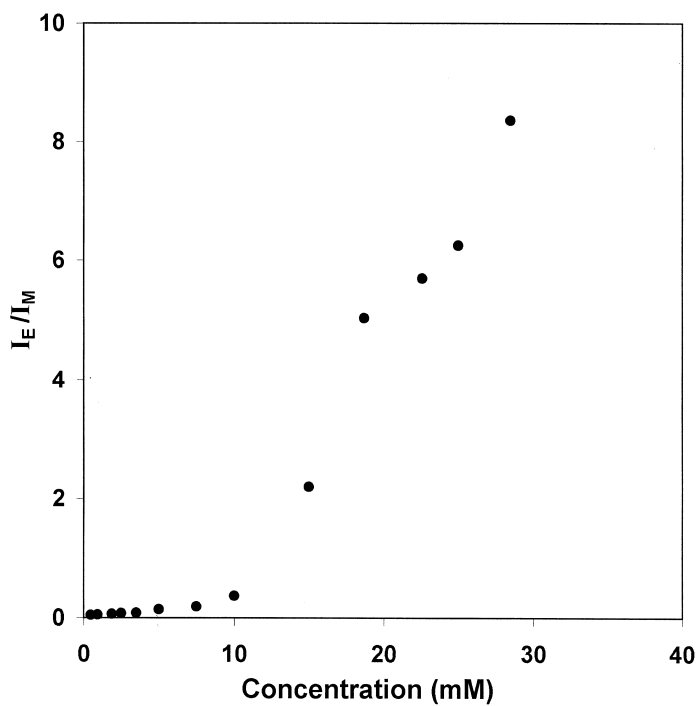


Figure 4. Dependence of the ratio of excimer and monomer fluorescence intensities, I_E/I_M , on the monomer concentration of 2VN dissolved in toluene.

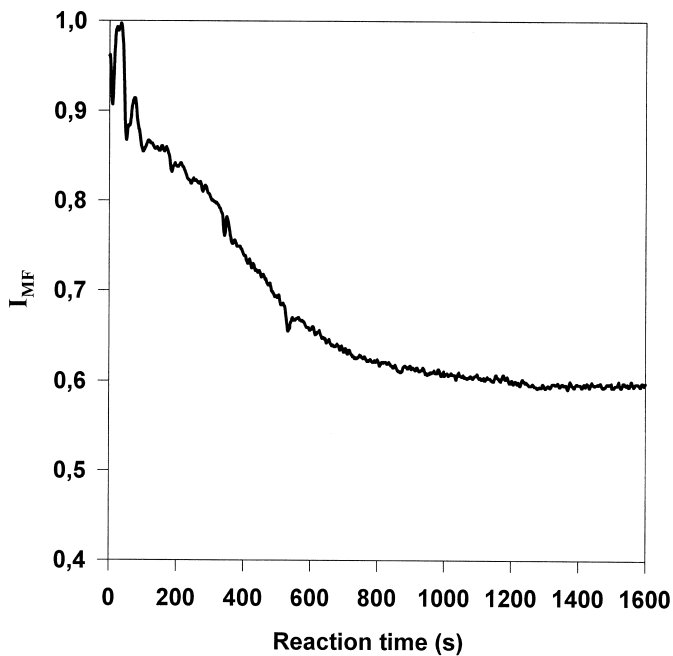


Figure 5. A typical spectrum of the normalized fluorescence intensity, I_{MF} , during the free-radical polymerization of 2VN at 60°C vs. the reaction time t .

tion of 2VN monomers. When the monomers chemically linked over the sequence of the polymer chains, the concentration of the free monomer decreases, and this gives rise to a decrease in fluorescence intensity. Since the initial concentration of the 2VN monomers is low enough and get lower and lower as the polymerization proceeds, there will be no self quenching effect on the fluorescence intensity. Therefore, the normalized fluorescence intensity, I_{MF} , coming from 2VN monomers will be proportional to the monomer concentration at time t during the polymerization reactions carried out at the temperatures 50, 60, 65, and 70°C.

The rate of the free radical polymerization R_p , is given by the following equation [2, 5]:

$$R_p = k_p [M][M\bullet] \quad (2)$$

where k_p is the propagation (or reaction) rate constant, $[M]$ is monomer concentration and $[M\bullet]$ represents the total concentration of all chain radicals irrespective of size. Substituting the definition of $R_p = -d[M]/dt$ in (2) one can get the following relation.

$$\frac{d[M]}{dt} = -k_p [M][M\bullet] \quad (3)$$

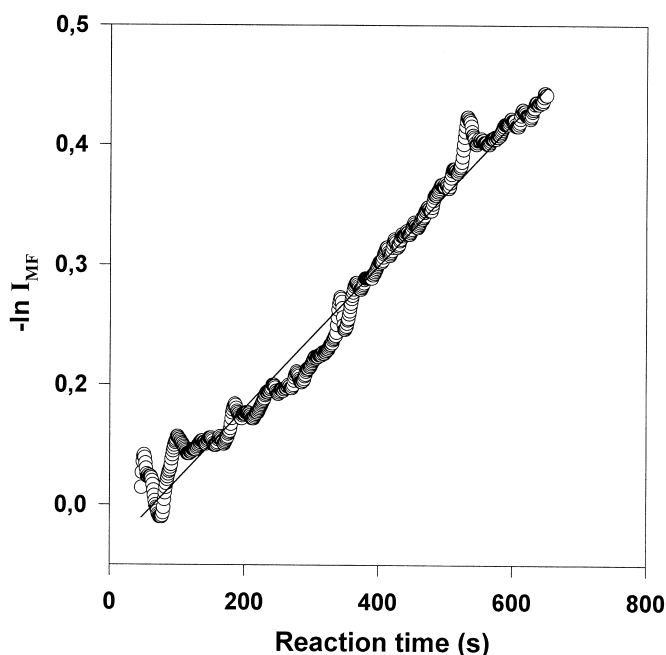


Figure 6. Logarithmic plot of fluorescence intensity, I_{MF} vs. time for the sample polymerized at 60°C. The product $k_p[M\bullet]$ was calculated from the slope of the curve.

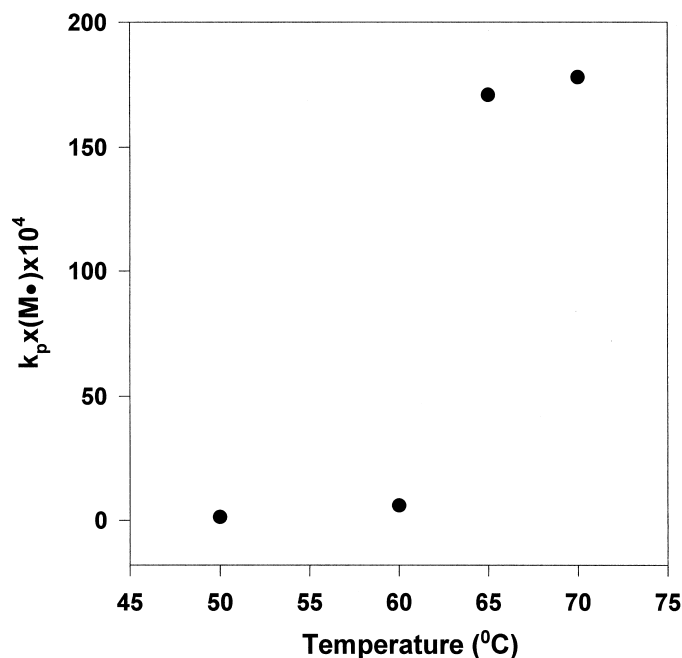


Figure 7. Dependence of the $k_p [M\bullet]$ to the temperature. A sudden change was observed at the temperature between 60 and 65°C.

Since the I_{MF} is proportional to the monomer concentration the above relation takes the following form with respect to I_{MF} .

$$I_{MF} = \exp(-k_p [M\bullet] t) \quad (4)$$

We fitted the logarithmic plots of the fluorescence intensity I_{MF} vs t , as shown in Figure 6, to determine the product $k_p [M\bullet]$. The results are shown in Figure 6. The values of the $k_p [M\bullet]$ produced from the slope of these curves were pictured in Figure 7 as a function of temperature. A very pronounced increase (about one hundred fold) in $k_p [M\bullet]$ was observed above the 60°C. This behavior shows that polymerization proceeds effectively just above 60°C. In conclusion, this work introduced a novel technique to study free-radical polymerization of chromophore including monomers, and some of the kinetic parameters can be calculated without disturbing the system mechanically.

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Received December 19, 2000

Revised date February 6, 2001