# Kinetics of Excimer Formation in Poly(1-naphthyl methacrylate)

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ABSTRACT: In poly(1-naphthyl methacrylate) the excimer to monomer ratio,  $I_e/I_m$ , is greatest in a poor (chain contracting) solvent and at high molecular weight. However, in poly(1-naphthyl acrylate), this ratio is virtually independent of solvent. This effect is discussed in terms of the increased chain flexibility and the existence of nearest neighbor interactions in the acrylate polymer. Binding energies of the PNMA excimer were estimated from steady-state measurements and range from 3 to 5 kcal/mol in various solvents. Transient measurements by single photon time correlation spectroscopy show that the rate of excimer formation,  $k_{DM}$ , follows an Arrhenius rate law, with an activation energy of about 3 kcal/mol. Evidence is presented suggesting a correlation between  $k_{DM}$  and the rate of rotational relaxation of several polymers.

The formation of excimers has been a well known phenomenon in the photophysics of small aromatic molecules since the original discovery of a concentration-dependent, unstructured emission in the fluorescence spectrum of pyrene.<sup>2–5</sup> A suitable kinetic scheme for the processes involved is given (Scheme I). The constants are defined as follows:  $k_{\rm FM}$ , radiative decay of the isolated chain unit (monomer emission);  $k_{\rm IM}$ , nonradiative decay of the isolated chain unit;  $k_{\rm DM}$ , excimer formation from an excited and a nonexcited chain unit;  $k_{\rm FD}$ , radiative decay of the excimer into two ground state chain units. The notation used is that of Birks.<sup>3</sup>

By definition, the excimer is stable only in the excited state and can be observed in the emission but not in the absorption spectrum. In addition, there may also exist nonradiative excimers, as has been suggested for the intermediate in the dimerization of anthracene. The usual model for excimer structure is that of a parallel sandwich with an interplanar distance of about 3 to 3.5 Å. However, work on intramolecular systems shows that the parallel alignment is not strictly required.<sup>6,8</sup> This is especially true for a large chromophore such as in poly(1-vinylpyrene).<sup>7</sup>

Hirayama<sup>9</sup> suggested that, for various diphenyl and triphenyl alkanes, excimers could form only in those compounds with chromophores separated by three carbon atoms: the "n = 3 rule".<sup>11</sup> Later work has shown that this rule is not generally valid, especially for larger chromophores.<sup>10,12,13</sup>

Excimer formation has been observed in most polymers bearing aromatic side groups (polystyrene, poly(vinyl naphthalene), etc.). The distinguishing feature of polymer excimers in dilute solution ( $\leq 10^{-1}$  M in monomer groups) is that they are independent of concentration and so are completely intramolecular.

The excimer intensity in polymers (expressed as the excimer to monomer ratio,  $I_e/I_m$ ) does not depend on the viscosity of the pure solvent. It does, for most polymers, depend on whether the solvent is "good" (chain expanding) or "poor" (chain contracting). Nishihara and Kaneko<sup>14</sup> found a linear relation between the ratio  $I_e/I_m$  where  $[\eta]$  is the intrinsic viscosity for polystyrene. They explained this according to the classical Flory theory for the intrinsic viscosity:

$$[\eta] = \frac{6^{3/2} \Phi \langle S^2 \rangle^{3/2}}{M}$$
(1)

where  $\Phi$  is a universal constant (= 2.1 × 10<sup>21</sup>),  $\langle S^2 \rangle$  is the mean square radius of gyration, and M is the molecular weight. The average density of polymer segments,  $\rho$ , is

Scheme I  $M + h\nu \rightarrow M^*$   $M^* + M \stackrel{k_{DM}}{\underset{k_{MD}}{\longleftarrow}} (M \cdots M)^*$   $k_{FM} \qquad k_{IM} \quad k_{FD} \qquad k_{ID}$  $M + h\nu \qquad M \ 2M + h\nu_{ex} \ 2M$ 

proportional to  $M/\langle S^2 \rangle^{3/2}$ , and hence for a given molecular weight

$$\rho \propto 1/[\eta] \tag{2}$$

A similar effect was noted by Somersall and Guillet<sup>15</sup> for excimer formation in poly(1-naphthyl methacrylate) (PNMA). Furthermore, no solvent effect was observed in poly(2-naphthyl methacrylate) (P2NMA).<sup>16</sup> This was attributed to the formation of excimers between nearest neighbors on this more flexible polymer chain. Molecular models confirm that the achievement of a planar geometry between adjacent rings should be more facile in the 2naphthyl ester.

The question arises as to whether excimers are formed between nearest or nonnearest neighbors on the polymer chain. Originally it was thought that those polymers with more restricted chain movement (e.g., PNMA) would not be able to form excimers between nearest neighbors on the polymer, but only between nonnearest neighbors. For this reason, a strong solvent dependence would be expected. On the other hand, less restricted polymer chains would be expected to form nearest-neighbor excimers and so would not show a solvent effect. While solvent independence seems to be an acceptable criterion for high chain flexibility and nearest neighbor interaction (cf., poly(1vinylnaphthalene)<sup>17</sup>), the solvent effect shown with polystyrene indicates that the situation may be more complex than originally supposed.

Tacticity also has an effect on the formation of excimers. In general,  $I_e/I_m$  is greater for isotactic than for atactic polymers (e.g., poly(*p*-methyl styrene)<sup>18</sup> and polystyrene).<sup>19,20</sup> This has been attributed to the formation of more stable configurations about the carbon skeleton in the isotactic form.

Excimer formation is of particular interest in polymers because of the possible role intramolecular energy transfer may play in excimer formation. In solid polystyrene scintillators, it was found<sup>21</sup> that energy transfer to the solute occurs from the excimers and not from the excited monomer. Virtually all of the polymer studies conducted so far have made use of steady-state measurements of excimer and monomer intensities as a function of temperature. Transient measurements have as yet been performed on only a few polymers.<sup>21,22</sup>

Another similar polymer, poly(N-vinylcarbazole) (PVCz), has been extensively examined for possible use as a photoconducting polymer in electrographic processes. In solid PVCz, energy transfer occurs by exciton hopping between chromophores, with trapping and either quenching or emission by excimer sites and chance impurities.<sup>23</sup>

In dilute polymer solution, excimer emission is preceded by energy migration down a polymer chain to an excimer trap on the same chain. This is of particular interest due to the parallel between this process and that of photosynthesis.<sup>24</sup>

#### **Experimental Section**

**Materials.** Solvents were Fisher reagent or spectroscopic grade. These were checked for residual absorbing and emitting impurities and were purified if necessary.

Methacrylyl chloride and acrylyl chloride (Pfalz and Bauer) and propionyl chloride (Eastman) were distilled before use. Isobutyryl chloride was prepared from isobutyric acid and thionyl chloride and was purified by distillation. Esters (monomers and their small molecule models) were prepared by a standard Schotten-Baumann reaction between sodium 1-naphtholate and the corresponding acid chloride.<sup>15</sup> The esters were extracted with ether, washed with dilute NaOH and water, dried, and vacuum distilled: 1-naphthyl methacrylate (NMA), mp 39–41 °C, bp 125 °C (1 torr); 1-naphthyl isobutyrate (NIBA), mp 28–31 °C, bp 120 °C (1 torr); 1-naphthyl propionate (NPA), bp 102 °C (1 torr); 1-naphthyl acrylate (NA), mp 28–31 °C, bp 100 °C (1 torr).

Poly(1-naphthyl acrylate) (PNA) and PNMA were prepared by free-radical polymerization in benzene solution degassed to  $\leq 0.005$  torr residual pressure. Decanoyl peroxide was used as initiator. The choice of solvent and initiator was based on their low tendency to add fluorescing and quenching impurities to the polymer chain, compared to other common solvents and initiators. PNMA and PNA were polymerized to ca. 100% yield for 70 h at 70 °C. The polymers were purified by multiple precipitation from benzene into methanol and were freeze dried from benzene. Further precipitation had no effect on the emission spectra (PNMA,  $M_n$ (osmometry, toluene) = 132000; PNA,  $M_n = 16000$ ).

Steady-State Measurements. Unless otherwise noted, fluorescent measurements (steady state and transient) were done in 13 mm o.d. round quartz degassed to a residual pressure of  $<10^{-4}$  torr by repeated freeze-thaw cycles on a vacuum line. Emission spectra were measured on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter and are shown uncorrected. These were analyzed in the same manner as in our previous paper.<sup>25</sup>

Fractionation was done in *n*-butyl acetate on a Bioglass column in a Waters Ana-Prep gel permeation chromatograph. To overcome an interfering Raman line in the spectrum of *n*-butyl acetate, the solvent was removed, and the fractionated polymer was examined in  $CH_2Cl_2$ .

**Transient Measurements.** Fluorescent lifetimes were measured by the technique of single photon time correlation using an apparatus similar to that described by Lewis and other workers.<sup>26-28</sup> Most of the components were obtained commercially from ORTEC Corp.; however, the flash lamp was constructed in this laboratory from a standard design.<sup>26,27</sup>

The samples were excited through a 280-nm interference filter (Pomfret Research Optics, 12 nm band-pass) and were viewed at an angle of 90° to the excitation through a Jarrell-Ash monochromator (band-pass = 15 nm). The lamp was run at 0.5 atm of  $H_2$  and 5 kV. Suitable precautions were taken to reduce scattered light to a minimum. A Corning 751 band-pass filter (310-410 nm) was placed at the exit slit of the monochromator. Lamp profile curves were obtained by scattering light from aluminum foil or from a solution of colloidal silica (DuPont Ludox) in 0.05 N NaCl-H<sub>2</sub>O.

The experimental decay law  $I_d(t)$  (for time divided into discrete channels) is given by the integral

$$I_{\rm d}(t_{\rm i}) = N_{\rm d} \int_0^{t_{\rm i}} I_{\rm F}(t_{\rm i} - t') G(t') \, {\rm d}t'$$
(3)

where  $N_{\rm d}$  is a normalization factor,  $I_{\rm F}(t-t_{\rm i})$  is the experimental



Figure 1. Normalized emission of PNMA at 23 °C (aerated  $CH_2Cl_2$ ) as a function of concentration.

lamp response curve, and G(t') is the true decay law. It is necessary to include the factor  $I_{\rm F}(t-t')$  due to distortion of the ideal decay law by the lamp.

Small molecule decays generally follow single exponential decay laws. The monomer emission from an excimer system is given by the sum of two exponentials:

$$G_{\rm m}(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \tag{4}$$

while emission from the excimer itself follows a difference of exponentials,

$$G_{\rm e}(t) = A_3[-\exp(-t/\tau_1) + \exp(-t/\tau_2)]$$
(5)

The true decay laws for both single and double exponentials were obtained by techniques similar to those described by Lewis and other workers.<sup>26-28</sup> The primary method was that of iterative convolution. The best fit lifetimes were taken as those values which minimized the weighted sum of the squares of the deviations  $(\chi^2 \text{ function})$  between the curve convoluted (by eq 3) from the lamp curve and test parameters and the experimental decay law. The criterion for a good fit was both a low reduced  $\chi^2$  value and reproducibility in the fit, using lamp curves taken at the beginning and end of the experimental decay measurements.

## **Results and Discussion**

Steady-State Experiments. The absorption spectrum of PNMA is identical with that of its small molecule analogue, NIBA. Similarly, the fluorescence emission from NIBA is identical with the naphthalene monomer emission from PNMA. Figure 1 shows the normalized fluorescence spectra of PNMA at 23 °C in nondegassed CH<sub>2</sub>Cl<sub>2</sub>, over a concentration range of about 10<sup>-2</sup> to 10<sup>-6</sup> M of monomer units. By comparison, the small molecule model NIBA only forms excimers at concentrations >1 M. The monomer emission is centered at about 335 nm, while the excimer emission is a broad structureless band centered at about 385 nm. As expected, there is no change in the ratio  $I_e/I_m$  with concentration, showing that this is strictly intramolecular excimer formation.

Figure 2 shows the fluorescence in three different solvents,  $CHCl_3$ ,  $CH_2Cl_2$ , and ethyl acetate (EtOAC), normalized to the same monomer emission. Intrinsic viscosities in each solvent and  $I_e/I_m$  are shown in Table I. The best solvent (defined as the one in which the intrinsic viscosity  $[\eta]$  is the greatest) is  $CHCl_3$ , the poorest solvent is EtOAc, and  $I_e/I_m$  increases in the order  $CHCl_3 < CH_2Cl_2 < EtOAc$ . Furthermore, the excimer intensity can also be increased by the addition of increasing amounts of a nonsolvent, either polar (MeOH) (Figure 3) or nonpolar (cyclohexane and heptane, Figure 4). The importance of



Figure 2. Emission of PNMA at 23 °C in degassed solution in several solvents.



Figure 3. Emission of PNMA at 23 °C in aerated  $CHCl_3$  solution as a function of added methanol.

Table I Solution and Emission Properties of Poly(1-naphthyl methacrylate) in Various Solvents

solvent	[η] (30°C) ± 0.005	$I_{e}/I_{m}$ (23 °C) ± 0.1	<sup>φ</sup> F,total (23°C) ± 10%					
EtOAc toluene	$\begin{array}{c} 0.040\\ 0.116\end{array}$	3.67 3.19	0.020 0.010					
CHCl <sub>3</sub> -cyclohexane (1:1)	0.125	2.81	0.015					
CH <sub>2</sub> Cl <sub>2</sub>	0.158 0.184	2.61	0.010					
011012	0.101	1.77	0.011					

chain contraction on excimer emission (eq 1 and 2) is readily apparent, and one may conclude from these experiments that the change in excimer intensity with solvent is not due to changes in the polarity or dielectric constant of the solvent.

Effect of Molecular Weight. In Figure 5 are shown the emission of fractions of PNMA over a molecular weight range of 40 000 to 360 000 in aerated  $CH_2Cl_2$  at 23 °C, normalized to the same monomer emission. It can be seen that the lowest molecular weight fractions have the lowest excimer emission, the same effect seen in the spectra of



Figure 4. Emission of PNMA at 23 °C in aerated CHCl<sub>3</sub> solution as a function of added cyclohexane.



Figure 5. Emission of PNMA at 23 °C in an aerated  $CH_2Cl_2$  solution as a function of molecular weight.

several unfractionated PNMA samples of different average molecular weight.

Evidently in an intramolecular system, chain length is important in providing a sufficient number of chromophore-chromophore interactions. Nishijima et al.<sup>29</sup> found a similar but much greater effect in a series of low molecular weight poly(1-vinylnaphthalene)s (molecular weight 1400 to 6000).

Effect of Temperature. According to Johnson,<sup>12</sup> if ln  $(I_e/I_m)$  is plotted vs. 1/T over a wide temperature range, an inverted U-shaped curve is usually obtained. In the low-temperature limit,  $k_{\rm M}$  and  $k_{\rm D}$  are assumed to be temperature independent and  $k_{\rm MD} \approx 0$ . Under these conditions, the excimer intensity drops with a reduction in temperature, and the activation energy  $E_{\rm DM}$  can be obtained from the slope of the low-temperature curve. In the high-temperature limit, it is assumed that  $k_{\rm MD}$ ,  $k_{\rm DM} \gg k_{\rm D}$ ,  $k_{\rm M}$ . Under these conditions, the ratio  $k_{\rm DM}/k_{\rm MD}$  gives a dynamic equilibrium constant, and the excimer intensity drops with increased temperature. An isoemissive point should be observed, and the slope of the plot ln  $(I_e/I_m)$  against 1/T gives the binding energy  $\Delta H_{\rm b}$ . The monomer and excimer should decay with a common lifetime  $\tau$ .

Figure 6 shows the emission spectrum of PNMA in EtOAc as a function of temperature (6 to 82 °C). As the



Figure 6. Emission of PNMA in degassed EtOAc as a function of temperature.

 Table II

 Binding Energy of Poly(1-naphthyl methacrylate)

 and Other Excimers

	solvent	$-\Delta H_{b}$ , kcal/mol	ref
poly(1-naphthyl methacrylate)	CH <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>	$2.8 \pm 0.2$	this work
- ,	$CHCl_3^a$	$3.7 \pm 0.2$	this work
	$EtOAc^{a}$	$4.6 \pm 0.2$	this work
1,3-bis( <i>N</i> -carbazolyl)- propane	2MeTHF <sup>a</sup>	1.9	12
	2MeTHF <sup>b</sup>	2.76	12
poly(N-vinylcarbazole)	2MeTHF <sup>a</sup>	2.8	34

<sup>a</sup> From steady-state measurements (variation in ln  $(I_e/I_m)$  vs. 1/T. <sup>b</sup> From transient measurements ( $\Delta H_b = E_{MD} - E_{DM}$ ).

temperature is lowered, both the total quantum yield and the ratio  $I_{\rm e}/I_{\rm m}$  increase. In Figure 7 ln  $(I_{\rm e}/I_{\rm m})$  is plotted vs. 1/T, and the excimer binding energy  $\Delta H_{\rm b}$  is obtained from the slope (Table II) for three solvents.

This treatment, although the same as that used by others,<sup>12,30</sup> is open to the same question raised by Johnson,<sup>12</sup> since it assumes an equilibrium between  $k_{\rm DM}$  and  $k_{\rm MD}$ , even though there is no isoemissive point in the spectra. Table II compares the binding energies  $\Delta H_{\rm b}$  for PNMA with those for 1,3-bis(N-carbazolyl)propane measured by the steady-state method and calculated from transient measurements ( $\Delta H_{\rm b} = E_{\rm MD} - E_{\rm DM}$ ). The lower value for the steady-state measurement on 1,3-bis(N-carbazolyl)propane was attributed to a "static quenching" of chromophores that have the proper configuration at the time of excitation. In that work, as in the present case, the condition  $k_{\rm MD} \gg k_{\rm D}$  is not fulfilled, and so quenching must also be considered in the present work. However,  $E_{\rm MD}$  is not easily obtainable from our measurements (since  $k_{\rm MD} \ll k_{\rm DM}$ ), and the values for  $\Delta H_{\rm b}$  can only be considered reasonable approximations. The relatively low values (3 to 5 kcal) for the binding energy of intramolecular excimers has been attributed to the existence of a bond-twisting repulsive force in addition to the expected electron overlap repulsion.<sup>30</sup>



Figure 7. Arrhenius plots for the PNMA excimer.

**Transient Measurements.** All of the naphthalenecontaining polymers we have studied show monomer fluorescence decays which cannot be described by a single exponential decay law. Figure 8a shows the fluorescence decay of the model compound NIBA in  $CH_2Cl_2$  which is accurately first order, with a lifetime  $\tau = 7.1 \pm 0.1$  ns. In contrast, the decay of monomer fluorescence from PNMA (Figure 8b) is not only nonexponential, but varies considerably with the solvent used. Although, as pointed out by Nemzek,<sup>27</sup> nonexponential decays may be expected when the rotational and emissive lifetimes are of the same order of magnitude, it is suggested that the phenomenon is better explained in terms of the formation and dissociation of an intramolecular excimer.

The kinetics can be described, following the notation of Scheme I, in the following treatment. For convenience, the rate constants are grouped as follows:

$$X = k_{\rm FM} + k_{\rm IM} + k_{\rm DM} \tag{6}$$

$$Y = k_{\rm FD} + k_{\rm ID} + k_{\rm MD} \tag{7}$$

The complete kinetic derivation is given in detail elsewhere.  $^{12,31}$ 

If a  $\delta$  function excitation pulse is assumed, then the expression for the decay of the monomer emission is of the form

$$I_{\rm m}(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$$
(8)

$$I_{\rm m}(t) = \frac{k_{\rm FM}(X-\lambda_2)}{\lambda_1-\lambda_2} \left( \exp(-\lambda_1 t) + \frac{\lambda_1-X}{X-\lambda_2} \exp(-\lambda_2 t) \right)$$
(9)

where

$$\lambda_{1,2} = \{ (X - Y) \pm [(X - Y)^2 + 4k_{\rm DM}k_{\rm MD}]^{1/2} \} \quad (10)$$

The excimer decay is given by

$$I_{\rm e}(t) = A_3[-\exp(-\lambda_1 t) + \exp(-\lambda_2 t)]$$
(11)

$$I_{\rm e}(t) = \frac{k_{\rm FD}k_{\rm DM}}{\lambda_1 - \lambda_2} [-\exp(-\lambda_1 t) + \exp(-\lambda_2 t)] \qquad (12)$$

It should be noted that various authors interchange the meaning of  $\lambda_1$  and  $\lambda_2$ . In this work,  $\lambda_1$  is always greater



Figure 8. Fluorescence of NIEA and PNMA in various solvents. (a) Decay of NIBA in degassed  $CH_2Cl_2$  at 23 °C: ( $\bullet$ ) experimental decay curve; (-) best fit decay ( $\tau = 7.07$  ns); (O) lamp curve. Scale = 0.4836 ns/channel. (b) Decay of PNMA monomer emission at 325 nm and 23 °C: ( $\Delta$ ) EtOAc, 0.1485 exp(-t/1.9490) + 0.0124 exp(-t/8.4780); ( $\bullet$ )  $CH_2Cl_2$ , 0.1217 exp(-t/1.375) + 0.0038 exp(-t/7.335); (O) CHCl<sub>3</sub>, 0.2463 exp(-t/1.026) + 0.0008 exp(-t/9.280). Scale = 0.3930 ns/channel.

than  $\lambda_2$ ;  $\tau_1$  (=1/ $\lambda_1$ ) is the lifetime of the short-lived part of the decay and  $\tau_2$  (=1/ $\lambda_2$ ) is the long lifetime.

It is assumed that

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$$k_{\rm FM} + k_{\rm IM} = k_{\rm M} \tag{13}$$

where  $k_{\rm M}$  is the rate of fluorescence decay of an isolated chain unit or of its model  $(=1/\tau)$  (e.g., ethylbenzene for polystyrene). Also,

$$k_{\rm FD} + k_{\rm ID} + k_{\rm MD} = 1/\tau_{\rm D}$$
 (14)

and

$$k_{\rm FD} + k_{\rm ID} = k_{\rm D} \tag{15}$$

where  $\tau_{\rm D}$  can be considered the fluorescence lifetime of the excimer.

Under conditions where  $k_{\rm MD} \ll k_{\rm DM}$  (at room temperature or below, depending on the system), the kinetics are greatly simplified. It can then be assumed that the monomer and excimer act as two independently emitting species, as such

$$X = k_{\rm IM} + k_{\rm FM} + k_{\rm DM} = \lambda_1 \tag{16}$$

If the preceding assumption holds, the value of  $k_{\rm DM}$  can be obtained directly from  $\lambda_1$  and  $k_{\rm M}$ .

The absolute values of the pre-exponential factors  $A_1$ and  $A_2$  in eq 8 are dependent upon various instrumental factors. Therefore, only the ratio  $A_1/A_2$  is used:

$$A_{1}/A_{2} = (X - \lambda_{2})/(\lambda_{1} - X)$$
(17)

If  $A_1 \gg A_2$ , then the long-lived component may be weak or not observed.  $k_{\rm DM}$  is obtained from eq 17. From eq 9 are obtained

$$\lambda_1 + \lambda_2 = k_{\rm M} + k_{\rm D} + k_{\rm MD} + k_{\rm DM}$$
 (18)

$$\lambda_1 \lambda_2 = k_{\rm DM} k_{\rm D} + k_{\rm M} k_{\rm MD} + k_{\rm M} k_{\rm D} \tag{19}$$

The only satisfactory criteria for determining (from transient measurements) whether excimer dissociation  $k_{\rm MD}$ 

is important are if a single exponential decay for the monomer emission is observed or if the condition  $A_1/A_2 \gg$ 1 is fulfilled, as was the case in this work. In addition, if the assumption that dissociation is negligible is made, then any value of  $k_{\rm MD}$  obtained from the monomer decay measurements is highly questionable. In this work no such assumption was made. However, the error in  $k_{\rm DM}$  is less than 10%, even if this assumption is made.

Earlier steady-state measurements on poly(1-vinylnaphthalene) suggesting that excimer dissociation is completely negligible were refuted by recent transient measurements, <sup>32,33</sup> thus showing the importance of these criteria.

The derivation for intermolecular excimer kinetics includes several concentration terms, and the rate equations can be solved by examining excimer decay as a function of concentration.<sup>3</sup> The concentration terms are dropped from the intramolecular case, since the concentration is a constant, but unknown, local term. As a pseudo-zeroorder rate constant,  $k_{\rm DM}$  should be given in units of M s<sup>-1</sup>. However, the convention adopted in previous publications has been to give it the same units as the first-order intermolecular constant, s<sup>-1</sup>.

In this work, the decay rates (Figure 8b) were measured by observing the monomer emission at 325 nm. The absence of residual excimer emission at this wavelength was verified by the independence of the decay rates with wavelength in the region about 325 nm.

In Figure 9, the rate of formation of the excimer,  $k_{\text{DM}}$ , in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, EtOAc, and a cyclohexane-CHCl<sub>3</sub> 1:1 mixed solvent is plotted vs. 1/T and is given an Arrhenius treatment,

$$k_{\rm DM} = A \, \exp(-E_{\rm DM}/RT) \tag{20}$$

$$e_{\rm DM} = (kT/h) \exp(\Delta S_{\rm DM}/R) \exp(-E_{\rm DM}/RT) \quad (21)$$

where  $\Delta S_{DM}$  is the entropy of activation.

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 Table III

 Kinetic Data for the Poly(1-naphthyl methacrylate) Excimer

solvent	$A_{\text{DM}}, \times 10^{-1}$ s <sup>-1</sup>	$E_{\rm DM}$ , kcal/mol	$\Delta S_{\mathbf{DM}}$ , eu	$k_{DM}^{a}$	$k_{MD}^{a}$	$k_{\mathbf{D}}^{a}$	$k_{M}^{a}$
CHCl,	$1.3 \pm 0.6$	$3.1 \pm 0.2$	$-7.7 \pm 0.7$	6.4	0.20	1.6	3.3
CH.Cl.	$1.5 \pm 0.2$	$3.2 \pm 0.1$	$-7.4 \pm 0.2$	5.9	0.20	1.4	1.5
EtŐAc	$0.17 \pm 0.05$	$2.2 \pm 0.2$	$-11.8 \pm 0.5$	3.9	0.40	1.4	0.90
$CHCl_{3}$ -cyclohexane (1:1)	$0.88 \pm 0.26$	$2.9 \pm 0.2$	$-8.4 \pm 0.7$	5.9	0.28	1.6	2.6

 $^{a} \times 10^{-8} \text{ s}^{-1}$  at 23 ° C.



Figure 9. Arrhenius plot for the rate of excimer formation  $k_{\text{DM}}$ .

The rate data are summarized in Table III. Since  $k_{\rm MD}$  is much smaller than  $k_{\rm DM}$  in this work, and since it is obtained by the difference between the larger constants, the results were not accurate enough to allow an Arrhenius treatment. Therefore, only room temperature (23 °C) data are provided.

The results for the excimer formation in the two good solvents,  $CH_2Cl_2$  and  $CHCl_3$ , and in the  $CHCl_3$ -cyclohexane 1:1 solvent mixture are identical within experimental error. The results in  $CHCl_3$  are open to the greatest possible error due to the low value of  $\tau_1$  (<1 ns) above room temperature. The reproducibility of the single photon apparatus is poor for lifetimes below 1 ns.

Excimer formation in ethyl acetate has a lower activation energy and also a more negative entropy of activation than in other solvents. The lower activation energy in ethyl acetate may reflect the chain contraction of the polymer in this solvent, resulting in a greater number of chromophores per unit volume and hence an easier path to the formation of excimer pairs.

The less negative entropy change for the polymer systems with respect to small molecules<sup>3</sup> is most probably due to the fact that the entropy loss caused by bringing together two units confined to the same chain is less than that involved in bringing together two widely separated molecules, as suggested by Tazuke and Banba.<sup>34</sup>

For the intramolecular excimer in 1,3-bis(N-carbazolyl)propane,<sup>35</sup> the relation between the rate of formation and solvent viscosity only held for a series of similar solvents. For a group of widely differing solvents, the rate of formation varied in a random fashion with solvent viscosity. This was discussed in a qualitative fashion in terms of a specific solvent-excimer interaction.

The evaluation of the rate constants summarized in Table III permits the estimation of the lifetimes of the



Figure 10. PNA emission at 23 °C from aerated solution.

monomer and excimer emission in PNMA from the relations

$$\tau_{\rm N}^{0} = (k_{\rm M} + k_{\rm DM})^{-1} \tag{22}$$

and

$$\tau_{\rm D}^{0} = (k_{\rm D} + k_{\rm MD})^{-1} \tag{23}$$

Using these relations, one obtains  $\tau_N^0 = 2.1 \pm 0.1$  ns and  $\tau_D^0 = 5.6 \pm 0.3$  ns for the monomer and excimer emission, respectively, in ethyl acetate at 23 °C.

Poly(1-naphthyl acrylate) was also examined in this work. The emission spectra in four solvents are shown in Figure 10. The excimer intensity is much greater here than in PNMA. This would be expected due to the increased flexibility of the acrylate chain backbone. The excimer intensity in PNA is virtually independent of solvent, in contrast to PNMA. Fisher-Hirschfelder models of PNMA and PNA show that the removal of the  $\alpha$ -methyl group makes nearest neighbor approach far less hindered. Similarly,  $k_{\rm DM}$  is about twice as large in PNA as in PNMA (at 23 °C in EtOAc,  $k_{\rm DM}$  for PNA is  $12 \times 10^8 \, {\rm s}^{-1}$ ; in CH<sub>2</sub>Cl<sub>2</sub>,  $k_{\rm DM} \approx 10 \times 10^8 \, {\rm s}^{-1}$ ). Measurements were taken at only one temperature for this polymer, since the lifetime  $\tau_1$  is less than 1 ns at room temperature, and so is at the limit for reproducible measurements. The rate of excimer formation,  $k_{\rm DM}$  at 23 °C, can be compared to the few intramolecular systems available. At 23 °C,  $k_{\rm DM}$  in 1,3-bis(*N*-carbazolyl)propane (a more hindered group than NMA) is equal to  $8.9 \times 10^7$  s<sup>-1</sup>.<sup>12</sup> On the other hand, in polystyrene, a much less hindered polymer,  $k_{\rm DM}$ , is of the order 1 to  $4 \times 10^9$  s<sup>-1</sup>, depending on tacticity.<sup>18</sup> An interesting correlation is apparent between the rate of excimer formation  $k_{\rm DM}$  and the rate of rotational relaxation of polymers in solution as measured by fluorescence depolarization.<sup>36</sup> The rates of main-chain rotational relaxation of poly(methyl acrylate), poly(methyl methacrylate), and PVCz are respectively  $\sim 8 \times 10^8$ ,  $2.5 \times 10^8$ , and  $4 \times 10^7$  s<sup>-1</sup>, at least comparable to the rates of excimer formation in polymers with similar chain structures. However, polystyrene, with one of the highest values of  $k_{\text{DM}}$ , has an anomalously slow rate of relaxation. It is clear that further studies must be made before firm conclusions should be drawn on this aspect of the phenomenon.

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#### **References and Notes**

- (1) Department of Chemistry, McGill University, Montreal, Canada H3A 2A7.
- Th. Förster and K. Kasper, Z. Phys. Chem. (Frankfurt am (2)Main), 1, 275 (1954).
- (3)J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970.
- (4) B. Stevens, Adv. Photochem., 8, 161 (1970).
- (5) A. C. Somersall and J. E. Guillet, J. Macromol. Sci., Rev. Macromol. Chem., 13, 135 (1975)
- (6)Y.-C. Wang and H. Morawetz, Makromol. Chem. Suppl., 1, 283 (1975).
- (7) J. R. McDonald, W. E. Echols, T. R. Price, and R. B. Fox, J.
- Chem. Phys., 57, 1746 (1972). A. H. Alwatter, M. D. Lumb, and J. B. Birks, "Organic Mo-lecular Photophysics", Vol. 1, J. B. Birks, Ed., Wiley, New York, 1973, Chapter 7.
- (9) F. Hirayama, J. Chem. Phys., 42, 3163 (1965).
- (10) E. A. Chandross and C. J. Dempster, J. Am. Chem. Soc., 92, 3586 (1970).
- W. Klöpffer, Chem. Phys. Lett., 4, 193 (1969).
   G. E. Johnson, J. Chem. Phys., 61, 3002 (1974).
- (13) W. Kühnle and K. Zachariasse, J. Photochem., 5, 165 (1976).

- (14) T. Nishihara and M. Kaneko, Makromol. Chem., 124, 84 (1969).
- A. C. Somersall, Ph.D. Thesis, University of Toronto, 1973; A. C. Somersall and J. E. Guillet, Macromolecules, 6, 218 (1973).
   R. B. Fox, T. R. Price, R. F. Cozzens, and W. H. Echols,
- Macromolecules, 7, 937 (1974). (17) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, J.
- Chem. Phys., 57, 534 (1972). (18) T. Ishii, S. Matsunaga, and T. Handa, Makromol. Chem., 177,
- 283 (1976).
- (19) W. Klöpffer, "Organic Molecular Photophysics", Vol. 1, J. B. (19) W. Riopher, Organic Hotecular Flotophysics Birks, Ed., Wiley, New York, 1973, Chapter 7.
   (20) J. W. Longworth, Biopolymer, 4, 1131 (1966).
- (21) F. Heisel and G. Laustriat, J. Chim. Phys. Phys. Chim. Biol., 66, 1895 (1969).
- (22) C. David, M. Piens, and G. Geuskens, Eur. Polym. J., 8, 1291 1972).
- (23) W. Klöpffer and D. Fischer, J. Polym. Sci., Polym. Symp., 40, 43 (1973), and references cited therein.
- (24) Chem. Eng. News (Feb. 16, 1976); ibid. (May 3, 1976).
- (25) J. S. Aspler, C. E. Hoyle, and J. E. Guillet, *Macromolecules*, 11, 925 (1978).
- (26)C. Lewis, W. R. Ware, L. J. Doemeny, and T. L. Nemzek, Rev. Sci. Instrum., 44, 107 (1973)
- (27) T. L. Nemzek, Ph.D. Thesis, University of Minnesota, 1975.
- (28) W. R. Ware, L. J. Doemeny, and T. L. Nemzek, J. Phys. Chem., 77, 2038 (1973).
- Y. Nishijima, K. Mitani, S. Katayama, and M. Yamamoto, (29)Rep. Prog. Polym. Phys. Jpn., 13, 421 (1970).
- (30) D. R. Rosseinsky, R. A. Hann, and E. J. Brunner, J. Lumin., 11, 291 (1975-1976).
- (31) J. B. Birks, Prog. React. Kinet., 5, 181 (1970).
  (32) K. P. Ghiggino, R. D. Wright, and D. Phillips, Chem. Phys. Lett., 53, 552 (1978).
- (33) K. P. Ghiggino, R. D. Wright, and D. Phillips, J. Polym. Sci., Polym. Phys. Ed., 16, 1499 (1978).
   (34) S. Tazuke and F. Banba, Macromolecules, 9, 451 (1976).
- (35) G. E. Johnson, J. Chem. Phys., 63, 4047 (1975).
- A. M. North and I. Soutar, J. Chem. Soc., Faraday Trans. 1, (36)68, 1101 (1972).

# Polymer Reaction. 11. Oxidative Pyrolysis of Poly(isoprene)<sup>1</sup>

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ABSTRACT: Poly(isoprene) has been oxidized at temperatures between 268 and 340 °C. The products were GC separated and on-line identified by an interfaced GC pyrolysis peak identification system. The most abundant products are methyl ethyl ketone, methyl vinyl ketone, and butyraldehyde, with lesser amounts of acetaldehyde, acetone, methacrolein, propionaldehyde, acrolein, and formaldehyde. A free-radical chain mechanism is proposed. The rate constants for the oxidative pyrolysis of poly(isoprene) have been determined; the overall activation energy is about 27 kcal/mol.

We have constructed an interfaced GC pyrolysis peak identification system for the investigation of high-temperature reactions of polymers with on-the-fly analysis of products. The pyrolyses of poly(propylene)<sup>3</sup> and poly-(isoprene)<sup>4</sup> in a stream of He carrier gas were found to be different from studies made in vacuo or in a stagnant inert atmosphere. Oxidative pyrolysis of poly(propylene) had also been investigated<sup>5</sup> with this system. Reaction mechanisms were formulated from the products and their distributions. It was found that the kinetics of oxidative degradation at temperatures between 240 and 289 °C can be calculated from rate constants determined for autoxidation between 71 and 140 °C.<sup>6,7</sup>

Our recent interests have been concerned with polymer degradation and stabilization associated with its combustion and flame retardancy. Therefore, even though there have been a number of reports on the aging and autoxidation of poly(isoprene) in the vicinity of 100 °C, data at much higher temperatures are scarce. The central purpose of this work is to determine the rates of oxidative degradation of poly(isoprene) at high temperatures, to remove the products rapidly from the reaction zone by a carrier gas thus simulating the conditions for a burning polymer, and to identify these oxidation products.

## **Experimental Section**

The poly(isoprene) used in this study contains 97% cis-1,4 and 3% 3.4 structural units. It is the product of Goodyear (Natsyn 2200) with a number average molecular weight of about 200 000. The in-process phenolic antioxidant was removed by repeated dissolution in toluene and reprecipitation with acetone and vacuum dried.

The pyrolysis temperatures were determined by TGA (DuPont 900 thermal analyzer) in air at a flow rate of 25 mL min<sup>-1</sup> and a heating rate of 30 °C min<sup>-1</sup>. To investigate its ignition char-