Table I
Dependence of Molecular Weight on the Feed Ratio of Diyne/BBr_3[a]

run	BBr_3, g (mmol)	diyne, g (mmol)	diyne/BBr_3 ratio	molec wt[b]
1	0.320 (1.28)	0.102 (0.96)	0.75	830
2	0.278 (1.11)	0.100 (0.94)	0.85	3320
3	0.423 (1.69)	0.169 (1.59)	0.94	6420
4	0.526 (2.10)	0.225 (2.11)	1.00	15500
5	0.403 (1.61)	0.178 (1.67)	1.04	28000
6	0.489 (1.95)	0.228 (2.15)	1.10	*c*

[a] Reactions were carried out in CH_2Cl_2 at −78 °C and then warmed up to room temperature. [b] GPC ($CHCl_3$, PSt standard), peak top molecular weight. [c] Gelation was observed when the system was warmed up to 0 °C.

From either **5b** or **5c**, the same product (**6**) was afforded by the reaction with ethanol (Scheme III). This result indicates that one B–C bond in trialkenylborane (**5c**) is reactive to ethanol to form B–OEt similarly to B–Br in **5b**. Accordingly, if the polymer **3** has a branched structure of the trialkenylborane moiety (**3c**) even in a small amount as mentioned above, a scission of B–C bonds should take place at this point under the conditions of GPC measurement. It may be possible that the molecular weight of the generated polymer before GPC measurement was higher in comparison with that estimated by GPC.

The structure of **3** was further confirmed by UV measurement. The polymer **3** and its model compound (**5b**) showed the same absorption maximum at 255 nm, which is assignable to the $C{=}C{-}B{-}C{=}C$ moiety. By using a molar absorptivity for **5b**, this structure was proven to exist almost quantitatively in **3**. To elucidate the stereochemistry of haloboration polymerization, acid hydrolysis of **3** with deuterated acetic acid was examined. 2,7-Dibromo-1,8-dideuterio-1,7-octadiene (**7**) was obtained in 90% yield (GC). From the results of ^1H NMR analysis, more than 77% of **7** was proven to contain the *Z* isomer. This result is taken to mean that the present haloboration polymerization proceeds mainly in cis addition of boron bromide to terminal acetylene.

The results of haloboration polymerization between **1** and **2** by changing the feed ratio of **2** to **1** are summarized in Table I. The molecular weight of the obtained polymer was increased when the ratio of **2** to **1** approached or slightly exceeded unity. As expected, a gelation was observed when excess **2** was used for this polymerization (run 6). The obtained gel in this experiment became soluble after treatment with ethanol. The soluble product showed lower molecular weight (GPC, $\bar{M}_n = 4100$, $\bar{M}_w = 12\,100$) than that of the polymer prepared by 1:1 feeding. This finding supports the assumption that one boron–carbon bond of the trialkenylborane moiety in the gel was cleaved by ethanol as described before.

The reactivity of B–Br in **3** was demonstrated as follows. Terminal monoyne compounds such as phenylacetylene were added to a dichloromethane solution of **3**. In this reaction, a further haloboration occurred to produce **8** as shown in Scheme II. The formation of **8** was supported by its ^1H NMR spectrum,[10] although **8** was decomposed during GPC measurement.

In a manner similar to the reaction with ethanol, **3** was reacted with water or diol compounds such as ethylene glycol to produce the corresponding gel by the intermolecular substitution reaction, which is illustrated in Scheme II.

3 was also subjected to the ether cleavage reaction. For example, when excess THF was introduced into a dichloromethane solution of **3** at 0 °C, the polymer structure was found to be changed into **9** (Scheme II) by its ^1H NMR.[11] After hydrolysis of **9**, followed by the purification with SiO_2 column chromatography, 4-bromo-1-butanol was isolated in 90% yield based on **3**. This reaction also demonstrates the characteristic property of **3** as a poly(Lewis acid).

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(9) **4**: ^1H NMR ($CDCl_3$) δ 1.27 (CH_3CO–, t, 3 H), 1.62 (–$CH_2CC{=}C$, m, 4 H), 2.54 (–$CH_2C{=}C$, m, 4 H), 4.09 (–OCH_2–, q, 2 H), 6.24 ($C{=}CHB$, 2 H).
(10) **8**: ^1H NMR ($CDCl_3$) δ 1.68 (–$CH_2CC{=}C$, m, 4 H), 2.60 (–$CH_2C{=}C$, m, 4 H), 6.59–7.05 (–$CCBr{=}CH$–, 2 H), 7.10–7.92 ($C_6H_5CBr{=}CH$–, m, 6 H).
(11) **9**: ^1H NMR ($CDCl_3$) δ 1.62 (–$CH_2CC{=}C$, m, 4 H), 1.84 (–$OCCH_2CH_2CBr$, m, 4 H), 2.54 (–$CH_2C{=}C$, m, 4 H), 3.47 (–CH_2Br, t, 2 H), 4.07 (–CH_2OB, t, 2 H), 6.24 ($C{=}CHB$, 2 H).

Yoshiki Chujo, Ikuyoshi Tomita, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

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Pyrene as a Fluorescent Probe for Monitoring Polymerization Rates

During the past few years monitoring of polymerization reactions using fluorescent probes has been the subject of numerous investigations. Changes in fluorescence yields,[2–6] polarization,[3,7] diffusion coefficient,[8] and the efficiency of intramolecular excimer formation[9–11] have been related to the changes in viscosity that occur during the polymerization event and, as such, are used in particular to monitor the extent of cure in certain applications.

An excimer (*exci*ted di*mer*) is formed by the diffusion-controlled reaction between a molecule in the excited state and another in the ground state and is characterized by a broad, structureless emission red-shifted with respect to the fluorescence emission of the monomer.[12] Provided that only two excited states are involved, the ratio of pyrene monomer to excimer emission is a linear function of the medium viscosity.

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Wang and co-workers[9-11] have used 1,3-bis(1-pyrenyl)propane, which forms intramolecular pyrene excimer, to monitor the cure of methyl methacrylate and epoxy resins after demonstrating that the ratio monomer to excimer varies linearly with viscosity in solutions of glycerol tripropionate in ethyl acetate.

A quantitative interpretation of the correlation above is not straightforward because of the complexity of the probe's photophysics. Measurements of fluorescence lifetimes for 1,3-bis(1-pyrenyl)propane, for example, indicate the presence of three kinetically related excited states.[13-18] As a consequence, the ratio monomer to excimer emission is, in general, not a simple function of solvent viscosity. Complex depenedence of this ratio has been observed for 1,3-bis(1-pyrenyl)propane in solvents[14,19] and during the polymerization of epoxy resins.[6] 1,3-Bis(2-pyrenyl)propane follows simpler kinetics.[18,20,21] However, this compound has, to our knowledge, not been used as a probe to monitor polymerizations. Similarly, the effect of viscosity on the ratio monomer/excimer has not been studied.

Our purpose is to develop a technique based on excimer formation that allows us to simply measure *quantitatively* the rate of polymerization of acrylate monomers at low conversions. Our ultimate purpose is that the method be easily adaptable to in situ monitoring of photopolymerizations both under steady-state and pulsed irradiation, and this formed the basis of our requirements. To this end, we have chosen pyrene itself as fluorescent probe for the following reasons: (a) the photophysics is well understood and, what is essential for our purposes, only two excited states, monomer and intermolecular excimer, need to be taken into account; (b) the ratio monomer to excimer emission can be easily controlled by adjusting the concentration of pyrene; and (c) due to the relatively high pyrene concentrations required, the penetration distance of the light used to excite the fluorescence is limited, thus minimizing complications, if any, introduced in the process by the fluorescent probe.

As a model system, to test the technique, we have studied the thermal polymerization of methyl methacrylate initiated by azobis(isobutyronitrile) and measured the reaction rate by monitoring the changes in the monomer/excimer emission ratio. Our results obtained with different initiator concentrations show that there is a linear relationship between the rate measured by fluorescence and that determined gravimetrically, thus demonstrating the validity of using this simple fluorescent probe method in the study of polymerization kinetics.

Experimental Section. Methyl methacrylate (MMA) was purified by vacuum distillation before use. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Pyrene (Aldrich, 99+%) was used as received. Fluorescence measurements were performed at 25 °C in a SPEX 212 Fluorolog spectrofluorimeter equipped with a constant-temperature cell holder. Excitation wavelength and band-pass were 322 and 5 nm, respectively. Polymerization was carried out in Pyrex cylindrical tubes. Fluorescence quenching experiments were performed in quartz cuvettes. Emission was measured using front-face detection, and, except for the spectra shown in Figure 1, the signal was averaged for 60 s to improve signal to noise ratio.

Samples containing MMA, AIBN, and pyrene were purged with argon for approximately 15 min. Polymerization was started by placing the solution in a water bath at 50 °C. Periodically the sample was removed and quenched at 0 °C. After warming to 25 °C the emission intensity was measured at 393 and 476 nm using a band-pass of 1 nm. Reproducibility of the ratio $I(393)/I(476)$ was better than 1%.

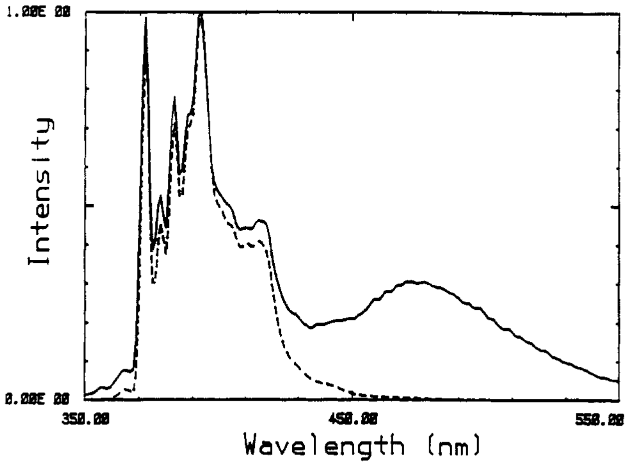

Figure 1. Normalized emission spectrum of pyrene (1.0×10^{-3} M) in MMA. Solid curve: before reaction. Broken curve: after 3.5 h of polymerization at 50 °C with AIBN (4×10^{-2} M). Emission intensities (in arbitrary units) at 393 nm. Before reaction = 1.10×10^4; after 3.5 h of polymerization = 1.39×10^6.

For gravimetric determinations the polymer was precipitated by addition of methanol and dried until a constant weight was obtained.

Results and Discussion. Figure 1 shows the change in the emission spectrum of pyrene (1×10^{-3} M) produced by polymerizing MMA for 3.5 h at 50 °C. In principle, the fluorescence intensity of either the monomer or the excimer, or their ratio, can be used to determine the progress of the reaction provided a correlation between fluorescence and rate of polymerization can be established.

(A) Control Experiments. Pyrene is a "foreign" substance, as we employed it in adding it to the polymerizing feed. As a control it is important to investigate its influence, if any, on the rate of MMA polymerization and to determine if it is reactive under the conditions of the experiment. In addition, azo compounds are efficient quenchers of the excited singlet state of aromatic hydrocarbons;[22] therefore, their presence may interfere with pyrene fluorescence. Control experiments were carried out to ascertain the effect of these factors in our kinetics results.

The rate of MMA polymerization in the presence of pyrene (1×10^{-3} M) was determined gravimetrically at six initiator concentrations between 1×10^{-2} and 0.1 M. The results can be represented by the equation

$$-\mathrm{d}[\mathrm{MMA}]/\mathrm{d}t = k[\mathrm{AIBN}]^{0.5}\ \mathrm{M\ min^{-1}} \qquad (1)$$

with k equal to $(6.4 \pm 0.1) \times 10^{-2}$ in the presence of pyrene (1×10^{-3} M) and $(6.6 \pm 0.1) \times 10^{-2}$ in its absence. Therefore, we conclude that within experimental error the presence of pyrene (1×10^{-3} M) has no effect on the rate of polymerization. Our results are in excellent agreement with what is predicted using literature values[23] for the rate constants of initiation, propagation, and termination, namely

$$-\mathrm{d}[\mathrm{MMA}]/\mathrm{d}t = 6.8 \times 10^{-2}[\mathrm{AIBN}]^{0.5}\ \mathrm{M\ min^{-1}} \qquad (2)$$

The stability of the probe, pyrene, under the polymerization conditions was determined by absorption spectroscopy. A sample containing AIBN (0.1 M, the highest concentration used in our work) and pyrene (1×10^{-3} M) in MMA was polymerized for 50 min. The solution

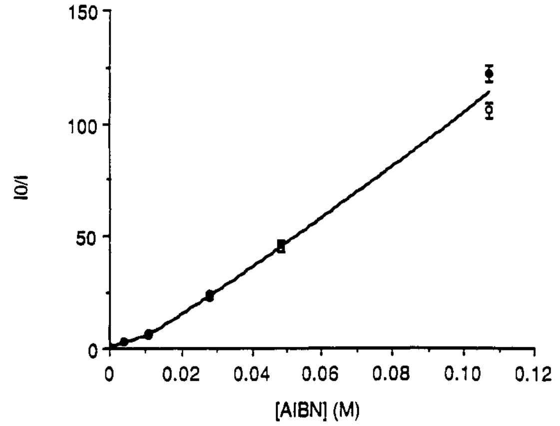

Figure 2. Stern–Volmer plot for the quenching of pyrene fluorescence by AIBN in MMA. Pyrene concentration is 1.1 × 10^{-3} M. Open circles = intensity at 393 nm (monomer emission). Closed circles = intensity at 476 nm (excimer emission).

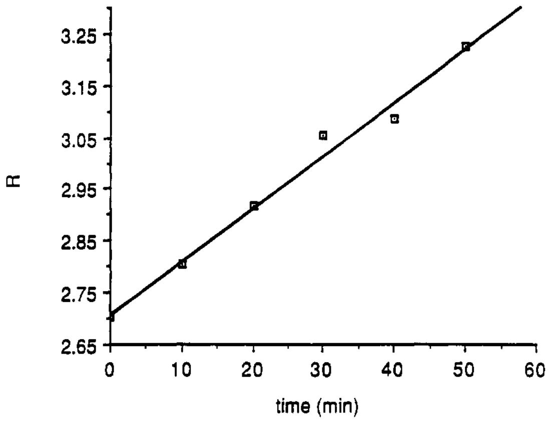

Figure 3. Increase in the fluorescence ratio during polymerization of MMA at 50 °C. [Pyrene] = 1.1 × 10^{-3} M; [AIBN] = 2.44 × 10^{-2} M. R is the ratio of fluorescence intensity at 393 nm to that at 476 nm. The slope and intercept of the line are (1.03 × 0.06) × 10^{-2} min^{-1} and 2.71 ± 0.03, respectively.

was diluted by a factor of approximately 20 with ethyl acetate and the absorption spectrum measured between 300 and 400 nm. As control we employed a sample that had been purged with argon but kept at room temperature. No difference was observed in the spectra of these two solutions, and we conclude that pyrene undergoes no chemical change detectable by absorption spectroscopy under the polymerization conditions.

AIBN quenches the fluorescence of pyrene in MMA. A Stern–Volmer plot is presented in Figure 2. Emission intensities are corrected for direct absorption by AIBN. At the highest AIBN concentration employed the correction amounts to approximately 4%. Data obtained at 393 nm (monomer emission) and 476 nm (excimer emission) can be described by the same Stern–Volmer curve. The ratio $I(393)/I(476)$ [monomer/excimer] is independent of the AIBN concentration and equal to 2.77 ± 0.14. The upward curvature of the Stern–Volmer plot indicates that both static (not requiring diffusion) and dynamic quenching are involved in the deactivation of pyrene excited state by AIBN.[24] Since the absorption spectra of the mixture pyrene + AIBN corresponds to the sum of the spectra of the individual species, we conclude there is no interaction in the ground state.

That the ratio $I(393)/I(476)$ does not depend on the AIBN concentration is evidence that only the monomer excited state is quenched by the initiator. A kinetic scheme describing the photophysics of pyrene[12] is presented below:

Kinetic scheme for pyrene

$$\text{Py} \rightarrow \text{Py}^* \quad I_a$$

$$\text{Py}^* + \text{Py} \rightarrow \text{PyPy}^* \quad k_1, k_{-1}$$

$$\text{Py}^* \rightarrow \text{Py} + h\nu_M \quad k_2$$

$$\text{Py}^* \rightarrow \text{Py} \quad k_3$$

$$\text{PyPy}^* \rightarrow 2\text{Py} + h\nu_E \quad k_4$$

$$\text{PyPy}^* \rightarrow 2\text{Py} \quad k_5$$

$$\text{Py}^* + \text{AIBN} \rightarrow \text{quenching (dynamic and static)}$$

$$F_M/F_E = (k_2/k_4)(k_{-1} + k_4 + k_5)/k_1[\text{Py}]$$

F_M and F_e are the integrated emission intensities of monomer and excimer, respectively.

Fluorescence quenching of aromatic hydrocarbons by azo compounds occurs by intermolecular singlet energy transfer.[22] From the UV spectrum of AIBN we obtain 73 kcal/mol for the energy of the lowest singlet state. The singlet energies of pyrene monomer and excimer are 77 and 69 kcal/mol, respectively.[12] From these values we expect that the rate constant for energy transfer from pyrene monomer to AIBN is close to that for a diffusion-controlled reaction. Because energy transfer from pyrene excimer to AIBN is endothermic by 4 kcal/mol, we expect the rate constant to be 3 orders of magnitude lower than that for diffusion-controlled energy transfer.[25] This difference in rate constants, along with the shorter lifetime of the excimer,[12] explains why under our conditions AIBN quenches only the monomer excited state.

(B) Rate Studies. Pyrene has been the subject of several investigations, and its photophysics is well understood.[12,26–31] Excimer formation is diffusion controlled. In the kinetic scheme above k_1 is inversely proportional to, and $(k_2/k_4)(k_{-1} + k_4 + k_5)$ is independent of, solvent viscosity. Therefore, we can write for the intensity ratio

$$R = I(393)/I(476) = A\eta[\text{Py}]^{-1} \tag{3}$$

where η is the viscosity coefficient, [Py] is the concentration of pyrene, and A is a constant that includes instrumental characteristics and factors that transform intensity at a single wavelength to integrated intensity.

A typical result obtained when we monitored the intensity ratio during the polymerization is presented in Figure 3. The conversion after 50 min is approximately 5%. For the polymer concentrations produced at 50° with 2.24 × 10^{-2} M AIBN the solution viscosity should change by 2–3 orders of magnitude and nonlinearly with polymer concentration.

From the result presented above we conclude that the fluorescence ratio is not a measure of the solution viscosity but of the microviscosity around the fluorescent probe. The differences between these two viscosities are well-known.[32–35] In particular, the microviscosity changes linearly with concentration up to 20–30% polymer and, beyond a certain degree of polymerization (approximately 60 for polyethylene), is independent of polymer molecular weight.

During the polymerization the microviscosity increases and the volume decreases. For low conversions we can derive the following expression relating the change in the fluorescence ratio and the rate of polymerization

$$(1/R_0)\,dR/dt = \{(1/\eta_0)\,d\eta/dc - (1/D_0)\,dD/dc\}R_p \tag{4}$$

where R_p is the rate of polymerization, D is density, c is the polymer concentration, and the subscript 0 indicates

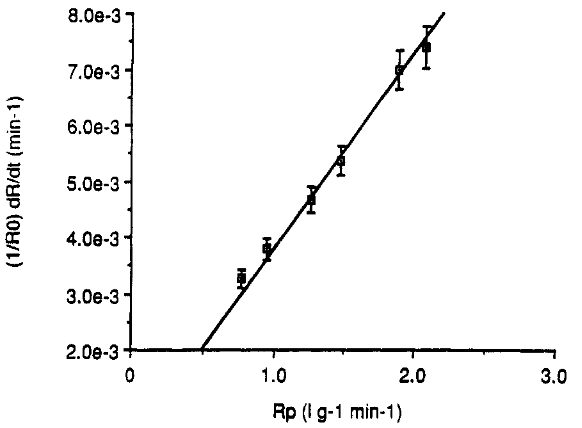

Figure 4. Correlation between the rate of increase in fluorescence ratio and the rate of polymerization measured gravimetrically. The slope and intercept of the line are (3.53 ± 0.10) × 10^{-3} L/g and (2.5 ± 2.1) × 10^{-4} min^{-1}, respectively.

the value in the absence of polymer. The term involving the density is the volume contraction factor and can be taken as 2.7 × 10^{-4} L/g.[23]

A correlation between the rate of polymerization determined gravimetrically and that measured by fluorescence is presented in Figure 4. On the basis of this relationship, we conclude that the rate of increase in the fluorescence ratio is a direct measure of the rate of polymerization. To the best of our knowledge, this is the first report showing a 1 to 1 correspondence between the fluorescence increase of a fluorescent probe and rate of polymerization determined at low conversions. In contrast, jubilidine malononitrile and similar probes developed by Loutfy[2-4] are insensitive at low conversions. As shown by this author,[2-4] the emission intensity remains almost constant up to 60% conversion.

From the slope of the line (Figure 4), using 2.7 × 10^{-4} L/g for the contraction factor, we obtain $(1/\eta_0)\, d\eta/dc$ = 3.8 × 10^{-3} L/g for poly(methyl methacrylate) in MMA. This value corresponds to the limiting viscosity number of a polymer containing 33 monomer units.[36] Thus, in analogy to what has been proposed for polyethylene[32] and poly(dimethylsiloxane),[35] we propose that 33 monomer units is the size of the segment whose motion controls the viscous flow at the microscopic level in poly(methyl methacrylate) solutions.

The ratio monomer to intermolecular excimer can be easily controlled by adjusting the concentration of pyrene. Preliminary results indicate that a pyrene concentration of 1 × 10^{-2} M has no effect on the rate of polymerization of methyl methacrylate. Thus, it should be possible to use this probe to study the polymerization of monomers considerably more viscous than MMA. The ability to control the ratio monomer/excimer by adjusting the concentration of the probe is a definite advantage over the intramolecular case[9-11] where, of course, no such control is possible. This lack of control is part of the reason why Stroeks and co-workers[6] were unable to study quantitatively the polymerization of epoxy resins.

Conclusion. We have presented evidence that quantitatively relates the fluorescence of a molecular probe included in a thermally polymerizing sample of MMA directly to the rate of polymerization of the monomer. In principle, this is a powerful tool that portends to substantially simplify such measurements of polymerization rates *and* to provide a straightforward probe wherein photopolymerization rates can be followed in situ and potentially in the transient time domain. Before application of the technique the influence of the monomer/initiator system on the photophysics of pyrene must be investigated.

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O. Valdes-Aguilera, C. P. Pathak, and D. C. Neckers*[,1]

Center for Photochemical Sciences
Bowling Green State University
Bowling Green, Ohio 43403

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