

Photoinitiated Polymerization of 1-Vinylimidazole

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Synopsis

The polymerization of 1-vinylimidazole differs from that of 1-vinyl-2-methylimidazole in that degradative chain addition to the monomer is an important factor, as previously indicated by Bamford and Schofield. The consequence of this is a dependence of rate on monomer concentration, which starts with the first power but levels off to a constant rate or even decreases slightly as the initial monomer concentration rises to 1–4 mol/L. Thus, the mechanism proposed by Bamford and Schofield appears to be confirmed. Initiator dependence of rate is best correlated by using the light absorbed by the initiator rather than the initiator concentration as the independent variable. The 0.72 power dependence found may be higher than the expected 0.5 power because the rates were measured at a monomer concentration (0.25 mol/L) just beyond the linear region. Low values of activation energy are expected, since photoinitiation rate is independent of temperature. The measured value reflects only the propagation and termination steps. Even then, the value found of 1.5 kcal/mol is low compared to the value of 3.9 kcal/mol for 1-vinyl-2-methylimidazole.

INTRODUCTION

Recently there has been interest in monomers and polymers containing the imidazole ring because of their interesting properties and their potential for diverse applications. Although polymers and copolymers of 1-vinylimidazole (VI) have been reported, the polymerization itself has not received much attention. There are few reports that deal specifically with the kinetics of polymerization of VI; some of these papers contain obvious errors, and the results reported by various researchers do not agree with each other.

SURVEY OF PREVIOUS WORK

The polymerization of VI was reported in patents more than twenty years ago.^{1,2} A few journal articles also appeared.^{3,4} Konsulov et al.⁵ appear to have been the first ones to study the kinetics of the homopolymerization of VI. They studied the polymerization in methanol and in bulk. According to them, the orders of the reaction in methanol are 0.7 and 1.6 with respect to initiator and monomer, respectively. Unfortunately, the plots they used to calculate these orders have obvious errors. The correct plots of their data points yield the orders 0.9 and 2.0 with respect to initiator and monomer, respectively, and their data points show considerable scatter. They also report an activation energy for the reaction; however, this activation energy was calculated from the wrong values for the orders and is unreliable. Skushnikova et al.⁶ studied the kinetics of ho-

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mopolymerization of VI as a function of solvent nature. For the polymerization in ethanol they reported orders of 0.53 with respect to initiator and 1.5 with respect to monomer. However, they presented no data to substantiate their claim. Hence, there is no way to check the validity of their conjecture. The values of $k_p/k_t^{1/2}$ and activation energies reported by them would be based on their values for the orders. Therefore, it is not possible to check their validity either. Konsulov⁷ studied the homopolymerization of VI in water. According to him, the initial rates of polymerization of VI in water can be represented by the equation

$$R_p = k_m [I]^{0.6} [VI]^{2.0} \quad (1)$$

where R_p is the rate of polymerization, $[I]$ is the initiator concentration, and $[VI]$ is the 1-vinylimidazole concentration.

Once again, from his data, the order with respect to monomer appears to be 1.7 rather than 2.0. There is no way to check the order with respect to initiator as no results are presented.

The study reported by Bamford and Schofield⁸ is the first significant work on the homopolymerization of VI. They found that the polymerization of VI does not follow the classical scheme for free-radical vinyl polymerization. They proposed a degradative addition reaction between propagating radicals and monomer molecules. Although they have not attempted to isolate the products of the proposed reaction, they have presented rate data that make a strong case for their proposed mechanism.

This paper describes a detailed study of the photoinitiated homopolymerization of VI in methanol. 2,2'-Diethoxyacetophenone was used as the photoinitiator. A few experiments were done with two other aromatic carbonyl-type photoinitiators.

EXPERIMENTAL

Materials. 1-Vinylimidazole (BASF) was purified by vacuum distillation (95°C/10 mm Hg). Benzoin methyl ether (Polyscience) was recrystallized from *n*-heptane, and benzoin isopropyl ether (Polyscience) was recrystallized from petroleum ether (bp 30–75°C). 2,2'-Diethoxyacetophenone (DEAP) (Polyscience) and methanol were reagent grade chemicals, used as received. Water was deionized and then distilled in all-glass still.

Techniques. The course of polymerization was followed by standard dilatometry. The details of experimental procedures and data treatments were reported previously.⁹ As noted in Ref. 9, it was not necessary to degas the reaction mixture with freeze-thaw cycles. Simply bubbling nitrogen through the reaction mixture kept about 10°C higher than the reaction temperature for about 5 min was sufficient. The induction periods were 2–3 min.

RESULTS AND DISCUSSION

The raw data in each experiment consist of a set of meniscus levels in the capillary (cm) vs. time (s) points. Four sets of data (Fig. 1) for polymerization of VI in methanol illustrate a typical feature, namely, dead-end polymerization (incomplete conversion). This is in marked contrast to the behavior of 1-

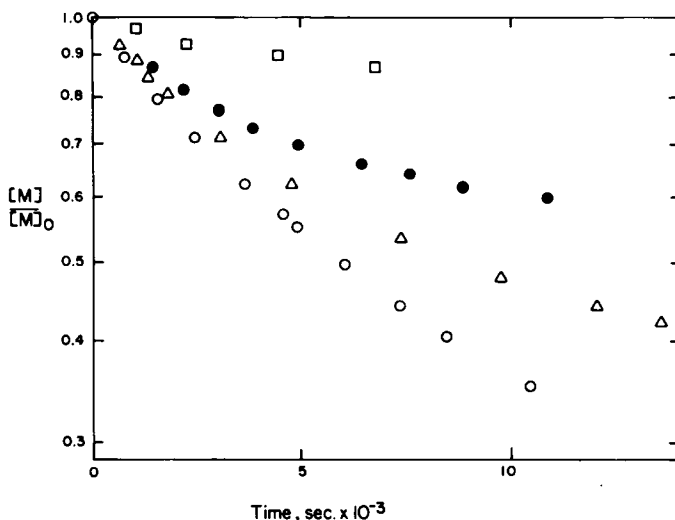


Fig. 1. Plots of fraction of monomer remaining vs. time for VI in methanol at 30°C. $[M]_0 = 0.25$ mol/L; initiator: DEAP; $[S]_0 = 1.00$ (\square), 5.00 (\bullet), 10.0 (Δ), and 25.0 (\circ) mmol/L.

vinyl-2-methylimidazole (MVI),⁹ with which nearly complete conversions are often obtained. Dead-end polymerization is a natural consequence of the slow propagation rate of VI compared to that of MVI. With VI, owing to slow prop-

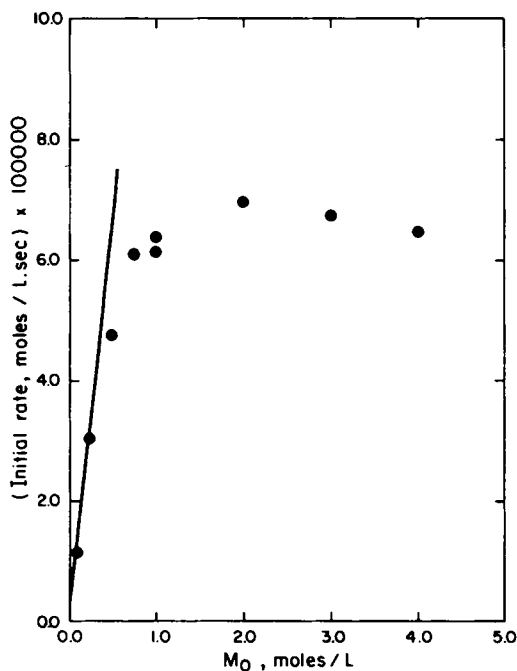


Fig. 2. Dependence of initial rate on initial monomer concentration for VI in methanol at 30°C. Initiator: DEAP; $[S]_0 = 5.00$ mol/L.

agation, the initiator is depleted significantly before all the monomer can be converted.

Only initial rate data are reported here. The raw information of meniscus height vs. time was converted to monomer concentration vs. time by the equation

$$\Delta[M] = \frac{\Delta h \pi D^2}{4} \frac{1}{K} \frac{1000}{V} \quad (2)$$

where Δh is the change in the meniscus level in the capillary (cm), $\Delta[M]$ is the change in monomer concentration corresponding to Δh (mol/L), D is the diameter of the capillary (cm), K is the shrinkage factor for the polymerization of VI (mL/mol), and V is the volume of the reaction bulb (mL).

The shrinkage factor K for VI was determined by measuring the densities of monomer and polymer solutions of known concentrations. For the polymerization of VI, $K = 19.1$ mL/mol.

Dependence on Monomer Concentration. The variation of initial rate of polymerization R_{p0} of VI in methanol with the initial monomer concentration $[M]_0$ is shown in Figure 2. The polymerization of VI does not follow the classical relation for free-radical polymerization

$$R_p = -\frac{d[M]}{dt} = \frac{k_p}{(2k_t)^{1/2}} [M](R_i)^{1/2} \quad (3)$$

where R_p is the rate of polymerization, k_p and k_t are the propagation and termination rate constants, respectively, $[M]$ is monomer concentration, and R_i is the rate of initiation.

The general character of variation of R_{p0} with $[M]_0$ is similar to that observed by Bamford and Schofield. In our work there is no plateau (where R_{p0} becomes independent of $[M]_0$) at high $[M]_0$ because in photoinitiated polymerizations the rate of initiation decreases with increase in monomer concentration especially at high monomer concentrations whenever monomer absorbs light in the same wavelength range as the initiator. This is due to absorbance of light by monomer, which reduces the amount of light available to initiator and thus reduces the rate of initiation.

In the mechanism of Bamford and Schofield, the major modification to "standard" kinetics is in the introduction of a degradative chain addition to monomer



where it is assumed that the product radical $X \cdot$ does not add to monomer to start a new polymer chain. Now the usual material balances for the consumption of monomer and production of radical chains can be written.

The only significant consumption of monomer should be in the propagation step so that

$$R_p = -d[M]/dt = k_p [M \cdot] [M] \quad (5)$$

Radical chains $M \cdot$ are produced by initiation R_i and are consumed by degradative

addition to monomer [eq. (4)] and by quadratic termination. With the usual steady-state assumption,

$$d[\text{M}\cdot]/dt = 0 = R_i - k_{fm}[\text{M}\cdot][\text{M}] - 2k_t[\text{M}\cdot]^2 \quad (6)$$

Eliminating $[\text{M}\cdot]$ between eqs. (5) and (6) gives

$$2(k_t/k_p^2)(R_p/[\text{M}])^2 + (k_{fm}/k_p)R_p - R_i = 0 \quad (7)$$

The solution of this quadratic equation is

$$R_p = \frac{k_{fm}k_p}{4k_t} [\text{M}]^2 \left\{ \left(1 + \frac{8R_i k_t}{k_{fm}^2 [\text{M}]^2} \right)^{1/2} - 1 \right\} \quad (8)$$

At low monomer concentrations, the equation reduces to the familiar form

$$R_p = k_p \left(\frac{R_i}{2k_t} \right)^{1/2} [\text{M}] \quad (9)$$

At high concentrations, the equation becomes

$$R_p = (k_p/k_{fm})R_i \quad (10)$$

That is, at high concentrations, the rate should approach a constant value as long as the rate of initiation does not depend on $[\text{M}]$. This is usually the case for thermal initiation. But in photoinitiation, the rate of initiation R_i may depend on $[\text{M}]$ when the monomer absorbs light in the same wavelength range as the initiator.

For photoinitiated polymerizations the rate of initiation is given by

$$R_i = 2\Phi I_a \quad (11)$$

where I_a is the value in moles (einsteins) of light absorbed and Φ is the quantum yield for production of radicals. If monomer absorbs light in the same wavelength range as the initiator, I_a is given by

$$I_a = I_0 \left[\left(\frac{\epsilon_s [\text{S}]}{\epsilon_s [\text{S}] + \epsilon_m [\text{M}]} \right) \{ 1 - \exp(-\epsilon_s [\text{S}]l - \epsilon_m [\text{M}]l) \} \right] = I_0 A \quad (12)$$

where I_0 is the intensity of incident light, ϵ_s and ϵ_m are the molar absorptivities of initiator and monomer, respectively, l is the path length, and $[\text{S}]$ and $[\text{M}]$ are the initiator and monomer concentrations, respectively. Equation (12) defines A , which is a convenient symbol for the expression in the braces. Substituting eqs. (11) and (12) in eq. (7) gives

$$2 \left(\frac{k_t}{k_p^2} \frac{R_{p0}^2}{[\text{M}]^2} \right) + \left(\frac{k_{fm}}{k_p} \right) R_{p0} - 2\Phi I_0 A_0 = 0 \quad (13)$$

where A_0 is given by

$$A_0 = \left(\frac{\epsilon_s [\text{S}]_0}{\epsilon_s [\text{S}]_0 + \epsilon_m [\text{M}]_0} \right) \{ 1 - \exp(-\epsilon_s [\text{S}]_0 l - \epsilon_m [\text{M}]_0 l) \} \quad (14)$$

In eqs. (13) and (14) the subscript 0 indicates initial conditions except for I_0 , which is the intensity of incident light. Equation (13) shows that a plot of $R_{p0}/[\text{M}]^2$ vs. A_0/R_{p0} should be linear. Such a plot is shown in Figure 3, which contains data points from Figure 2 as well as Figure 4 (see next section). The plot is linear, but there is some scatter, which could be due to use of a constant

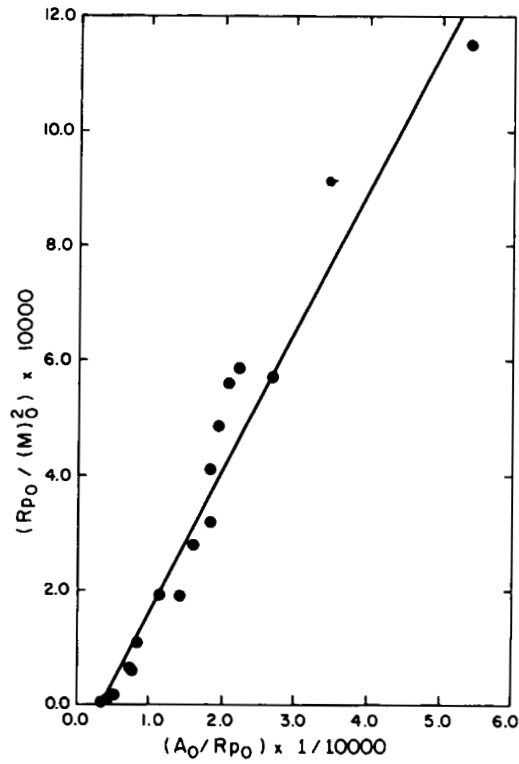


Fig. 3. Plot of $R_{p0}/[M]_0^2$ vs. A_0/R_{p0} [eq. (13)]. Monomer: VI; initiator: DEAP; $T = 30^\circ\text{C}$.

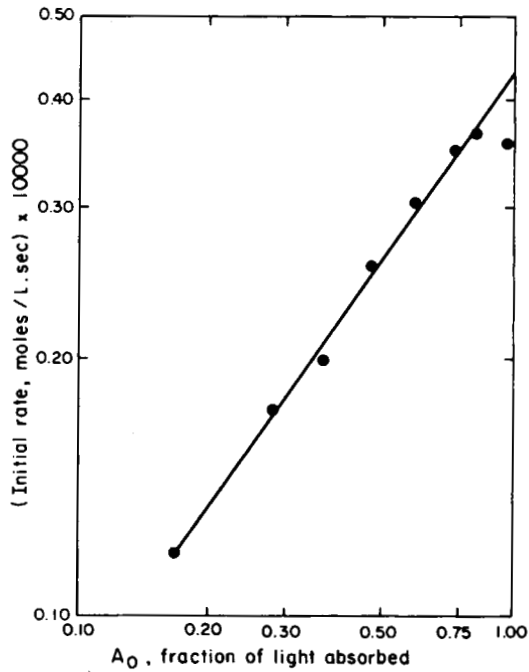


Fig. 4. Dependence of initial rate on the fraction of incident light absorbed by the initiator for VI in methanol at 30°C . $[M]_0 = 0.25$ mol/L; initiator: DEAP.

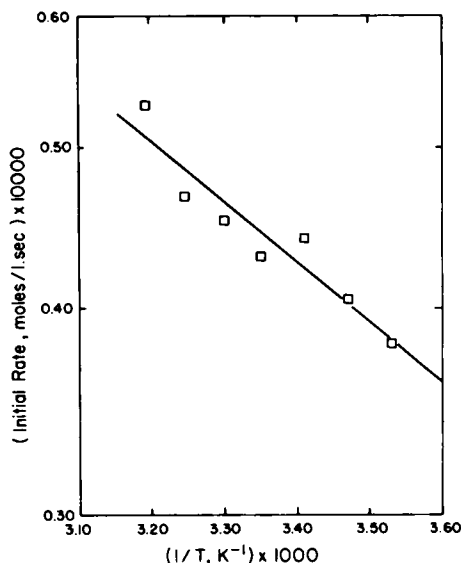


Fig. 5. Arrhenius plot for polymerization of VI in methanol. $[M]_0 = 0.5$ mol/L; initiator: DEAP; $[S]_0 = 5.00$ mmol/L.

value for molar absorptivity of monomer for concentrations from 0.25 to 4.0 mol/L. Deviations from Beer's law can be expected at high concentrations.

Dependence on Initiator Concentration. The expression for the rate of polymerization of VI [eq. (7)] reduces to the classical expression [eq. (9)] at low monomer concentrations. Our experiments show that the initial rate of polymerization of VI increases linearly with initial monomer concentration $[M]_0$ up to $[M]_0 = \sim 0.25$ mol/L. Hence we decided to investigate the dependence of rate of polymerization of VI on initiator concentration at initial monomer concentration of 0.25 mol/L. As was indicated earlier,¹⁰ in photoinitiated polymerizations the appropriate way to find out the dependence on initiator concentration is to see the variation of rate with the fraction of incident light absorbed by the initiator. Equation (12) shows that the fraction of incident light absorbed by the initiator is equal to A ; thus we should look at the variation of rate with A . Figure 4 is a plot of $\ln(R_{p0})$ vs. $\ln(A_0)$. The plot is linear, but the slope is 0.72 instead of 0.5. A slope of 0.5 would have resulted if the classical expression for free-radical polymerization was valid at the monomer concentration of 0.25 mol/L. In the plateau region (high monomer concentration) the expression for the rate of polymerization reduces to eq. (10). In other words, at high monomer concentration the slope of the plot of $\ln(R_{p0})$ vs. $\ln(A_0)$ will be 1.0. Thus it is possible that a monomer concentration of 0.25 mol/L is in the transition zone between the linear and plateau regions. It is also possible that the expression for R_p developed by Bamford and Schofield is not valid for the polymerization of VI in methanol, owing to complications such as active-center deactivation by chain transfer to solvent.

Activation Energy. We determined the overall activation energy for the photoinitiated polymerization of VI by carrying out the polymerizations at various temperatures between 10°C and 40°C. Figure 5 shows the Arrhenius

TABLE I
 Comparison among Various Initiators^a

Initiator	Concn [S] ₀ (mmol/L)	Absorbance (1 - e ^{-c[S]₀l})	R _{p0} × 10 ⁵	Φ _i /Φ _{DEAP}
DEAP	5.00	0.64	3.04	1.0
BME	1.80	0.64	1.80	0.35
BIPE	1.47	0.64	1.43	0.21

^a [M]₀ = 0.25 mol/L; T = 30°C; solvent = MeOH.

plot. The activation energy is quite low, 1.5 kcal/mol. The plot shows some scatter; hence one cannot put much confidence in the exact value. It is clear, however, that the rate of photoinitiated polymerization of VI is relatively insensitive to temperature variation. The experiments reported in Figure 5 were carried out at an initial monomer concentration of 0.5 mol/L. If the mechanism proposed by Bamford and Schofield is accepted, the initial rate of polymerization of VI at the initial monomer concentration of 0.5 mol/L is given by eq. (8).

From eq. (8) it is evident that we cannot equate the measured overall activation energy to $(\Delta E_p - \Delta E_t/2)$ as we did for photoinitiated polymerization of MVI.⁹ The overall activation energy will be given by a complex expression that will contain not only activation energies for various reactions but the frequency factors also.

Comparison of Initiators. In Ref. 9 we referred to the controversy about the efficiency of various benzoin derivatives. In a few experiments, we compared three initiators, BME, BIPE, and DEAP (Table I). Again, the efficiencies are in the order DEAP > BME > BIPE, but the efficiency of BIPE is not much lower than that of BME. In the photoinitiated polymerization of MVI, the efficiency of BIPE was much lower than that of BME. The initiators are compared at constant absorbance rather than at constant concentration, as pointed out earlier.⁹

Estimation and Correlation of Molecular Weights. As mentioned previously, the polymerization of VI did not go to completion in most of the experiments. The residual monomer could not always be removed completely, owing to its adsorption on the polymer. This complicated the recovery of the polymer samples. In some cases the polymer did not precipitate out properly, as a colloidal suspension was obtained. This occurred more often with polymer samples obtained with high initial monomer concentration, as they contained relatively more residual monomer. Sometimes a portion of the polymer sample was lost. All these factors have made the correlation of molecular weight with the conditions of polymerization not satisfactory.

Poly(VI) is a polyelectrolyte, and the viscosity plots (reduced viscosity vs. concentration) of its solutions in various solvents show concave-upward curvature typical of many polyelectrolyte solutions. Tan and Sochor¹¹ circumvented the problem of curvature in the viscosity plots by adding neutral salts to the solution of poly(VI). They also reported the Mark-Houwink relationship for the polymer in various solvents and stated that a 0.01M solution of tetrabutylammonium bromide (TBABr) in methanol is a good solvent for the polymer. Hence it was used for viscosity measurements. The measurement of reduced viscosity as a

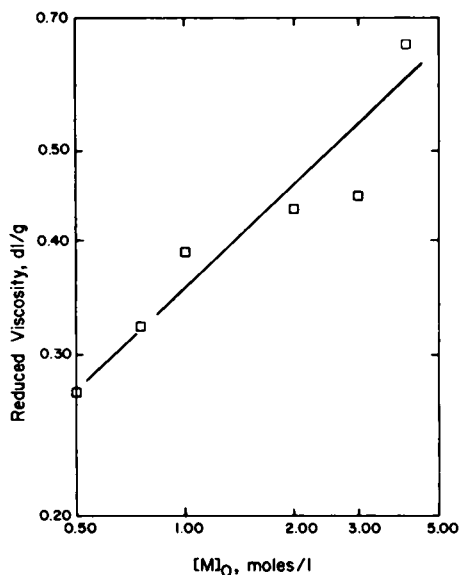


Fig. 6. Variation of molecular weight of final polymer sample with initial monomer concentration. Monomer: VI; initiator: DEAP; $[S]_0 = 5.00$ mmol/L; $T = 30^\circ\text{C}$; solvent: methanol.

function of concentration yielded a value of almost zero for the Huggins constant. Tan¹² obtained 0.441 for the same constant. This casts doubts on the reliability of extrapolation to infinite dilution and the calculation of intrinsic viscosity. Therefore, we decided to use the value of reduced viscosity of the polymer samples at a fixed concentration (2.0 g/dL) as a qualitative measure of the mo-

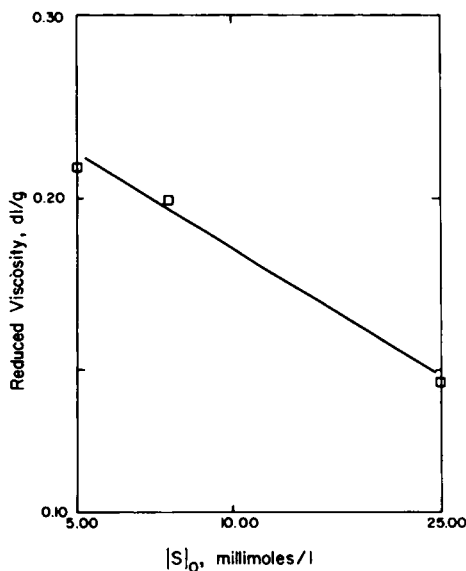


Fig. 7. Variation of molecular weight of final polymer sample with initial initiator concentration. Monomer: VI; $[M]_0 = 0.25$ mol/L; initiator: DEAP; solvent: methanol; $T = 30^\circ\text{C}$.

lecular weight. The variations of reduced viscosity of the recovered polymer samples with initial monomer concentration and initial initiator concentration are shown in Figures 6 and 7, respectively. These results show the qualitative trends expected from the theoretical considerations.

CONCLUSIONS

The photoinitiated polymerization of 1-vinylimidazole (VI) does not follow the classical kinetic scheme for free-radical polymerization. Kinetic results for VI suggest a degradative addition reaction between the macroradical and the monomer molecule to produce a relatively stable, unreactive radical that does not reinitiate polymerization readily. The overall activation energy for the photoinitiated polymerization of VI is low, 1.5 kcal/mol. Among the three aromatic carbonyl-type photoinitiators tried, 2,2'-diethoxyacetophenone (DEAP) has the highest quantum efficiency for initiating the polymerization of VI. Of the other two photoinitiators, benzoin methyl ether (BME) is more efficient than benzoin isopropyl ether (BIPE). Under the experimental conditions used, the polymerization of VI does not proceed to complete conversion, and the phenomenon of dead-end polymerization is observed.

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