

# The Kinetics of Photoinitiated Polymerization of 1-Vinyl-2-Methylimidazole

MAKARAND G. JOSHI and FERDINAND RODRIGUEZ, *School of Chemical Engineering, Cornell University, Ithaca, New York 14853*

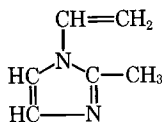
## Synopsis

The kinetics of isothermal, photoinitiated, solution polymerization of 1-vinyl-2-methylimidazole (MVI) was studied using the standard dilatometric technique. The photoinitiators used were aromatic carbonyl compounds. Most of the experiments were carried out using methanol as solvent, but other solvents were also used. The reaction follows the classical kinetic scheme for free radical polymerization. The activation energy for the polymerization is 3.9 kcal/mol. The polymerization is greatly accelerated by the presence of water in reaction medium. Among the three photoinitiators tried, 2,2'-diethoxyacetophenone (DEAP) has the highest quantum efficiency for the polymerization of MVI.

## INTRODUCTION

Polymers and copolymers containing the imidazole ring exhibit interesting properties. For example, catalysis by these polymers of the solvolysis of phenyl esters exhibits features characteristic of enzymatic reactions.<sup>1-3</sup> Many are water soluble and can form complexes with a variety of substances including metal ions.<sup>4-6</sup> It is possible to make strong ion exchange resins using them.<sup>7,8</sup> Consequently, these polymers find many applications in diverse fields such as photography,<sup>9-11</sup> textiles,<sup>12,13</sup> papermaking,<sup>14</sup> dyes,<sup>15</sup> adhesives,<sup>16</sup> and organic reaction catalysis.<sup>17,18</sup> Nevertheless, the kinetics of polymerization of these compounds has not been investigated extensively.

A few investigators<sup>19-22</sup> have reported the polymerization of 1-vinyl-2-methylimidazole (MVI) under various conditions. However, no attempts have been made to evaluate the kinetic parameters:



1-vinyl-2-methylimidazole

In the present work, the photoinitiated polymerization of MVI was studied using a standard dilatometric technique. The rate equation for the reaction was developed, and the effect of various solvents on the rate of the reaction was investigated. Three different photoinitiators were tried, and their efficiency in initiating the polymerization was compared.

## EXPERIMENTAL

1-Vinyl-2-methylimidazole was purified by vacuum distillation (90°C/10 mm Hg). Benzoin methyl ether (BME) was recrystallized from *n*-heptane, and benzoin isopropyl ether (BIPE) was recrystallized from petroleum ether (bp 30–75°C). 2,2'-Diethoxyacetophenone (DEAP), methanol, and ethanol were reagent-grade chemicals and were used as received without any further purification. The water used was distilled twice. The second distillation was carried out in an all-glass still.

The dilatometer (Fig. 1) is made from Pyrex glass. The reaction bulb is constructed by fusing two flat 3.175 mm ( $\frac{1}{8}$  in.) thick Pyrex plates (not optically smooth) to a 25.4 mm (1-in.) length of 50.8 mm (2-in.) diameter tube. To the top of this "lollipop"-shaped reaction vessel, a 304.8 mm (12-in.) length of 1 mm inside diameter, precision-bore, graduated capillary tubing is fused. The other parts of the dilatometer are the filling bulb and the tube for loading the dilatometer with the reaction mixture, and a port which allows a small magnetic stirring bar to be placed in the bulb. The stopcock on the filling tube has a Teflon plug and is attached close to the reaction bulb in order to eliminate dead space. Likewise, the plug for the port is closed at the inner end so that there is no stagnant liquid inside it when it is inserted. The volume of the reaction bulb is  $45.85 \pm 0.05$  mL at 30°C when it contains the stirring bar. The least count of the graduations on the capillary is 1 mm. The total useful length of the capillary is 285 mm. During an experiment the dilatometer is placed in a constant temperature bath. The temperature of the bath is controlled within  $\pm 0.01^\circ\text{C}$  of the set value. The water in the bath is well stirred and is checked for its UV absorbance at regular intervals. The UV absorbance has been found to be negligible at all times. The constant temperature bath has a window made of 6.35-mm (0.25-in.) thick Pyrex glass. The reaction bulb is kept parallel to the window. The light source is a 100-W Osram superpressure mercury lamp. Light from the lamp is collimated using a 50-mm-diam double convex lens with a focal-length of 81 mm. The source is kept at the focus of the lens to produce a parallel beam.

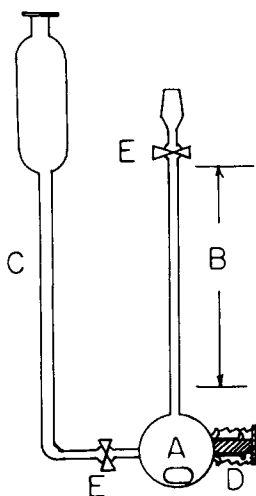


Fig. 1. Front view of dilatometer with: (A) reaction bulb; (B) graduated capillary tube; (C) capillary filling tube; (D) plug, and (E) Teflon stopcocks.

The intensity of the collimated beam is checked by a UV light meter before each experiment and has been found to vary slightly, but not enough to change the observed rates significantly. Hence the rates reported here have not been corrected for the changes in the light intensity.

The dilatometer was purged with nitrogen for 20–30 min before loading it with the reaction mixture. Nitrogen was bubbled through the reaction mixture kept at a temperature at least 5–10°C above the reaction temperature for 5 min. The time at higher temperature did not exceed 8 min in any experiment. The reaction mixture was poured into the filling bulb of the dilatometer immediately after bubbling nitrogen through it and while the dilatometer was still being purged with nitrogen. Nitrogen was bubbled through the reaction mixture in the filling bulb for 1 min and then the mixture was allowed to flow into the reaction bulb by gravity. No appreciable induction period was observed by following this procedure. At no time the induction period was more than 2–3 min. High vacuum techniques were not necessary.

## RESULTS AND DISCUSSION

The change in volume of mixture during the course of polymerization is used as a quantitative measure of monomer being converted to polymer. The change in monomer concentration can be calculated from the change in the height of meniscus in the capillary attached to the reaction bulb using the expression

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

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

When the change in the height of meniscus in the capillary with time is recorded, the monomer concentration vs. time data can be obtained by using eq. (1) and the value of the initial monomer concentration.

If we assume the usual radical termination processes and the steady state, the rate of polymerization is given by

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

where  $k_p$  = the rate constant for the propagation reaction,  $k_t$  = the rate constant for the termination reaction,  $R_i$  = the rate of radical production, and  $[M]$  = the monomer concentration. Recently it has been shown<sup>23</sup> that the rate of radical production in photoinitiated polymerizations using initiators with high molar absorptivity is more accurately represented by

$$R_i = 2\Phi I_0 (1 - e^{-\epsilon[S]l}) \quad (3)$$

where  $\Phi$  = the quantum yield for radical production,  $I_0$  = the intensity of the incident light,  $\epsilon$  = the molar absorptivity of the initiator,  $[S]$  = the initiator concentration, and  $l$  = the path length in the system. Equations (2) and (3) can be combined to give

$$R_p = \frac{k_p}{k_t^{1/2}} [\Phi I_0 (1 - e^{-\epsilon[S]l})]^{1/2} [M] \quad (4)$$

In many instances eq. (4) is found to hold with minor modifications. For example, the power on monomer concentration may be different from 1.0.

### DEPENDENCE ON MONOMER CONCENTRATION

The initial rate of polymerization of MVI was studied over monomer concentration range of 0.1–1.0 mol/L. The plot of log (initial rate) vs. log (monomer concentration) (Fig. 2) was linear with a slope of 0.94 which is in nominal agreement with eq. (4). Once the order with respect to the monomer concentration is established, eq. (4) can be integrated. If it is assumed that the rate of radical production remains constant, then the integration yields

$$-\ln \frac{[M]}{[M]_0} = \frac{k_p}{k_t^{1/2}} [\Phi I_0 (1 - e^{-\epsilon[S]_0 t})]^{1/2} t \quad (5)$$

or

$$-\ln \frac{[M]}{[M]_0} = kt \quad (6)$$

where the subscript 0 indicates initial conditions (except for intensity).

Figure 3 shows the plot of  $\ln [M]/[M]_0$  vs. time for a few experiments with identical initial initiator concentrations but different initial monomer concentrations. The plot of  $\ln [M]/[M]_0$  vs. time is linear in most of the cases up to 60–70% conversion. This confirms the order with respect to monomer and also shows that the rate of radical production does indeed remain constant over the time scale under consideration. The data points for all experiments lie on the same line. This is very significant as it indicates that the rate of radical production is the same for all cases.

The variations in the slope  $k$  of the linear section of the plot of  $\ln[M]/[M]_0$  against time can be used to determine the dependence of rate on initiator concentration and the activation energy. This procedure is much better than using the initial rate which is more susceptible to inaccuracies, especially in the dilatometric technique. Hence this method was used to examine the effects of different variables on the rate. Similar results were obtained by using the initial rate, but there was much less scatter when the slope  $k$  was used.

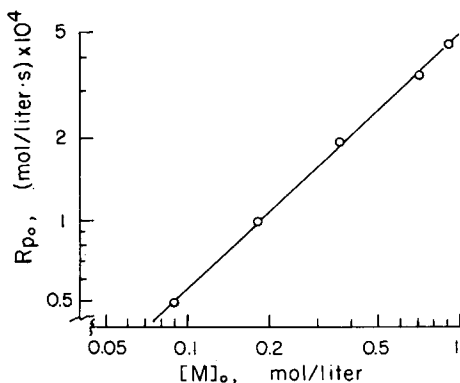


Fig. 2. Dependence of initial rate  $R_{p0}$  on monomer concentration with DEAP  $[S]_0 = 5.09$  mmol/L and  $T = 30^\circ\text{C}$ .

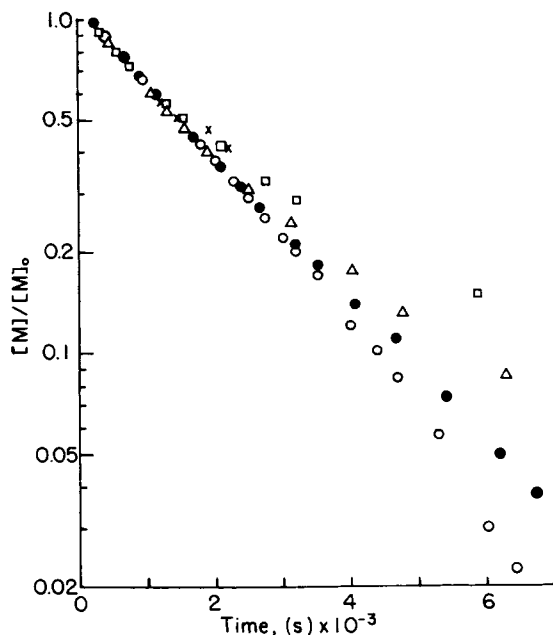


Fig. 3. Course of polymerization with DEAP  $[S]_0 = 5.09$  mmol/L and  $T = 30^\circ\text{C}$ . Monomer concentrations (mol/L) are: 0.1 ( $\square$ ); 0.2 ( $\Delta$ ), 0.4 ( $\times$ ); 0.75 ( $\bullet$ ); and 1.0 ( $\circ$ ).

### DEPENDENCE ON INITIATOR CONCENTRATION

In the past, investigators have tended to plot the initial polymerization rate vs. initiator concentration raised to 0.5 with the hope that a straight line would be obtained. In many cases their plots have shown marked curvature.<sup>24,25</sup> A straight line will be obtained only when the rate of radical production can be approximated by

$$R_i = 2\Phi I_0 \epsilon [S] l \quad (7)$$

As was shown recently,<sup>23</sup> this approximation is only valid for initiators with low molar absorptivity and at low initiator concentrations. From eq. (4) it can be seen that a more appropriate way to analyze data would be to plot  $\log$  (initial rate) vs.  $\log$  (absorbance) in the system or, as was pointed out earlier, a still better way would be to plot  $\log k$  vs.  $\log$  (absorbance). Ideally, a straight line with a slope of 0.5 should result. The polymerization of MVI using DEAP as initiator was carried out at various initiator concentrations. A straight line with a slope of 0.61 is obtained (Fig. 4). It can be shown that a slope greater than 0.5 will result if monomer and polymer also absorb UV light in the same region as the initiator. This is because monomer and polymer absorb some of the incident light and reduce the rate of radical production. This effect is more acute at low initiator concentrations than at high end. This leads to increase in the slope observed. Both MVI and poly(MVI) absorb UV light in the range of wavelengths used. The plot of  $\ln k$  vs.  $\ln[S]_0$  (Fig. 5) does not yield a straight line. It should be noted that the section of the plot at low initiator concentrations is linear with a slope around 0.45.

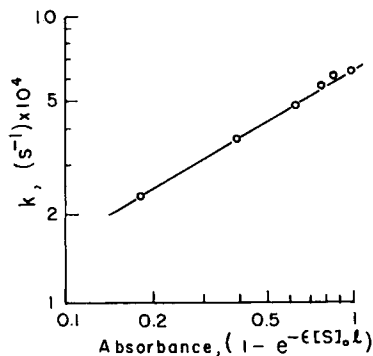


Fig. 4. Dependence of  $k$  [eq. (6)] on absorbance for  $[M]_0 = 0.25$  mol/L at 30°C. Molar absorptivity for DEAP at 325 nm is 80.2 L/mol-cm.

### THE ACTIVATION ENERGY

The overall activation energy for the photoinitiated polymerization of MVI was determined by carrying out polymerizations at various temperatures between 10°C and 35°C. The overall activation energy for the polymerization was found to be 3.9 kcal/mol (Fig. 5). This value compares well with the activation energy for photoinitiated polymerization of acrylamide<sup>26</sup> (1.5 kcal/mol) and *N*-vinyl-

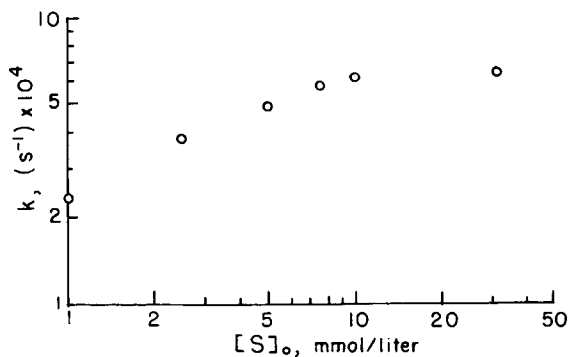


Fig. 5. Variation of  $k$  [eq. (6)] with initial initiator concentration for  $[M]_0 = 0.25$  mol/L at 30°C.

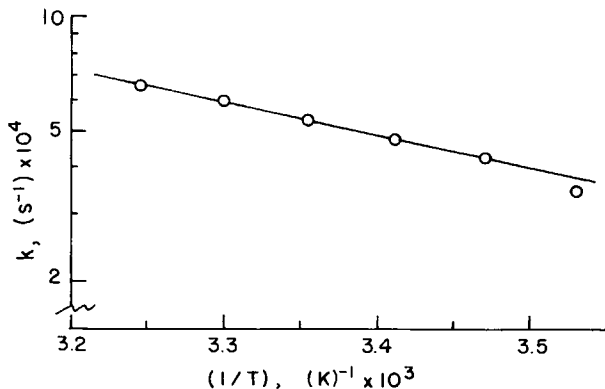


Fig. 6. Arrhenius plot for  $[M]_0 = 0.25$  mol/L and  $[S]_0 = 4.96$  mmol/L. The activation energy of 3.90 kcal/mol is based on a correlation that neglects the  $k$  at 10°C.

pyrrolidinone<sup>27,28</sup> (5.9–6.2 kcal/mol). Unlike thermal production of radicals, photochemical production of radicals is not highly temperature-dependent. This results from the fact that quantum yield  $\Phi$  does not depend strongly on temperature. In photoinitiated polymerization the overall activation energy is given by

$$\Delta E_a \cong \Delta E_p - \frac{1}{2} \Delta E_t \quad (8)$$

where  $\Delta E_p$  and  $\Delta E_t$  are the activation energies for propagation and termination reactions, respectively. The activation energy for the propagation reaction is often about 7 kcal/mol.<sup>29</sup> The termination could be by coupling and/or by disproportionation. Termination by disproportionation has much higher activation energy, but coupling of chain radicals has a low activation energy. Thus, if the termination occurs by disproportionation, a relatively low overall activation energy would be expected for photoinitiated polymerizations.

### THE EFFECT OF SOLVENT

Recently much attention has been paid to the effect of solvent on the rate of polymerization of ionizable monomers with functional groups which can react with a solvent, especially those which form hydrogen bonds.<sup>30–32</sup> Konsulov<sup>32</sup> reported that the rate of polymerization of 1-vinylimidazole was appreciably increased by addition of small amounts of water. A maximum in the rate was observed when a equimolar mixture of water and the monomer was used. In order to investigate similar effects in the case of MVI, polymerizations were carried out using various solvents (Table I). The rate is increased greatly by the presence of water. There is not much difference between the rates when MeOH or EtOH is solvent. It was not possible to carry out polymerization using only water as the solvent since the initiator is not soluble in pure water. More work is necessary to understand the effect of solvent on the rate. The fact that poly(MVI) is soluble only in a few common solvents limits the range of solvents that can be used.

### COMPARISON BETWEEN VARIOUS INITIATORS

Osborn and Sandner<sup>33</sup> found that DEAP was more efficient than benzoin alkyl ethers in their study of curing of acrylate ester coatings. On the other hand, Ledwith<sup>34</sup> observed DEAP to be much less efficient than benzoin methyl ether

TABLE I  
Effect of Solvent on Kinetics<sup>a</sup>

Monomer concn [M] <sub>0</sub> (M)	Initiator concn [S] <sub>0</sub> (mM)	Solvent <sup>b</sup>	$k \times 10^4$ (s <sup>-1</sup> )
0.5	5.35	MeOH	6.09
0.5	5.29	75% H <sub>2</sub> O—25% MeOH	15.53
0.5	5.33	90% H <sub>2</sub> O—10% MeOH	13.00
0.25	6.00	MeOH	6.02
0.25	5.90	75% H <sub>2</sub> O—25% MeOH	19.93
0.25	5.63	EtOH	5.71

<sup>a</sup>  $T = 30^\circ\text{C}$  for all experiments. Subscript 0 indicates initial conditions.

<sup>b</sup> Percentages are vol %.

TABLE II  
 Comparison between Various Initiators<sup>a</sup>

Initiator	Concn [S] <sub>0</sub> (mM)	Absorbance (1 - e <sup>-ε[S]<sub>0</sub>l</sup> )	k × 10 <sup>4</sup>	φ <sub>i</sub> /φ <sub>DEAP</sub>
DEAP	5.38	0.86	5.23	1.0
BME	1.80	0.86	2.14	0.246
BIPE	1.43	0.86	1.63	0.097

<sup>a</sup> [M]<sub>0</sub> = 0.25M, T = 30°C, and solvent = MeOH for all the three experiments.

(BME) for polymerization of methyl methacrylate in bulk at 30°C. Ledwith speculated that the apparent lower efficiency of DEAP in solution studies might result from increased self-quenching in the case of DEAP as compared with BME. It was also proposed by him that the discrepancy between his results and those reported by Osborn and Sandner could be due to basic differences between his system (solution polymerization) and their system (film curing). A few experiments were carried out to study the relative efficiencies of these initiators for polymerization of MVI. Since the initiators have molar absorptivities (Table II) that differ by as much as fourfold, they are best compared at constant absorbance, (1 - e<sup>-ε[S]<sub>0</sub>l</sup>), rather than at constant concentration. The results are presented in Table II. The values of φ<sub>i</sub>/φ<sub>DEAP</sub> were calculated from the values of k in eq. (6). In these experiments the monomer concentration and the absorbance in the system were held constant. Thus, the ratio of k values for two initiators i and DEAP is

$$(k_i/k_{\text{DEAP}})^2 = (\phi I_0)_i / (\phi I_0)_{\text{DEAP}} \quad (9)$$

If I<sub>0</sub> is assumed to be constant, then

$$\phi_i / \phi_{\text{DEAP}} = (k_i/k_{\text{DEAP}})^2 \quad (10)$$

It is evident that DEAP is a much more efficient initiator for polymerization of MVI than BME or BIPE. In the present work the system employed is quite similar to that used by Ledwith, but the results are very different. Hence the differences in the experimental system may not be the major reason for the difference in the efficiencies observed. Osborn and Sandner have indicated that DEAP does not undergo α-cleavage but rather follows Norrish Type II photochemistry. It could be that photodecomposition of DEAP follows different pathways in different systems (monomer and solvent). Evidently more research needs to be done in this area.

## CONCLUSIONS

The photoinitiated polymerization of MVI follows conventional kinetics. The polymerization is greatly accelerated by the presence of water in the reaction medium. It is possible that, in the presence of water, monomer molecules form short hydrogen-bonded chains which make the continuation of kinetic chain more favorable and lead to an increase in the observed rate of polymerization. Out of three initiators investigated, DEAP was found to have the highest quantum efficiency for the polymerization of MVI. The rate of radical production appears to remain constant until at least 50% of the monomer is converted to polymer. More research work is necessary to understand these phenomena in a better way.



The authors wish to thank the Eastman Kodak Co. for financial support of this project.

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Received November 12, 1982

Accepted February 17, 1982