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## AIBN-Initiated Polymerization of Methyl Methacrylate in Pyridine

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### ABSTRACT

The AIBN-initiated polymerization of methyl methacrylate in pyridine at 50°C proceeds to higher conversion than that carried out in bulk. The increased values of the overall rate constant are due to the increased values of the initiation rate constant. The overall activation energy (13.1 kcal/mole monomer) and the activation energy for initiator decomposition (12.6 kcal/mole) are lower than those given in the literature. In addition to anomalies of the kinetic and energetic parameters, an increase in the frequencies of the  $\gamma$ -skeletal modes (5-20  $\text{cm}^{-1}$ ) of methyl methacrylate on its mixing with pyridine (molar ratio 1:1.33) is also observed. At this ratio, an increase in the band strength of the methyl methacrylate  $\nu(\text{C}=\text{O})$  vibrations is also observed. The most plausible explanation of the obtained anomalies in the polymerization of methyl methacrylate in pyridine (6.215-7.991 mole/liter) is the formation of a weak complex which affects the initiation step. The values of  $k_p/k_t^{1/2} = 0.24$ ,  $E_p = 1/2 E_t = 6.8$  kcal/mole, and  $E_p \approx 6.8$  kcal/mole do not differ much from the values in literature. The average value of the transfer

constant for pyridine in methyl methacrylate polymerization at 50°C is about  $1 \times 10^{-4}$ . The activation energy for the transfer to pyridine is 22.4 kcal/mole. Abstraction of a hydrogen atom from every pyridine carbon atom is possible in the transfer reaction of poly(methyl methacrylate) radical to pyridine. This is possible in greatest degree in the  $\alpha$  and  $\gamma$  positions.

## INTRODUCTION

The character of the interaction between a growing radical and its medium is not yet clear. In many cases anomalous values for the kinetic parameters are explained by formation of a complex in the reaction medium.

Data about the AIBN-initiated polymerization of methyl methacrylate in pyridine are not available in the literature. The present study was undertaken in order to study some peculiarities of the radical polymerization of methyl methacrylate in pyridine.

Poly(methyl methacrylate) radical is an electron acceptor [1, 2]. A free electron pair on the nitrogen atom and a system of  $\pi$  bonds are characteristic of the pyridine molecule. The latter is able to form molecular complexes [3]. Hence, pyridine acts as an electron donor or proton acceptor [4]. It is a polar compound. The negative charge of the dipole is concentrated on the nitrogen atom, while carbon atoms are positively charged.

The AIBN-initiated polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate in benzene was studied by Burnett and Loan [5], who observed that the rate of polymerization decreases with the increase of solvent concentration in a concentration limit, characteristic of the monomer. In the polymerization of vinyl acetate in benzene low values of the overall polymerization rate were explained by the formation of a complex between the growing radical and benzene [6]. This complex is comparatively inactive in the propagation reaction. Such retardation was observed also in the AIBN-initiated polymerization of styrene in carbon tetrabromide [7]. The polymerization of methyl methacrylate in halogenated benzenes and in naphthalene at 60°C in the presence of AIBN [8-10] was studied by Burnett and co-workers. It was found that the polymerization rate is higher than in cases when the solvent acts as an inert diluent. Burnett and co-workers [11] suggested that three macro-radical species may contribute to propagation in methyl methacrylate polymerization: an uncomplexed species, a species complexed with solvent, and a species complexed with monomer.

Initiated polymerization of methyl methacrylate is possible under the action of initiation systems such as pyridine. For example, the system pyridine (electron donor)-liquid  $\text{SO}_2$  (electron acceptor)- $\text{CCl}_4$  initiates at usual and elevated temperatures [12, 13]. This initiation is of radical character. Another example is the system poly-2-vinylpyridine (polymer electron donor)-liquid  $\text{SO}_2$  (electron acceptor)- $\text{CCl}_4$  [13]. In this case the polymerization also proceeds through intermediate products with a radical character. In methyl methacrylate polymerization initiated with low concentrations of  $\text{SO}_2$ , the influence of pyridine is higher [14] than that of other solvents. Pyridine in low concentrations accelerates the polymerization of methyl methacrylate initiated by trialkylborane in the presence of oxygen at  $30^\circ\text{C}$ . Moreover, the accelerating influence of pyridine is higher than that of quinoline and pyrrole. The polymerization proceeds by a radical mechanism and a participation of peroxides is supposed.

### EXPERIMENTAL

Pyridine was of ultraviolet spectroscopy grade (Lachema, Brno).

The purification of monomer and evacuation of reaction mixtures were the same as described in our previous papers [15-17]. The polymerization experiments were carried out in sealed glass ampoules and dilatometers. Polymerization of methyl methacrylate was carried out in an ultrathermostat. The polymer was isolated from the polymerization mixture by quantitative precipitation in a 20-fold amount of cyclohexane [18]. The poly(methyl methacrylate) obtained was separated from cyclohexane solution by filtration, dried at about  $70^\circ\text{C}$  in vacuo for 2 hr [19] and thereafter to constant weight. The degree of conversion was determined by weight determination of polymer obtained from each ampoule and dilatometer. The overall polymerization rate  $R_p$  (in mole/liter-sec) was calculated from Eq. (1):

$$R_p = [\text{Polymer}]/M_m vt \quad (1)$$

where  $M_m$  is the molecular weight of the monomer,  $v$  is the volume of the solution before the polymerization (in liters), and  $t$  is time (in seconds).

The volume contraction of the reaction mixture was determined in dilatometers. The monomer conversions to polymer at given time intervals  $R_c$  were calculated from Eq. (2):

$$R_c = (R_c' / \Delta V') \Delta V \quad (2)$$

where  $R_c'$  is the monomer conversion to polymer at the end of the polymerization (in %),  $\Delta V'$  is the volume contraction of the reaction mixture at the end of the polymerization (in ml), and  $\Delta V$  is the volume contraction of the reaction mixture in the definite time intervals (in ml).

The results obtained from Eq. (2) correspond with those obtained by weight determinations.

The kinetic order in monomer was calculated by numerical and graphical solutions of the relation

$$R_p = K [I]^{1/2} [M] \quad (3)$$

The overall rate constant  $K$  (in liter/mole-sec) was calculated from Eq. (3).

The intrinsic poly(methyl methacrylate) viscosity was determined in benzene solution at  $30 \pm 0.02^\circ\text{C}$ .

The number-average molecular weight  $\bar{M}_n$  of poly(methyl methacrylate) was calculated from Eq. (4) [20].

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76} \quad (4)$$

The chain-transfer constant of pyridine  $C_s$  in AIBN-initiated polymerization of methyl methacrylate was calculated by graphical solution of the relation (5)

$$1/\bar{P}_n = (1/\bar{P}_0) + C_s ([S]/[M]) \quad (5)$$

where  $[M]$  is the initial monomer concentration and  $[S]$  is solvent concentration.

The values  $1/2(1 + \lambda) k_t/k_p^2$  were calculated by Eq. (6) by using the values for  $C_s$  from Eq. (5) at a definite  $[S]/[M]$  ratio.

$$\frac{1}{\bar{P}_n} = \frac{1}{2} (1 + \lambda) \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_m + C_s \frac{[S]}{[M]} \quad (6)$$

where  $\lambda$  is the portion of the polymer radicals which disproportionate in the termination reaction,  $C_m$  is transfer constant for monomer, given [21] in the literature as  $C_m = 8.5 \times 10^{-5}$ .

In order to obtain the values for the ratio  $k_p/k_t^{1/2}$  using  $1/2(1 + \lambda)(k_t/k_p^2)$  it is necessary to know  $\lambda$ . The latter can be obtained by numerical or graphical extrapolation of literature values [22] for the ratio  $k_{td}/k_{tc}$  at the desired temperatures (Table 1) where  $k_{td}, k_{tc}$  are rate constants for disproportionation and combination of macroradicals in the termination reaction respectively.

In calculations, the numerical values of  $\lambda$  are used (Table 1).

The overall activation energy and the frequency factor were calculated by graphical solution of the relations

$$\log K = \log A - (E/2.303RT) \quad (7)$$

$$\log R_p = \log A - (E/2.303RT) \quad (8)$$

where  $E$  is the overall activation energy for the polymerization (in cal/mole monomer),  $A$  is the frequency factor (in liter/mole-sec),  $R = 1.986$  cal/deg-mole is the gas constant, and  $T$  is Kelvin temperature. Equation (8) was used only for low conversions.

The difference between the activation energy for propagation and the half of the activation energy for termination,  $E_p - 1/2 E_t$ , was calculated by graphical solution of Eq. (9):

TABLE 1.

Temperature (°C)	Method of extrapolation	$\frac{k_{td}}{k_{tc}}$	$\lambda$
50	Numerical	4.72	0.83
50	Graphical	4.63	0.82
61	Numerical	5.89	0.85
61	Graphical	5.95	0.86
70	Numerical	7.17	0.88
70	Graphical	7.14	0.88

$$\log(k_p/k_t^{1/2}) = \log A_p - 1/2 \log A_t - (1/4.57T)[E_p - (E_t/2)] \quad (9)$$

where  $A_p$  and  $A_t$  are the frequency factors for propagation and termination, respectively (in liter/mole-sec).

The activation energy for the initiator decomposition  $E_d$  (in cal/mole) was calculated from Eq. (10).

$$E = 1/2E_d + [E_p - (E_t/2)] \quad (10)$$

The frequency factor for the initiator decomposition  $A_d$  (in liter/mole-sec) was calculated from Eq. (11).

$$A = A_d^{1/2} (A_p/A_t^{1/2}) \quad (11)$$

The activation energy for the degree of polymerization  $E_{\bar{P}_n} = E_p - E_{tr}$  and the value of the ratio  $A_p/A_{tr,s}$  were calculated by graphical solution of the relation

$$\begin{aligned} -\ln \left\{ \frac{[M]}{[S]} \left( \frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_0} \right) \right\} &= \ln \frac{k_p}{k_{tr,s}} \\ &= \ln \frac{A_p}{A_{tr,s}} - \frac{(E_p - E_{tr,s})}{RT} \end{aligned} \quad (12)$$

where  $k_{tr,s}$ ,  $A_{tr,s}$ ,  $E_{tr,s}$  are, respectively, the rate constant, the frequency factor, and the activation energy for the transfer reaction of pyridine.

The activation energy for transfer to solvent  $E_{tr,s}$  (in cal/mole) was calculated [23] from Eq. (13).

$$E_{\bar{P}_n} = E_p - E_{tr,s} \quad (13)$$

## RESULTS

All experimental data for polymerization in bulk as well as in pyridine, were obtained at constant AIBN concentration ( $6.19 \times 10^{-3}$  mole/liter).

Polymerization of Methyl Methacrylate in Bulk

In four independent measurements the following values for the overall polymerization rate at  $50^\circ\text{C}$  were obtained from Eq. (1):  $103.14 \times 10^{-6}$ ,  $106.13 \times 10^{-6}$ ,  $108.79 \times 10^{-6}$ , and  $109.43 \times 10^{-6}$  mole/liter-sec. The literature value [24] is  $92.4 \times 10^{-6}$  mole/liter-sec at the same initiator concentration.

The calculated value of the overall rate constant  $K$ ,  $1.44 \times 10^{-4}$ , from Eq. (3) agrees well with the literature value [25] of  $1.27 \times 10^{-4}$ .

The experimental values for  $1/\bar{P}_0$  ( $10.423 \times 10^{-5}$  and  $10.937 \times 10^{-5}$ ) are also in agreement with the literature value [24] of  $9.1 \times 10^{-5}$ .

Polymerization of Methyl Methacrylate in Pyridine

The order of the monomer concentration at 41.6, 50, 61, and  $70^\circ\text{C}$  ranges from 0.98 to 1.02. This order was calculated numerically by using Eq. (3) at every monomer: solvent ratio. The graphical determination of the order at  $50^\circ\text{C}$  is shown in Fig. 1.

The average value for  $1/2(1 + \lambda) k_t/k_p^2 = 16.57$  is calculated by numerical solution of Eq. (6). The average value of the ratio  $k_t/k_p^2 = 18.21$  is calculated at  $\lambda = 0.83$  (Table 1), and  $k_p/k_t^{1/2} = 0.24$ . In the AIBN-initiated polymerization of methyl methacrylate in ethyl acetate [26], a value  $k_p/k_t^{1/2} = 0.535$  was found.

The values  $E_p - (E_t/2) = 6.8$  kcal/mole and  $A_p/A_t^{1/2} = 1 \times 10^4$  liter/mole-sec were obtained by graphical solution of Eq. (9) at 41.6, 50, 61, and  $70^\circ\text{C}$  (Fig. 7).

It is known from the literature [27] that  $E_t \approx 1$  kcal/mole. If we accepted this value,  $1/2 E_t \approx 0$  and  $E_p - (E_t/2) \approx E_p - 0 \approx E_p \approx 6.8$  kcal/mole. The literature values for  $E_p$  are 6.0 kcal/mole [22] and 4.4 kcal/mole [27]. It should be noted here that in calculating the values for the activation energies an error of  $\pm 2$  kcal/mole monomer



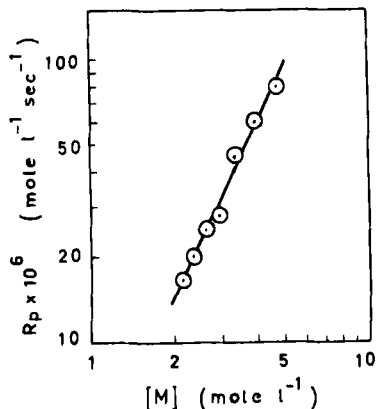


FIG. 1. Determination of the kinetic order in monomer in the polymerization of methyl methacrylate in pyridine.  $[AIBN] = 6.19 \times 10^{-3}$  mole/liter;  $50^\circ\text{C}$ .

is not considered large [28]. The difference for  $E_{P_n}^- = E_p - E_{tr,s} = -15.6$  kcal/mole and  $\log(A_{tr,s}/A_p) = 6.49$  as well as the ratio  $A_p/A_{tr,s} = 7.08 \times 10^{-7}$ , were calculated by graphical solution of Eq. (12).

## DISCUSSION

On mixing methyl methacrylate with pyridine in a molar ratio of 1:1.33 an increase in the frequencies ( $5\text{-}20\text{ cm}^{-1}$ ) of the  $\gamma$ -skeletal modes of the former is observed (Figs. 2 and 3, spectrum 1). This increase may be due to the formation of a weak hydrogen bond [29], to the large volume of the donor in the complex, or to dielectric or other effects [30]. The center of the maximum for one of the  $\gamma$ -skeletal modes of methyl methacrylate is at  $1025\text{ cm}^{-1}$  (Figs. 2 and 3, spectrum 2). This mode increases its frequency (spectrum 1) and coincides with the  $\gamma$  (CNC) of pyridine at  $1038\text{ cm}^{-1}$  (spectrum 3). Parallel with this an increase in the band strength of  $\nu$  (C=O) vibrations of methyl methacrylate in a mixture with pyridine is observed (Table 2). In other words, on dilution of methyl methacrylate with pyridine, a smaller decrease in the band strength of  $\nu$  (C=O)

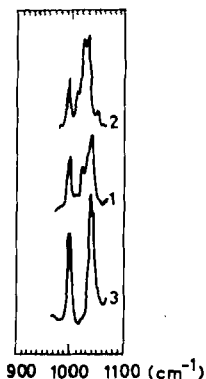


FIG. 2. Increase in the frequencies of  $\gamma$ -skeletal modes of methyl methacrylate (1) on mixing with pyridine (molar ratio 1:1.33); (2) spectrum of pure methyl methacrylate in the region of  $\gamma$ -skeletal modes; (3) spectrum of pyridine. Spectrum is obtained on mixing cyclohexane solutions of methyl methacrylate (0.2337 mole/liter) and pyridine (0.3107 mole/liter) at room temperature.

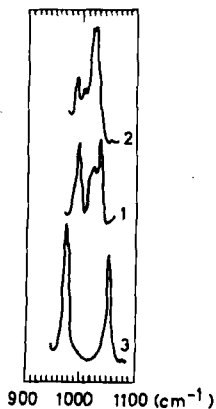


FIG. 3. Increase in the frequencies of  $\gamma$ -skeletal modes of methyl methacrylate (1) on mixing with pyridine (molar ratio 1:1.33); (2) spectrum of pure methyl methacrylate in the region of the  $\gamma$ -skeletal modes; (3) spectrum of pyridine. Spectrum obtained on mixing pyridine with methyl methacrylate in a layer; room temperature.

TABLE 2. Increase in the Band Strength of  $\nu(\text{C}=\text{O})$  Vibrations of Methyl Methacrylate in a Mixture with Pyridine (Molar Ratio 1:1.33)<sup>a</sup>

Components	Fundamental frequency ( $\text{cm}^{-1}$ )	Group	$I_0$ (mm)	$I$ (mm)	$\log \frac{I_0}{I} = E$	$c$ (mole/liter)	$\ell$ (cm)	$\epsilon$ (liter/cm-mole)
Methyl methacrylate	1738	$\nu(\text{C}=\text{O})$	95.5	7.6	1.0992	0.234	0.016	294
Methyl methacrylate on mixing with pyridine <sup>b</sup>	1738	$\nu(\text{C}=\text{O})$	98.0	16.4	0.7764	0.117	0.016	415

<sup>a</sup>  $I_0$  is the intensity of incident radiation on an absorbing path,  $I$  is the intensity of transmitted radiation through the absorbing path,  $\log(I_0/I) = E$  is the absorbance (extinction),  $c$  is the sample concentration in cyclohexane,  $\ell$  is the thickness of the cell (path length), and  $\epsilon$  is the molar absorption coefficient (molar extinction).

<sup>b</sup> The spectrum was obtained by mixing cyclohexane solutions of methyl methacrylate (0.2337 mole/liter) and of pyridine (0.3107 mole/liter).

vibrations is observed than was expected. The increase in the band strength of  $\nu(\text{C}=\text{O})$  vibrations probably is related to some effect of pyridine which increases the polarity of the methyl methacrylate molecule.

It is known that the polarity increases with the dielectric constant  $\epsilon$  and the dipole moment  $\mu$  of the solvent molecules. In our case, the components of the polymerization mixture have the following values for these constants: pyridine,  $\epsilon = 12.4$  at  $21^\circ\text{C}$ ,  $\mu = 2.37$  at  $25^\circ\text{C}$  [31]; methyl methacrylate,  $\epsilon = 2.9$  (temperature not indicated),  $\mu = 1.675$  at  $25^\circ\text{C}$  [31]. Therefore the polarity of pyridine may play a role in the complex formation.

The kinetic and energetic parameters are of greatest interest in the study of influence of solvent on radical polymerization. The polymerization of methyl methacrylate in pyridine proceeds more speedily (Fig. 4, curves 1-3) than that in bulk (Fig. 4, curves 4-7). It is seen in Fig. 5 that the overall rate constant  $K$  (curve 1) and the

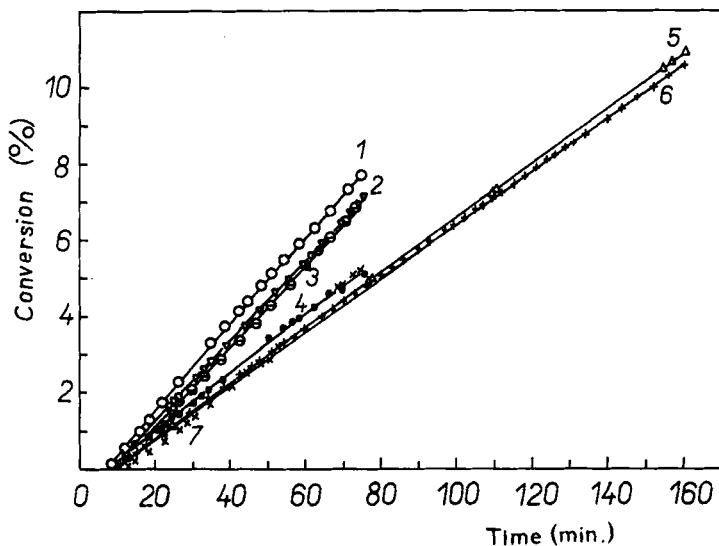


FIG. 4. Effect of pyridine on conversion of methyl methacrylate at  $[\text{AIBN}] = 6.19 \times 10^{-3}$  mole/liter and  $50^\circ\text{C}$ : (1) pyridine = 7.991 mole/liter, methyl methacrylate = 3.339 mole/liter; (2) pyridine = 8.977 mole/liter, methyl methacrylate = 2.597 mole/liter; (3) pyridine = 9.322 mole/liter, methyl methacrylate = 2.337 mole/liter; (4-7) block polymerizations.

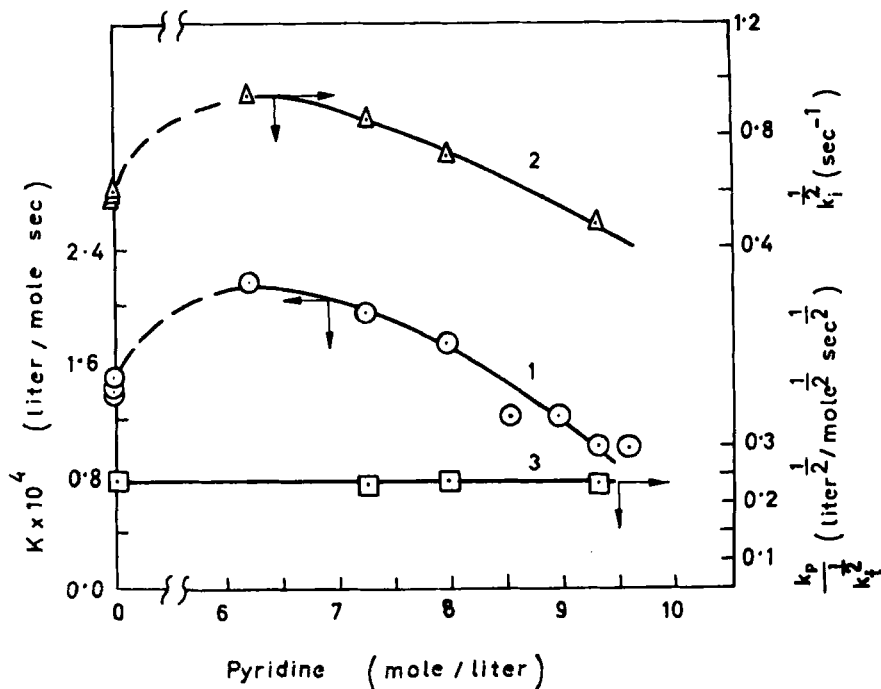


FIG. 5. Influence of pyridine concentration on (1)  $K$ , (2)  $k_i^{1/2}$ , and (3)  $k_p/k_t^{1/2}$  in polymerization of methyl methacrylate. Pyridine = 6.215-7.991 mole/liter;  $[AIBN] = 6.19 \times 10^{-3}$  mole/liter;  $t = 50^\circ\text{C}$ .

initiation rate constant  $k_i$  (curve 2) are higher than these in bulk. Both rate constants gradually decrease with increasing concentration of pyridine. The changes in values of  $K$  are due to changes in values of  $k_i$ . This is because no material changes are observed for the value of the ratio  $k_p/k_t^{1/2}$  (curve 3).

The value for the overall activation energy 13.1 kcal/mole monomer was calculated by graphical solution (Fig. 6) of Eq. (7). The frequency factor is  $1.74 \times 10^5$  liter/mole-sec. If the same relation (7) is applied to low conversions, the value for the overall activation energy is 11.3 kcal/mole monomer. The frequency factor is  $1.00 \times 10^4$

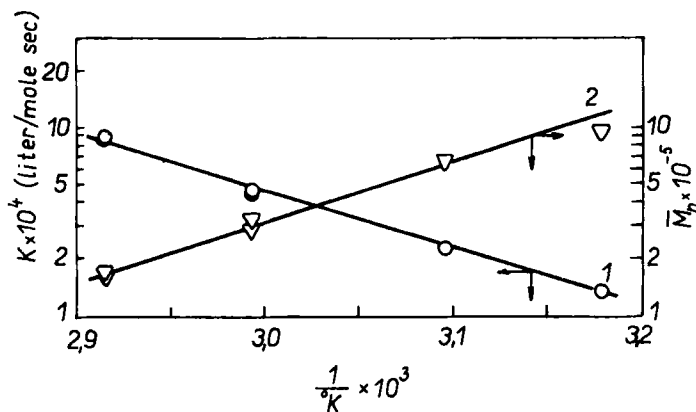


FIG. 6. Dependence of (1) the polymerization rate constant and (2) the molecular weight of the polymer in methyl methacrylate polymerization in pyridine on temperature.  $[AIBN] = 6.19 \times 10^{-3}$  mole/liter; pyridine = 6.215 mole/liter.

liter/mole-sec. When Eq. (8) is applied to low conversions, the overall activation energy is 11.2 kcal/mole monomer, and the frequency factor is  $0.29 \times 10^4$  liter/mole-sec. The literature value [23] for the overall activation energy of AIBN-initiated polymerization is usually about 20 kcal/mole monomer.

It is known that the rate of a reaction depends mostly on the activation energy. If the effect of the solvent is to reduce this value, the polymerization is accelerated. Just this dependence is observed in our case.

In the AIBN-initiated polymerization of vinyl acetate in benzene, the rate decreases with increasing the solvent concentration [5]. Moreover a significantly higher overall activation energy (37.6 kcal/mole) was obtained. These data are logically related to our results for the AIBN-initiated polymerization of methyl methacrylate in pyridine. In our case, in the presence of pyridine an acceleration of the polymerization and a lower overall activation energy are observed.

According to Eq. (10),  $E_d = 12.6$  kcal/mole when  $E = 13.1$  kcal/mole monomer. According to the same relation,  $E_d = 8.6$  kcal/mole in the case when  $E = 11.3$  kcal/mole monomer (the value at low

monomer conversion). The literature value of  $E_d$  for azo initiators is about 30 kcal/mole [23, 32]. In our case, the lower overall activation energy is due to the lower activation energy for initiation. The most plausible explanation for these anomalies is the formation of a complex [1] between pyridine and the methyl methacrylate [or the poly(methyl methacrylate) radical]. Possibly this complex concerns the initiation step.

From Eq. (11) we calculated  $A_d = 3.03 \times 10^2$  liter/mole-sec for  $A = 1.74 \times 10^5$ .

In our case (Fig. 6), the well known dependence [23] is also observed: with the increase of the reaction temperature, the reaction rate also increases while the molecular weight of the polymer decreases.

The higher the value of the activation energy for a reaction, the higher the increase in rate with increasing temperature. At  $E = 0$  the rate of the reaction does not depend on temperature. The obtained activation energy for the propagation reaction is low (6.8 kcal/mole). The activation energy for the termination reactions is about 1kcal/mole. Hence, the value of the ratio  $k_p/k_t^{1/2}$  increases only slowly with temperature. Just this dependence is shown in Fig. 7. The

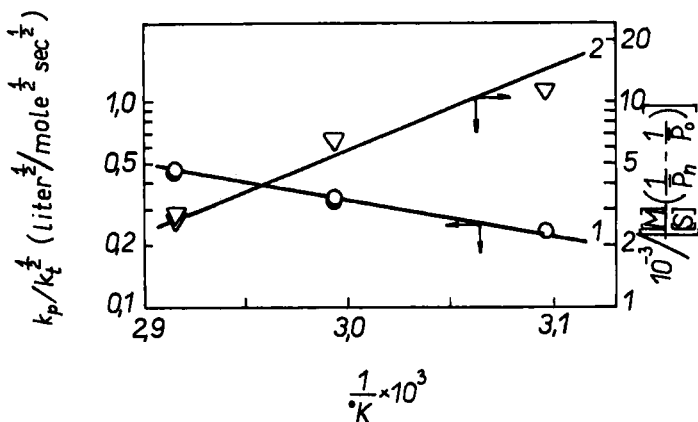


FIG. 7. Dependence on temperature of (1)  $k_p/k_t^{1/2}$  and (2)  $1/([M]/[S])(1/\bar{P}_n - 1/\bar{P}_0)$  in methyl methacrylate polymerization in pyridine.  $[AIBN] = 6.19 \times 10^{-3}$  mole/liter; pyridine = 6.215 mole/liter.

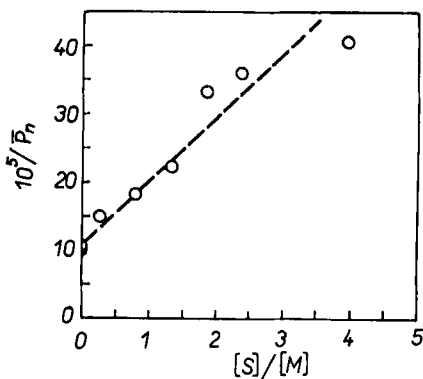
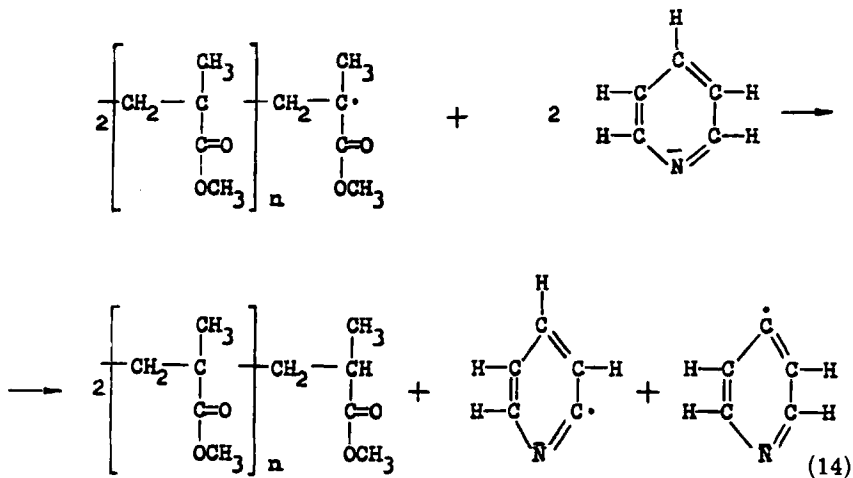


FIG. 8. Determination of pyridine chain transfer constant in methyl methacrylate polymerization. [AIBN] =  $6.19 \times 10^{-3}$  mole/liter; 50°C.





obtained activation energy for the transfer reaction with pyridine  $E_{tr,s}$  is comparatively high (22.4 kcal/mole) which explains why the value of the ratio  $k_p/k_{tr,s} = \{1/([M]/[S])[(1/\bar{P}_n) - (1/\bar{P}_0)]\}$  depends on temperature. In Fig. 7, line 2 it is seen that  $\log \{1/([M]/[S])[(1/\bar{P}_n) - (1/\bar{P}_0)]\}$  decreases with increasing temperature analogously to  $\bar{M}_n$  (Fig. 6).

The determination of the transfer constant of pyridine in methyl methacrylate polymerization is given in Fig. 8.

The average transfer constant of poly(methyl methacrylate) radical to pyridine  $C_s$  as calculated by graphical solution (Fig. 8) of Eq. (5) is  $1.0 \times 10^{-4}$ . The most probable value for the transfer constant of polystyrene radical to pyridine is  $6 \times 10^{-5}$  [2]. This value is calculated only from one experimentally established degree of polymerization.

It may be expected that, in the transfer reaction, a poly(methyl methacrylate) radical can split off hydrogen from every pyridine carbon atom, mostly in the  $\alpha$  and  $\gamma$  positions. [Eq. (14)].

Some literature data are of interest for the transfer reaction described in this manner [3, 33].

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