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Kinetic Study of Cationic Polymerization of α -Methylstyrene Initiated by BuOTiCl_2 in Dichloromethane Solution

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ABSTRACT

The cationic polymerization of α -methylstyrene initiated by $n\text{-BuOTiCl}_2$ has been studied at -70°C in dichloromethane solution by using a calorimetric technique. Polymerizations were performed under high vacuum either in dry conditions for which low monomer conversions were observed (4-12%), or in the presence of added cocatalyst (H_2O or HCl). In these last cases, yields were quantitative, and it was shown that polymerization rate was proportional to added water concentration and first order with respect to catalyst and to monomer. A kinetic scheme is proposed, based on a monomer-independent initiation step and on a unimolecular termination process. At -70°C , the initiation rate is higher than termination rate during the whole course of the polymerization, and the concentration of active centers increases continuously. The following rate constants were found at -70°C : $k_i = 17 \pm 6$, $k_p = 2.2 \pm 1.1 \times 10^4$, $k_{\text{term}} = 30 \pm 15$ liter/mole-sec, and $k_t = 0.54 \pm 0.05 \text{ sec}^{-1}$. At

-50 and -30° C, the concentration of active centers goes through a maximum during the polymerization and incomplete monomer conversions were observed, showing that all the catalyst is consumed. The different rate constants were tentatively estimated at these temperatures by using a simulation method, and this led to a negative value of ca. -7 kcal/mole for the apparent activation energy for propagation, and to a value of ~5 kcal/mole for E_1 . The observation of a negative ($E_{p'app}$) might be explained either by a shift of the dissociation equilibrium of the growing ends or by a solvation process of these growing ends by monomer prior to the propagation step.

Cationic polymerization of α -methylstyrene initiated by Lewis acids was extensively studied during the fifties, but surprisingly no major work has been published on the subject in fifteen years. Early kinetics were proposed by Jordan and Mathieson [1] for $AlCl_3$ initiation in ethyl chloride and carbon tetrachloride, by Dainton and Tomlinson [2] for $SnCl_4-H_2O$ initiation in ethyl chloride, and for $BF_3 \cdot Et_2O$ by Worsfold and Bywater [3] and Okamura [4], using, respectively ethylene dichloride and mixtures of chloroform-hexane and toluene-hexane, as solvents. The results showed some scatter, and even if the proposed schemes for $SnCl_4$ and BF_3 catalysis are in good agreement, no conclusive information was given on the initiation mechanism. Thus, initiation kinetics and active centers concentrations are unknown and the reported (k_p/k_t) values, obtained through the too generally used quasistationary-state assumption, may be questioned.

Re-examination of α -methylstyrene polymerization by Lewis acids was undertaken in our laboratory with use of either *n*-butoxytitanium trichloride or titanium tetrachloride as catalysts and methylene dichloride as solvent. Preliminary results with $TiCl_4$ have been published [5]. We report here on initiation mechanism and polymerization kinetics with the $BuOTiCl_3$ catalyst system.

EXPERIMENTAL

Materials

All reagents were thoroughly purified and dehydrated by using high vacuum techniques as previously described [6-8].

Monomer

Commercial α -methylstyrene (Fluka, pure grade) was carefully distilled, and gas chromatograms of middle fractions showed that impurities content was less than 10 ppm. Dehydration was performed under vacuum in sealed vessels, using successively CaH_2 and several sodium mirrors treatments, until living carbanions appear at $+60^\circ\text{C}$. Monomer was then stored in graduated tubes equipped with break-seals.

Solvent

Methylene dichloride (Matheson Coleman and Bell, spectrophotometric grade) was refluxed on oleum (one day), washed, dried, and distilled with an efficient column. Dehydration was obtained on several successive phosphorus pentoxide and sodium films. Solvent was stored in darkness on sodium mirrors. Details on solvent purification techniques have been published elsewhere [7].

Catalyst and Cocatalyst Solutions

n-Butoxytitanium trichloride was synthesized, purified, and finally stored in 4-ml bulbs as previously reported [6].

Hydrogen chloride was dehydrated in the gaseous phase on P_2O_5 films and stored in convenient bulbs of known volume. Aqueous solutions in methylene chloride were prepared by dilution of a saturated solution of which the exact water content had been determined by NMR.

Polymerization

Monomer consumption was followed by using an adiabatic calorimeter [8] of the Biddulph-Plesch type [9], equipped with suitable breakers for catalyst and cocatalyst bulbs. The polymerization vessel—bottom apart—was flamed several hours and sealed under very high vacuum (better than 5×10^{-7} Torr). The whole sealed apparatus was then rinsed several times with anhydrous solvent kept on sodium film, before introducing reagents by bulb to bulb distillation. Details on polymerization runs and thermograms treatment are given elsewhere [8]. Polymers were precipitated in methanol, filtered, and dried under high vacuum. Oligomer content was always quite negligible. Molecular weight were determined by osmometry on toluene solutions by using a Mechrolab membrane dynamic osmometer.

Polymerization enthalpy was found equal to $\Delta H_p = -9.6 \pm 0.7$ kcal/mole at -70°C (mean value of eleven polymerizations with corresponding polymers of $3 \times 10^4 < \overline{M}_n < 7 \times 10^4$)

RESULTS

The polymerization of α -methylstyrene in methylene chloride solution is rapid and always quantitative when performed at -70°C with added cocatalyst. Incomplete conversion was observed at -50 and -30°C .

The monomer polymerization curve $[M] = f(t)$ is S-shaped, showing that initiation is relatively slow. The point of inflection on the curve is close to the starting time and we considered the inflection slope to be the "initial" overall rate of the polymerization, R_0 . As a nonnegligible amount of monomer is consumed at this time, we used the values of R_0 only to determine the partial orders with respect to each reagent.

Evidence for a Cocatalytic Effect of Proton Donors

It may be seen from Table 1 that very low polymer conversions are observed when polymerizations are performed without added cocatalyst in ultimate dehydration conditions. Further addition of water or hydrogen chloride leads to rapid and complete conversions, and it may be noted that the initial rate is about twice as high with HCl as cocatalyst as with H_2O . Nevertheless no direct comparison between these two rates is really permissible, as at -80°C water was frozen and precipitated from its dichloromethane solution in the cocatalyst bulb and as, in the second experiment, the gaseous HCl bulb was broken above the reactant medium and the dissolution rate was unknown. It is also difficult to state whether the low yield observed during the so-called "prepolymerization" results from residual traces of cocatalyst or from a direct initiation as observed with the same monomer and TiCl_4 [5] at low temperature. Several prepolymerizations (yield $< 2\text{-}5\%$) were followed by bulb to bulb distillation of reagents, but these tentative condensation polymerizations led to only about 10% conversion.

Effects of Initial Cocatalyst, Initiator and Monomer Concentrations: External Orders with Respect to the Reagents

Results of polymerizations at -70°C with increasing initial water concentrations are summarized in Table 2. It may be seen that conversion becomes quantitative at very low cocatalyst concentration ($\sim 5 \times 10^{-4}$ mole/liter), and a linear dependence is observed between

TABLE 1. Cocatalytic Effect of Water and Hydrogen Chloride at -80°C

Expt.	$[M]_0 \times 10^1$ (mole/ liter)	$[I]_0 \times 10^3$ (mole/ liter)	Prepolymerization		Polymerization after cocatalyst addition		Overall yield (%)	$\bar{M}_n \times 10^{-sb}$
			$(R_0)_1 \times 10^2$ (liter/mole- sec)	Yield (%) ^a	Cocatalyst (1×10^{-3} mole/liter)	$(R_0)_2 \times 10^2$ (liter/mole- sec)		
I	3	1	1.8	4	H ₂ O	5	100	1.35
II	3	1	1.3	12	HCl	9.4	100	1.60

^a Estimated from thermograms.

^b Measured on the final polymer.

TABLE 2. Influence of Initial Concentration of Added Water^a

Expt.	$[M]_0$	Added $[H_2O]_0 \times 10^3$ (mole/liter)	$\frac{[H_2O]_0}{[I]_0}$	$[M]_{infl}$ (mole/liter)	$R_0 \times 10^2$ (liter/mole-sec)	Yield (%)	$\bar{M}_n \times 10^{-3}$
III	0.31	0	—	~ 0.3	0.48 ^b	< 6	48
IV	0.29	0.42	0.35	0.25	3.29 ^b	96	57.5
V	0.28	0.62	0.52	0.22	5.60	100	57
VI	0.28	0.79	0.66	0.21	7.07 ^b	100	48
VII	0.30	1.03	0.85	0.22	8.47	100	60

^aConditions: $T_0 = -70^\circ C$; $[I]_0 = 1.2 \times 10^{-3}$ mole/liter; polymerization time, 5 min; solvent CH_2Cl_2 .
^bInitial rate corrected for a monomer concentration at the inflection time equal to $|M_{infl}| = 0.22 M$.

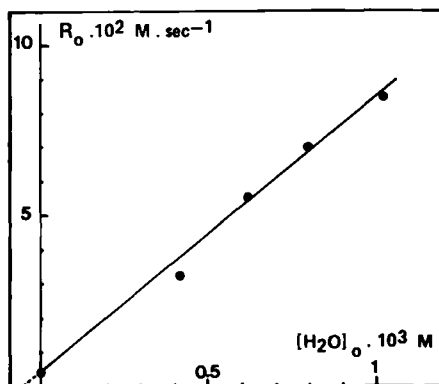


FIG. 1. Linear dependence between initial rate of polymerization and added water concentration. $T_0 = -70^\circ\text{C}$; $[I]_0 = 1.2 \times 10^{-3}$ mole/liter, $[M]_0 \sim 0.3$ mole/liter.

initial rate and water concentration (Fig. 1) for experiments where the $[\text{cocatalyst}]/[\text{catalyst}]$ ratio is lower than unity. Extrapolation at $R_0 = 0$ of the plot of Fig. 1 would indicate a residual water concentration of about 6×10^{-5} mole/liter which seems incompatible with our drying techniques. Thus, in this case, the small yield of the polymerization cannot be explained by residual water in reagents or on the walls of the vessels. A linear relationship is also observed between initial rate and monomer concentration (see Table 3 and Fig. 2a). When plotting R_0 against initiator concentration, this proportionality is observed only for cocatalyst/catalyst ratios equal to or lower than unity (Fig. 2b). Values of R_0 are higher than expected when water is in excess with respect to the initiator, which might be explained by the evolution of hydrogen chloride resulting from the partial hydrolysis of BuOTiCl_3 . As HCl seems to be a more efficient cocatalyst than water, the number of active centers formed with time is higher than expected, leading to deviating values of R_0 .

Effect of the Temperature of Polymerization

The kinetic study was mainly carried out at -70°C , but two experiments were done at higher temperatures (-50 and -30°C). Results are listed in Table 4. The overall rate of polymerization decreases

TABLE 3. Influence of Initial Concentrations of Monomer and Initiator^a

Expt.	$[M]_0 \times 10^2$ (mole/liter)	$[I]_0 \times 10^3$ (mole/liter)	$\frac{[H_2O]_0}{[I]_0}$	$[M]_{infl.} \times 10^2$ (mole/liter)	$R_p \times 10^2$ (mole/liter-sec)	Yield (%)	$\bar{M}_n \times 10^{-3}$
VIII	6.29	1.05	1	4.7	1.65	100	31
IX	11.4	"	"	8.6	3.53	100	35
X	22.6	"	"	17.9	6.30	100	57
XI	30	"	"	22.3	8.82	100	58.5
XII	30	0.48	2.2		4.71	100	56
XIII	"	0.56	1.87		6.30	100	67
XIV	"	0.78	1.36		7.56	100	62
XV	"	1.05	1		8.10	b	
XVI	"	1.15	0.91		8.47	100	60
XVIII	"	1.44	0.73		10.47	100	66

^aConditions: $T_0 = -70^\circ C$; $[H_2O]_0 = 1.05 \times 10^{-3}$ mole/liter.^bStopped after incomplete conversion.

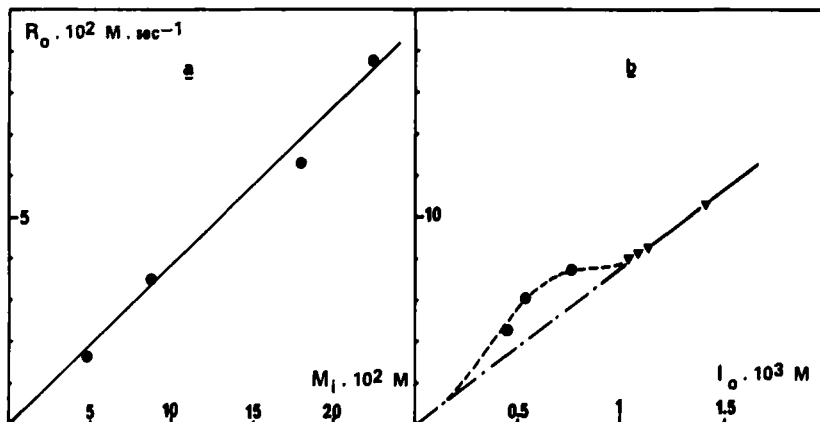


FIG. 2. Overall first orders with respect (a) to monomer and (b) to catalyst at $T_0 = -70^\circ\text{C}$: (a) M_1 = monomer concentration at inflection point, $[I]_0 = [H_2O]_0 = 1.05 \times 10^{-3}$ mole/liter; (b) $[M]_0 = 0.3$ mole/liter, $[H_2O]_0 = 1.05 \times 10^{-3}$ mole/liter, (\blacktriangle) $[H_2O]_0/[I]_0 \leq 1$, (\bullet) $[H_2O]_0/[I]_0 > 1$.

TABLE 4. Influence of Initial Temperature of Polymerization

Expt.	T ($^\circ\text{C}$)	$R_0 \times 10^2$ (mole/liter-sec)	Yield (%)	$\bar{M}_n \times 10^{-3}$
XVIII	-30	2.6	77	< 7.0
XIX	-50	4.6	95	20.7
XI	-70	8.8	100	58.5

^aConditions: $[M]_0 = 0.3$ mole/liter; $[I]_0 = 1.05 \times 10^{-3}$ mole/liter; $[H_2O]_0 = 1.05 \times 10^{-3}$ mole/liter.

with increasing temperature, and monomer conversion, which goes to completion at -70°C , becomes incomplete at higher temperature. The decrease of molecular weights is also very large.

Kinetics

According to the overall first order with respect to monomer, the most probable scheme would be a partial zero order for initiation and a first order for propagation:

$$R_i = k_i [H_2O] [I] \quad (1)$$

$$R_p = k_p [M^*] [M] \quad (2)$$

At -70°C , as we shall see further, the concentration of catalyst and cocatalyst consumed during the polymerization does not exceed 15%. It is possible to write, as a first approach,

$$R_i = k_i [H_2O]_0 [I]_0 \quad (3)$$

Assuming unimolecular termination, this leads to

$$d[M^*]/dt = k_i [H_2O]_0 [I]_0 - k_t [M^*] \quad (4)$$

Integration between $t = 0$ and t yields $[M^*]$. Hence

$$\begin{aligned} (R_p/[M]) &= k_p [M^*] \\ &= (k_i k_p / k_t) [H_2O]_0 [I]_0 (1 - e^{-k_t t}) \end{aligned} \quad (5)$$

According to this equation, plots of $(R_p/[M])$ versus time are superimposed for experiments with constant $[I]_0$ and $[H_2O]_0$. This was observed at -70°C within experimental error (see Table 3 and Fig. 3, Expts. IX, X, XI. The experiment at lowest $[M]_0$ was not used, as the thermogram did not allow an accurate enough determination).

The correct value of k_t is that which fits with relation (5), i.e., which gives linear plot of $R_p/[M]$ against $(1 - \exp \{-k_t t\})$. For each of the above experiments this constant was determined and the observed values were satisfactorily close, leading to a mean of $0.54 \pm 0.05 \text{ sec}^{-1}$ at -70°C . Slopes of corresponding plots yield values of the $(k_i k_p)$ products (see Fig. 4 and Table 5).

As the concentration of active centers is independent of monomer concentration, the conversion versus time plots must also be independent of $[M]_0$ for experiments where $[I]_0$ and $[H_2O]_0$ are the same.

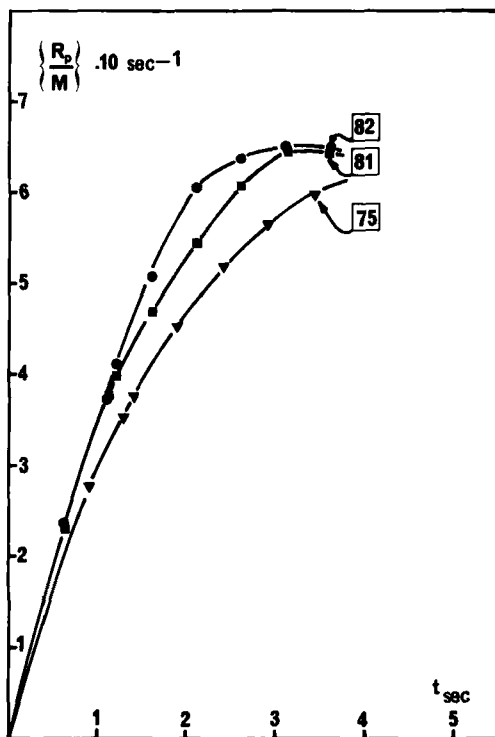


FIG. 3. Variation of concentration of active centers during the polymerization at -70°C (see Table 3): (\bullet) expt. IX; (\blacksquare) expt. XI; (\blacktriangledown) expt. X. Numbers in squares represent the monomer conversion (%) at the last significant point of each plot.

This was experimentally observed at -70°C (Fig. 5). Completion is obtained after a polymerization course of 10 ± 1 sec as shown by analysis of thermograms.

For each polymer sample, the total concentration of macromolecules, determined from $[M]_0$ and \bar{M}_n , is the sum of initiated and transferred chains.

$$[P] = [P_i] + [P_{tr}] \quad (6)$$

$[P]_i$ is determined from

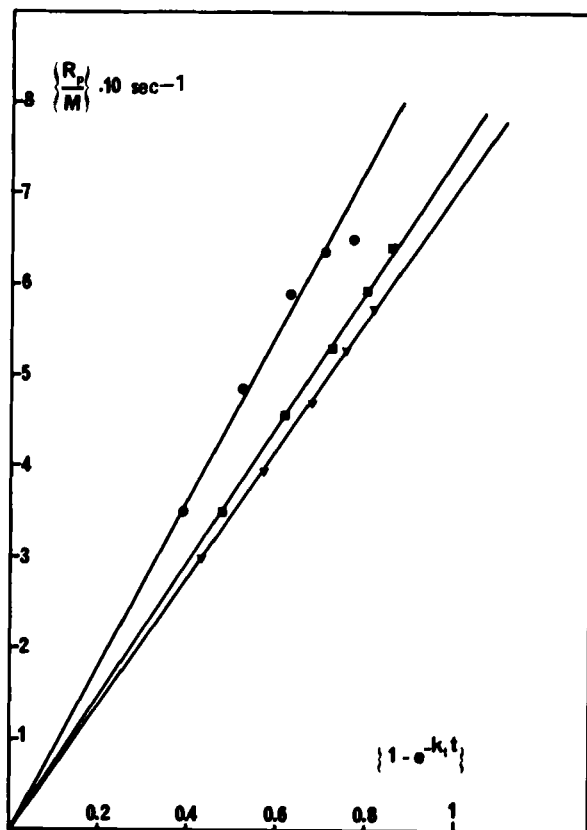


FIG. 4. Determination of k_t and of $(k_i k_p)$ at -70°C (see text). Symbols are the same as in Fig. 3.

$$d[P_i]/dt = k_i [I] [H_2O] = k_i [I]^2 \quad (7)$$

as in these experiments $[I]_0 = [H_2O]_0$

$$d[P_i]/dt = k_i ([I]_0 - [P_i])^2 \quad (8)$$

integration leads to

TABLE 5. Values of Initiation, Propagation, and Termination Rate Constants at Different Temperatures

T (°C)	k_t (sec ⁻¹)	$k_i k_p$ (liter/mole-sec) ²	k_i (liter/mole-sec)	k_p (liter/mole-sec)
-70 ^a				
Expt. XI	0.60 ± 0.05	(4 ± 0.3) × 10 ⁵		(2.3 ± 1.1) × 10 ⁴
Expt. IX	0.50 ± 0.05	(4 ± 0.3) × 10 ⁵	17 ± 6	(2.3 ± 1.1) × 10 ⁴
Expt. X	0.52 ± 0.05	(3.3 ± 0.3) × 10 ⁵		(2.0 ± 1) × 10 ⁴
Avg.	0.54 ± 0.05	(3.8 ± 0.3) × 10 ⁵		(2.2 ± 1.1) × 10 ⁴
-50	1 ± 0.1 ^b	(2.1 ± 0.5) × 10 ⁵ c	60 ± 10 ^b	(4.5 ± 0.5) × 10 ³ b
-30	1 ± 0.1 ^b	(1.4 ± 0.4) × 10 ⁵ c	120 ± 20 ^b	(1.3 ± 0.5) × 10 ³ b
(E) _{app} (kcal/ mole)	0.5 to 2	-2.1 to -2.4	+4.5 to 5	-6.5 to -7.5

^a Expts. IX, X, and XI; values of constants are kinetically determined.

^b Values estimated by simulation (see text).

^c Calculated from Eq. (13).

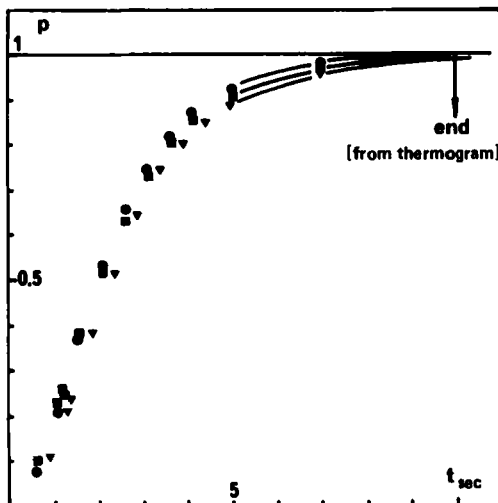


FIG. 5. Variation of the extent of polymerization p with time for different initial concentrations of monomer at -70°C : (\bullet) $[\text{M}]_0 = 0.11$ mole/liter; (\blacktriangledown) $[\text{M}]_0 = 0.23$ mole/liter; (\blacksquare) $[\text{M}]_0 = 0.30$ mole/liter. $[\text{I}]_0 = [\text{H}_2\text{O}]_0 = 1.05 \times 10^{-3}$ mole/liter.

$$P_i = k_i [\text{I}]_0^2 t / (1 + k_i [\text{I}]_0 t) \quad (9)$$

If transfer to monomer is the major transfer process, $[P_{\text{tr}}]$ is obtained from

$$d[P_{\text{tr}}]/dt = k_{\text{trm}} [\text{M}^*] [\text{M}] \quad (10)$$

After replacing $[\text{M}^*]$ by its expression [Eq. (5)] and introducing the extent p of polymerization, integration gives

$$P_{\text{tr}} = (k_i k_{\text{trm}} / k_t) [\text{I}]_0^2 [\text{M}]_0 \int_0^t (1 - e^{-k_i t}) (1 - p) dt \quad (11)$$

Thus the overall concentration of chains formed during the whole course of the polymerization is

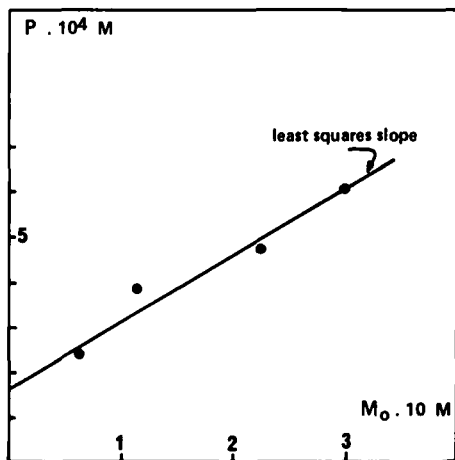


FIG. 6. Linear dependence between the total concentration of formed macromolecules and the initial monomer concentration at -70°C [see Eq. (12)].

$$[P] = \frac{k_i [I]_0^2 t_{\infty}}{1 + k_i [I]_0 t_{\infty}} + \frac{k_i k_{trm}}{k_t} [I]_0^2 [M]_0 \int_0^{t_{\infty}} (1 - e^{-k_t t}) (1 - p) dt \quad (12)$$

A plot of $[P]$ versus $[M]_0$ was found to be linear (Fig. 6). It may be noted that the intercept represents $[P]_i$, i.e., the concentration of catalyst consumed during the polymerization. The observed value (1.6×10^{-4} mole/liter) is 15% of $[I]_0$ at -70°C .

With $t_{\infty} = 10 \pm 1$ sec, k_i is obtained from the intercept and k_{trm} from the slope. The integral

$$\left\{ \int_0^{t_{\infty}} (1 - e^{-k_t t}) (1 - p) dt \right\}$$

is independent of $[M]_0$ and may be graphically determined. Accuracy on values of k_i and k_{trm} is not better than 40-50%:

$$k_i = 17 \pm 6 \text{ liter/mole-sec}$$

$$k_{\text{term}} = 30 \pm 15 \text{ liter/mole-sec at } -70^\circ \text{C}$$

The propagation rate constant may be computed for each experiment at -70°C from the above value of k_i and from those of $(k_i k_p)$ products (slopes in Fig. 4). The mean value is found to be

$$k_p = (2.2 \pm 1.1) \times 10^4 \text{ liter/mole-sec at } -70^\circ \text{C}$$

Influence of Temperature on Initiation, Termination, and Propagation Rate Constants

If at -70°C the concentration of active centers is continuously increasing, at -50 and -30°C maxima are observed, as shown on Fig. 7.

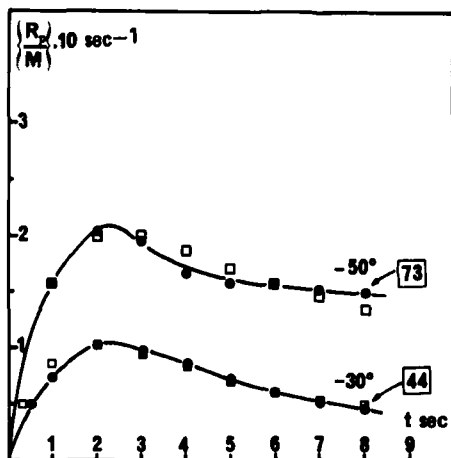


FIG. 7. Variation of concentrations of active centers during the polymerization at -30 and -50°C : (\bullet) experimental points; (\square) theoretical points obtained by simulation by use of the best fitting values of k_t , k_i , k_p . Numbers in square represent the monomer conversion (%) at the last significant point of each plot.

At these temperatures, partial yields are obtained. Catalyst and cocatalyst are consumed before the end of the polymerization and obviously Eq. (5) is no longer valid. An order of magnitude of the different rate constants might nevertheless be attained by computing theoretical curves of $R_p/[M]$ versus time for different sets of k_i , k_t , and k_p values until they fit with the experimental plot (Fig. 7).

Values chosen for k_i and k_p were not independent, since their product was known from the initial slope of the plot of $R_p/[M]$ versus time which is expressed by

$$\begin{aligned} \frac{d}{dt} \left(\frac{R_p}{[M]} \right)_0 &= k_p \left(\frac{d[M^*]}{dt} \right)_0 \\ &= k_p k_i [H_2O]_0 [I]_0 \end{aligned} \quad (13)$$

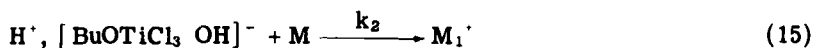
Values of $(k_i k_p)$, k_i , k_p and the corresponding activation energies are listed in Table 5, but it must be kept in mind that this is only a tentative approach and then a rough approximation.

DISCUSSION AND CONCLUSION

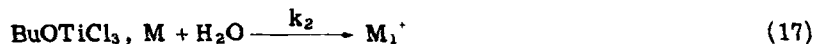
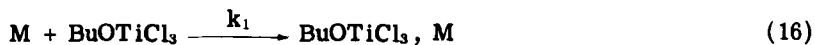
We have shown, in this work, that α -methylstyrene can be readily polymerized by $BuOTiCl_3$ in dichloromethane solution. As the polymerization systems were subjected to exhaustive drying, it appeared that initiation requires a protogenic cocatalyst like water or hydrogen chloride. Attempts to stop the polymerization completely were unsuccessful. In these stopping experiments, low yields (4-15%) were always observed for the so called prepolymerization, and we are unable to settle the question of the effect of remaining traces of cocatalyst and of a possibility of direct initiation. This last hypothesis might be reasonable as, with $TiCl_4$, quantitative polymerization of α -methylstyrene takes place in superdried systems within a wide temperature range (0 to $-70^\circ C$) [10]. In the case of initiation by the less acidic $BuOTiCl_3$, a smaller participation of the direct mechanism may be expected and this might explain the incomplete polymerization we observed in dry conditions.

The kinetic study was performed with equal amounts of catalyst and cocatalyst, and the value of the initiation constant found at $-70^\circ C$ for α -methylstyrene ($k_i = 17$ liter/mole-sec) may be compared with

the value of this constant in the case of cyclopentadiene polymerization [11] with same solvent and initiator ($k_1 = 11$ liter/mole-sec). In these two systems, the initiation step was found to be kinetically independent of monomer concentration, and that should lead to the same value of the constant. The close values experimentally observed account for this but we are unable to specify whether initiation results from a relatively slow reaction of protogen onto Lewis acid [Eqs. (14), (15)] (with $k_1 = k_i \ll k_2$)



or onto a monomer-Lewis acid preformed complex [Eqs. (16), (17)]. (with $k_1 \gg k_2 = k_i$)



At -30 and -50°C , values of ($k_p [M^*]$) go through a wide maximum and then decrease slowly (Fig. 7). The maximum is reached when the initiation rate becomes equal to the termination rate, which means that at -30 and -50°C , initiator is much more rapidly consumed than at -70°C . The positive activation energy found for the initiation step ($E_1 \approx 5$ kcal/mole) agrees with this behavior.

It is interesting to note that a negative apparent activation energy for propagation is also found for this α -methylstyrene cationic polymerization. As it was discussed for cyclopentadiene and *p*-methoxystyrene polymerizations initiated by trityl cations [12, 13], a simple explanation might be a strong temperature effect on the ion pair \rightleftharpoons free ions equilibrium, associated to a solvation process. The value of k_p on free ions obtained by radiation-induced polymerization and reported [14, 15] to be of the order of 10^6 liter/mole-sec is much higher than our k_p apparent values and makes the above hypothesis reasonable.

An alternative explanation based on the early proposal of Fontana and Kidder [16] and which we recently advanced in the case of *p*-methoxystyrene polymerization [13] might also account for this large

difference between $(k_p)_{app}$ and k_{p+} values : a solvation of active centers by monomer, prior to propagation step itself, would lead at equilibrium to an apparent value of k_p close to $(k_p K_S)$ and thus much lower than the true propagation rate constant.

The kinetic scheme we proposed and the whole kinetic treatment is based on a zero order with respect to monomer for the initiation step. Even if experimental results fit well with such a scheme, it may be argued that initiation might be first order with respect to monomer, and propagation zero order. In fact, it may be easily shown that this hypothesis would lead to a different rate expression,

$$R_p = k_i k_p [I]_0 [H_2O]_0 [M] \frac{\int_0^t (1-p) e^{-k_t t} dt}{(1-p) e^{-k_t t}}$$

For each experiment at -70°C , values of the complex time function in above relation were computed using a wide range of arbitrary k_t . No value of k_t satisfied a linear relationship between $(R_p/[M])$ and the time function, and this second scheme appears unlikely.

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