the method of Meissner and Redding[9] to be 222.0°. This temperature must be quite near the *true* critical temperature, since vapor pressure measurements at 220° were exceedingly difficult to make. For the temperature range 110–210°, log *p* is approximately a linear function of the reciprocal of the absolute temperature; the value at 220° was not included in the derivation of the relationship

$$\log p \text{ (atm.)} = 4.3609386 - \frac{1409.0428}{(T + 273.16)} + 0.000244348(T + 273.16)$$

where T is in °C.

The maximum deviation between the experimental vapor pressure and the vapor pressures calculated by the above equation is 0.30%; this equation reproduces 9 of the 11 experimental points to 0.15% or less.

The compressibility values are believed to be accurate to within 0.1 to 0.2%. The decomposition of 1,2-difluoro-1,1-dichloroethane proceeded slowly enough even at the highest temperatures to provide accurate P–V–T data; the vapor pressure values are changed more by a slight decomposition than are the compressibility values.

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KINGSVILLE, TEXAS

[9] H. P. Meissner and E. M. Redding, *Ind. Eng. Chem.*, **34**, 521 (1942).

[CONTRIBUTION FROM THE DIVISION OF APPLIED CHEMISTRY, NATIONAL RESEARCH COUNCIL (CANADA)]

Cationic Polymerization of α-Methylstyrene

BY D. J. WORSFOLD AND S. BYWATER

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The kinetics of polymerization of α-methylstyrene with a boron trifluoride–ether–water complex have been studied. The reaction rate has been found to be governed by the expression $- \mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_i[\mathrm{c}][\mathrm{M}]\ (2 + k_\mathrm{p}[\mathrm{M}]/k_\mathrm{t})$ and the degree of polymerization by $\overline{\mathrm{DP}} = 2 + k_\mathrm{p}[\mathrm{M}]/k_\mathrm{t}$. The nature of the termination step has been investigated. The cause of the low degree of polymerization has been identified as a low propagation rate compared with the termination reaction.

The heat of polymerization of α-methylstyrene is known to be only of the order of 8 kcal. This would lead to the conclusion that the ceiling temperature for polymerization, as defined by Dainton and Ivin,[1] would be somewhat above room temperature. It is known, moreover, that the radical polymerization of this monomer is very difficult and at ambient temperature only low molecular weight polymers are produced with the Friedel–Crafts type of catalysts. It would seem desirable therefore to carry out kinetic measurements at lower temperatures using cationic catalysis whereby rather higher molecular weight polymers are formed in order to determine more certainly the cause of the low degree of polymerization. The two principal previous studies of this reaction, one by Jordan and Mathieson,[2] using aluminum chloride in carbon tetrachloride solution and one by Dainton and Tomlinson[3] using stannic chloride in ethyl chloride solution, are so contradictory that the study of a third system would seem worthwhile. The system chosen was boron trifluoride etherate in the presence of excess water and diethyl ether in ethylene chloride solution. The kinetics were found to follow very closely the mechanism proposed by Dainton and Tomlinson for their system.

Experimental

Materials.—Ethylene chloride was stirred with concentrated sulfuric acid for four days, washed, dried and distilled from aluminum chloride, and after a final wash was fractionally distilled over phosphoric oxide. The product was degassed and stored under vacuum.

α-Methylstyrene was fractionally distilled under vacuum, and stored under vacuum. Boron trifluoride was sublimed under vacuum and stored at liquid nitrogen temperature. Diethyl ether was distilled from sodium wire and then from phosphorus pentoxide into a trap on the vacuum system.

Procedure.—Since it has been reported that cationic polymerizations are rendered more reproducible by having a fair excess of water present, the concentration of water in practically all runs was at such a level that a very limited exposure to the atmosphere was considered permissible in that the water pick up would be negligible compared to the added water.

Solutions of monomer and water in ethylene chloride and boron trifluoride and ether in ethylene chloride, were prepared under vacuum, and blanketed with dry nitrogen. The reaction was started by pipetting a little of the catalyst solution into the monomer solution.

Samples were siphoned from the reaction vessel at intervals and the residual monomer estimated with mercuric acetate in methanol solution.[4] The initial rates were found from the first 10% or less of the reaction; rates given are in units of moles/l./minute. The molecular weights were determined after 10% reaction using the viscosity relationship, for benzene solution at 30°.

$$[\eta]_{\mathrm{sp0}}/c = 0.0105 + 1.787 \times 10^{-5}\, M$$

obtained from cryoscopic measurements on unfractionated polymer samples.

Results

The effect of temperature on the initial rates and degree of polymerization at various monomer concentrations was investigated at five temperatures between +20° and −20°.

At +20° the initial rates are very nearly dependent on the first power of the monomer concentration (Fig. 1), but at the lower temperatures the order increases and the whole series is adequately described by the expression

$$\text{Initial rate} = K_1[\mathrm{M}](C + K_2[\mathrm{M}])$$

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[1] F. S. Dainton and K. J. Ivin, *Nature*, **162**, 705 (1948).

[2] D. O. Jordan and A. R. Mathieson, *J. Chem. Soc.*, 2354 (1952).

[3] F. S. Dainton and R. H. Tomlinson, *ibid.*, 151 (1953).

[4] R. W. Martin, *Anal. Chem.*, **21**, 921 (1949).

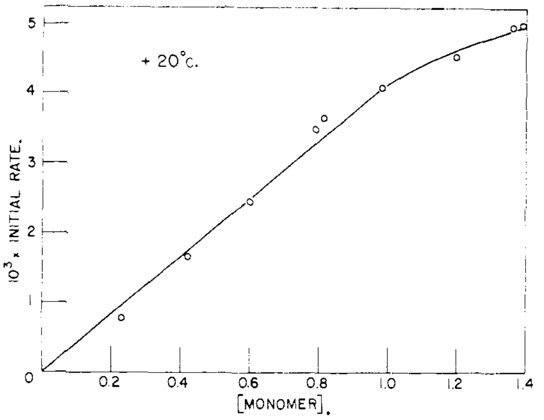

Fig. 1.—[BF$_3$] = 2.73 × 10^{-4}, [H$_2$O] = 3.11 × 10^{-3}, [C$_4$H$_{10}$O] = 2.68 × 10^{-2}.

and plots of initial rate/[Monomer] against [Monomer] are linear (Fig. 2). Some deviations are found at concentrations above molar in monomer at the lower temperatures, but these probably are due to the considerable change in the environment at these high concentrations.

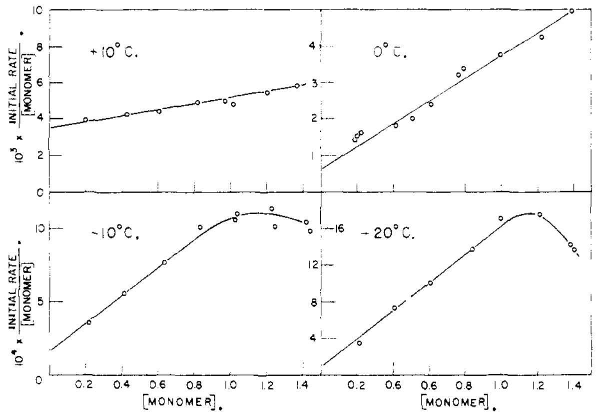

Fig. 2.

Temp.	10^3 × [BF$_3$]	10^3 × [H$_2$O]	10^2 × [C$_4$H$_{10}$O]
+10	1.09	3.11	2.68
0	1.09	3.11	2.41
−10	3.05	9.33	2.68
−20	1.09	3.11	1.25

The plots of $\overline{DP}$ against monomer concentrations are also linear at these temperatures and extrapolate back to a value close to 2 (Fig. 3). They are described by the equation

$$\overline{DP} = 2 + K_3[M]$$

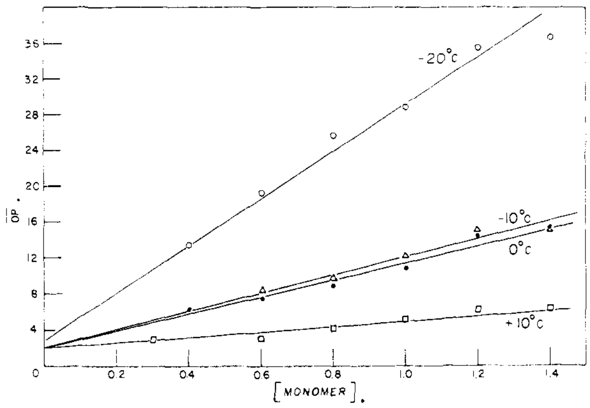

Fig. 3.—Reactant concentrations as in Fig. 2.

The variation of initial rate with boron trifluoride, water and ether concentrations was measured at −10° together with the corresponding degrees of polymerization, with the results shown in Tables I, II and III.

TABLE I

VARIATION OF INITIAL RATE AND $\overline{DP}$ WITH [BF$_3$]

[H$_2$O] = 3.11 × 10^{-3} M, [C$_4$H$_{10}$O] = 2.68 × 10^{-2} M, [C$_9$H$_{10}$] = 1 M, temp. = −10°

10^3 × [BF]$_3$	10^4 × initial rate	$\overline{DP}$
3.05	35.0	15.5
3.05	36.7	
2.41	25.4	15.2
1.87	18.8	15.7
1.37	9.1	15.8
1.37	12.3	
1.30	11.7	
1.29	11.0	
0.61	4.2	14.9

TABLE II

VARIATION OF INITIAL RATE AND $\overline{DP}$ WITH [H$_2$O]

[BF$_3$] = 3.05 × 10^{-3} M, [C$_4$H$_{10}$O] = 2.68 × 10^{-2} M, [C$_9$H$_{10}$] = 1 M, temp. = −10°

10^3 × [H$_2$O] added	10^4 × initial rate	$\overline{DP}$
0	124	18.7
0	78.3	
1.46	119.5	16.8
3.11	33.0	15.5
3.11	35.0	
3.11	41.3	
3.11	36.7	
6.22	19.7	17.8
9.33	11.4	12.5
9.33	10.8	
12.44	6.45	16.6

TABLE III

VARIATION OF INITIAL RATE AND $\overline{DP}$ WITH [C$_4$H$_{10}$O]

[H$_2$O] = 3.11 × 10^{-3} M, [BF$_3$] = 1.37 × 10^{-3} M, [C$_9$H$_{10}$] = 1 M, temp. = −10°

10^2 × [C$_4$H$_{10}$O]	10^4 × initial rate	$\overline{DP}$
0	*ca.* 5000	(15.8)
1.29	93.5	19.6
1.59	52.7	19.2
2.68	12.3	15.8
5.38	2.98	13.1

It is seen that both water and ether concentration have a large effect on the reaction, both considerably reducing the rate with increasing concentration in the range covered. In the complete absence of ether, however, the rate achieves a very high value indeed. But as the water concentration decreases the rate becomes very variable and seems to level off or perhaps fall. The order with respect to boron trifluoride is rather greater than unity, but a simple relationship is perhaps not to be expected in this complex initiating system.

The degree of polymerization shows far smaller variations than does the rate. It appears to be completely independent of the boron trifluoride concentration, nearly independent of the water, and only decreases slowly with higher ether concentrations. These results tend to exclude the possibility of any transfer with water and to permit a very little with ether. The principal effect of varying these reactants is on the initiation reaction.

All reactions would go to completion and there was no evidence for catalyst or co-catalyst consumption.

Discussion

The initiation of cationic polymerization is generally thought to occur through the reaction of the monomer with a proton donating complex of the Friedel–Crafts catalyst with some protonated compound such as water. In this investigation when water was present it is assumed that the initiating agent is some hydrate of boron trifluoride formed in competition with the etherate. Two hydrates have been isolated, an unstable monohydrate, and a comparatively stable dihydrate.[5] The structures suggested for the two complexes are $H^+(\bar{B}F_3OH)$ and $(H_3^+O)(\bar{B}F_3OH)$. Quite possibly the former would be a stronger proton donating agent, and account for the fall in rate as the water concentration increases due to the formation of more of the dihydrate. It also has been suggested that water reacts with boron trifluoride etherate to form a complex of structure $(C_2H_5O^+H_2)(\bar{B}F_3OC_2H_5)$,[6] similar to that of the alcoholate, this too could be the initiating agent.

It is possible that under rigorously dry conditions the rate would fall to zero, although solvent cocatalysis and the more likely ether cocatalysis are both feasible. There was little evidence for solvent cocatalysis as a polymer of molecular weight 1600, formed with no water deliberately added to the reaction mixture, had less than 0.05% chlorine present. The infrared spectrum of the polymer showed no evidence of ether linkages, but this in itself would not eliminate the possibility of ether cocatalysis.

The role of the ether probably is to reduce both the free boron trifluoride concentration and that of the monohydrate in the form $H^+(BF_3OH)^-$, by solvating the proton.

Chain termination can occur in a variety of ways. Since each boron trifluoride, water or ether molecule is capable of initiating many chains, chain termination must occur through proton expulsion to reform the catalyst, or through some intermediate such as water, ether, solvent or monomer to give chain transfer. The possible reactions are

$$BF_3 + C_4H_{10}O + H_2O \longrightarrow C$$

$$\begin{array}{lll}
\text{Initiation} & C + M & \xrightarrow{k_1} M^+C^- \\
\text{Propagation} & \left\{\begin{array}{l} M^+ + M \\ P_n^+ + M \end{array}\right. & \begin{array}{l} \xrightarrow{k_2} P_1^+ \\ \xrightarrow{k_2} P_{n+1}^+ \end{array} \\
\text{Transfer} & \left\{\begin{array}{l} P_n^+ + I \\ I^+ + M \end{array}\right. & \begin{array}{l} \xrightarrow{k_3} P + I^+ \\ \xrightarrow{k_4} M^+ \end{array} \\
\text{Monomer transfer} & P_n^+ + M & \xrightarrow{k_5} P + M^+ \\
\text{Termination} & P_n^+ & \xrightarrow{k_6} P + H^+ \\
\text{Monomer termination} & P_n^+ + M & \xrightarrow{k_7} P + H^+
\end{array}$$

where C is an active complex of BF_3, water and ether, and I may be any transfer agent.

The transfer reactions involving water or monomer can both be eliminated since they give kinetic equations which are either incompatible with the dependence of the initial rate or the degree of polymerization with monomer concentration, or both. On the same grounds monomer termination can also be eliminated. Solvent transfer cannot be eliminated on kinetic grounds, but can be ignored since the polymer contained virtually no chlorine.

Transfer with ether, however, is feasible, on kinetic grounds, and the variation of degree of polymerization with ether concentration at −10° suggests that at this temperature $2k_3 \sim k_6$. With the low concentration of ether present, however, this reaction can only play a minor role. It is possible that the ether extracts the proton to form an oxonium ion.

The major part of the reaction, consequently, seems to be governed by the reactions 1, 2 and 6, leading to the rate expressions

$$-\frac{d[M]}{dt} = k_1[C][M]\left\{2 + \frac{k_2}{k_6}[M]\right\}$$

where [C] is the concentration of active catalyst species, and

$$\overline{DP} = 2 + \frac{k_2}{k_6}[M]$$

Plots of initial rate/[Monomer] and $\overline{DP}$ against monomer concentration should both be linear giving intercepts of $2k_1[C]$ and 2, respectively, and this linearity is found. Also the ratio slope/intercept and slope/2 for the two equations respectively are both $k_2/2k_6$, and should be equal. These values from the experimental results are shown in Table IV, where good agreement is found at all except the highest temperature.

TABLE IV

Temp., °C.	−20	−10	0	+10
From Fig. 2, slope/intercept	14.0	5.9	4.8	0.5
From Fig. 3, slope/2	13.1	5.2	4.9	2.5

As k_6 grows larger and exceeds k_2 so the reaction will tend to first-order kinetics and very low molecular weights as is found. This is in accord with the scheme suggested by Dainton and Tomlinson using stannic chloride as a catalyst.

Since one catalyst molecule is capable of forming many chains, and transfer reactions appear to be of little importance, if the initiation step is proton addition the terminating step must be proton expulsion. Proton expulsion can occur by two processes, it can either regenerate the double bond, or else the chain end may cyclize by the carbonium ion substituting the penultimate phenyl ring, to give a hydrindene derivative[3]

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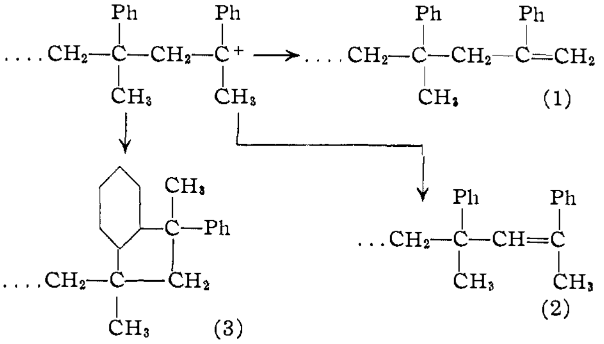
(5) N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, 1915 (1951).

(6) N. N. Greenwood and R. L. Martin, *Quart. Revs. (London)*, **8**, 17 (1954).



The structures of the corresponding dimers have been studied previously. Two are known, one saturated, the other unsaturated. Bergmann, Taubadel and Weiss[7] identified the former with structure 3, the latter with structure 2. Hukki[8] has shown, however, that for *p*-methyl-α-methylstyrene the two corresponding dimers have structure 3 for the saturated form and a 5:1 mixture of 1 and 2 for the unsaturated one.

The infrared spectrum of the polymer produced by boron trifluoride at 20°, of molecular weight 560, had several bands not found in very high molecular weight poly-α-methylstyrene. Strong bands were found in 900 and 1620 cm.$^{-1}$, which correspond to unsymmetrically disubstituted double bonds and appear in the monomer, and a weaker band at 840 cm.$^{-1}$ corresponding to a trisubstituted double bond. None of these bonds appear in the spectrum of the saturated dimer, nor did any of the bands that seemed characteristic of this compound and could be attributed to an *ortho*-disubstituted phenyl ring appear in the low polymer spectrum. Analysis of this polymer by bromination indicated that 4 out of every 5 molecules contained double bonds.

It is suggested that the polymer produced at this temperature mostly contained the end structure 1, with some of the structure 2. There is the probability that there was some of the saturated structure 3. The proportion of structure 3 probably increases as the temperature at which the polymer is formed is raised, polymer formed at 30° on analysis showed only 50% of the polymer molecules unsaturated, that at 0° was all unsaturated within experimental error.

The kinetic scheme shown above has none of the characteristics typical of polymerization near the ceiling temperature in which depolymerization is prominent. Subsequent work on the anionic polymerization[9] of α-methylstyrene has shown, however, that both propagation and depropagation reactions are important where the active polymer chains are long in the temperature range -40 to 0°. Roberts and Jessup[10] have measured the heat of polymerization of α-methylstyrene and found it to be dependent on the molecular weight of the resulting polymer. The highest polymer formed in this investigation at $-20°$ had a molecular weight of *ca.* 4,000. According to Roberts and Jessup a polymer of molecular weight 3,750 has a heat of polymerization of -9.04 kcal. For this value of ΔH and assuming $\Delta S = -27$ e.u. as found for high polymer,[9] the equilibrium monomer concentration where the forward and reverse reactions are equal would be 0.025 M instead of 0.24 M for high polymers. Thus the depropagation step is too slow to be important for low molecular weight chains at normal concentrations of monomer. Similar results were found at the other temperatures. The reason for the low molecular weight products formed at these temperatures must be the high rate of termination compared with the propagation step, and not the onset of depropagation, which would only become important if the chains were able to grow longer, as is the case for the anionic system where termination is negligible. In the cationic polymerization there is probably an abnormally low propagation rate, due to steric factors, compared with a reasonably normal termination rate.

OTTAWA, ONTARIO, CANADA

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[7] E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, **64**, 1493 (1931).

[8] J. Hukki, *Acta Chem. Scand.*, **3**, 279 (1949).

[9] S. Bywater and D. J. Worsfold, *J. Polymer Sci.*, in press.

[10] D. E. Roberts and R. S. Jessup, *J. Research Natl. Bur. Standards*, **46**, 11 (1951).