707. The Kinetics of Catalytic Polymerisations. Part XII.[1] Heat and Mechanism of Polymerisation of α-Methylstyrene catalysed by the Chloroacetic Acids.[1]

By C. P. Brown and A. R. Mathieson.

The heat of polymerisation of α-methylstyrene catalysed by trichloroacetic acid in ethylene dichloride at 20° is 8280 ± 90 cal. mole^{-1}. The polymer formed is a mixture of unsaturated dimer and trimer, and saturated esterified dimer–pentamer. The heat of polymerisation and infrared spectra are in agreement with the presence of trichloroacetate-substituted phenylindane end-groups in the saturated esterfied fraction. The ceiling temperature for polymerisation is 60°. The established kinetics of polymerisation have been confirmed by an adiabatic method. The mechanism of polymerisation is similar to that for styrene with the addition of depropagation and a two-step termination. Formation of the monomer–catalyst complex before initiation can explain differences between kinetic orders obtained from the initial rates and during the course of reaction.

The methyl substituent in α-methylstyrene increases the rate of cationic polymerisation but confines it to the formation of very low polymer at ordinary temperatures.[1] Evans and Polanyi [2] and Flory [3] suggested that for 1 : 1-disubstituted ethylenes there is steric hindrance to polymerisation, and in general heats of polymerisation ($-\Delta H_p$) for disubstituted monomers are 3—9 kcal. mole^{-1} smaller than the values estimated from heats of formation and hydrogenation, allowance being made for increased branching in the polymers and end effects.[4] For dienes and phenyl-substituted vinyl monomers the loss of resonance stabilisation on polymerisation must be also taken into account. The discrepancy is considered to be due to the energy of steric repulsion between the side-groups on the polymer chain.[4, 5] Estimated values of $-\Delta H_p$ of 22·3, 18·7, and 18·0 kcal. mole^{-1} have been given for ethylene, styrene, and α-methylstyrene respectively,[4] and values of 16·1—17·54 have been obtained experimentally for styrene.[6, 7] This indicates only a small degree of steric repulsion corresponding to about 1 kcal. mole^{-1}, loss of resonance stabilisation accounting for about 4 kcal. mole^{-1}.

Roberts and Jessup [8] measured the heat of polymerisation for four fractions of poly-α-methylstyrene formed during the industrial distillation of α-methylstyrene. The heat of polymerisation decreased as molecular weight ($\overline{M}_n$) increased from 10·13 kcal. ($\overline{M}_n = 1300$) to 8·83 kcal. mole^{-1} ($\overline{M}_n = 5400$), and obeyed the relation

$$-\Delta H_p = 8{\cdot}424 + 2194/\overline{M}_n$$

Extrapolation, if valid, shows that the infinite polymer has $-\Delta H_p = 8{\cdot}4$ kcal. mole^{-1} and the values for the dimer, trimer, and tetramer are 17·7, 14·6, and 13·0 kcal. mole^{-1} respectively. These figures apply to saturated polymers containing no catalyst fragments. The value for the infinite polymer indicates a very large steric effect accounting for about 9 kcal. mole^{-1}, while the dimer shows little, if any, steric hindrance. McCormick [9] gives $-\Delta H_p = 6{\cdot}96$ kcal. mole^{-1} for the polymerisation with a sodium–naphthalene catalyst, calculated from measurements of the ceiling temperature. In view of the partial

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[1] Part XI, Brown and Mathieson, *J.*, 1958, 3445.
[2] Evans and Polanyi, *Nature*, 1943, **152**, 738.
[3] Flory, *J. Amer. Chem. Soc.*, 1943, **65**, 372.
[4] Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, pp. 249—256.
[5] Roberts, *J. Res. Nat. Bur. Stand.*, 1950, **44**, 221.
[6] Tong and Kenyon, *J. Amer. Chem. Soc.*, 1947, **69**, 1402.
[7] Roberts, Watson, and Jessup, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 627.
[8] Roberts and Jessup, *ibid.*, 1951, **46**, 11.
[9] McCormick, *J. Polymer Sci.*, 1957, **25**, 488.

incorporation of catalyst for chloroacetic acid catalysis,[1] measurement of $-\Delta H_p$ for this system might give information on the structure of the polymer, and perhaps on its mechanism of formation. The opportunity was taken to confirm the kinetic orders of the polymerisations with the adiabatic calorimeter.

RESULTS AND DISCUSSION

Heat of Polymerisation.—The heat of polymerisation of α-methylstyrene catalysed by trichloroacetic acid in ethylene dichloride solution was measured calorimetrically at 20° (Table 1); the results were averaged to give 8280 ± 90 cal. mole^{-1} for $-\Delta H_p$, the accuracy being estimated from the reproducibility since the calorimetric measurements were more accurate than the polymerisations were reproducible.

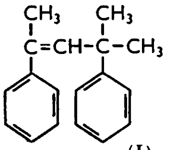
The molecular weight and distribution of the polymer formed were $\overline{M}_n = 370$; fraction 236—350, 58·9%; fraction 350—500, 25·3%; fraction 500—800, 13·9%; the constitution was unsaturated dimer, 47%; unsaturated trimer, 12%; dimer ester, 25%; trimer—pentamer ester, 14% (w/w).[1]

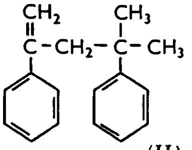
The value of $-\Delta H_p$ is close to that for an infinite polymer,[8] but for a comparable polymer of $\overline{M}_n = 370$, Roberts and Jessup's results predict $-\Delta H_p = 14{\cdot}35$ kcal. mole^{-1}, greatly in excess of the value obtained here. The polymer studied by Roberts and Jessup was saturated and incorporated no catalyst fragments. The double bonds and trichloroacetate groups in our polymer will have a large influence on $-\Delta H_p$.

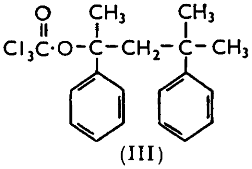
TABLE 1. *Heat of polymerisation of α-methylstyrene.*

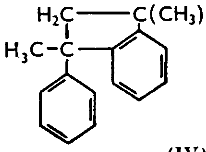
Monomer polymerised (mole)	0·0737	0·1370	0·0608	0·1410	0·1350
Corrected reaction temp. rise (°)...	2·009	3·452	1·772	3·471	3·524
Corrected rating temp. rise (°)......	0·902	0·432	0·945	0·543	0·543
Electrical energy supplied (cal.) ...	272·41	142·24	271·65	182·98	170·68
Thermal equivalent (cal.)	302·00	329·26	287·46	336·97	314·33
Heat evolved (cal.)	606·72	1136·61	509·38	1168·99	1107·69
Heat of polymerisation (cal.)	8232·2	8292·7	8377·2	8290·8	8205·1

Structure of the Polymer.—Head-to-tail addition being assumed, the simplest structures for the unsaturated dimer are (I) and (II). Corresponding structures could be written for head-to-head and tail-to-tail addition. The polymer could be a mixture of (I) and (II), as already reported,[10] which might behave as a single structure in heterolytic reactions. If there is no steric strain in this dimer, as implied by Roberts and Jessup's results,[8] its heat of formation from monomer will be equal to the heat of formation of a hypothetical unstrained infinite polymer from this dimer, the heats of formation being reckoned per monomer unit. The heat of formation of saturated dimer from monomer (17·7 kcal. mole^{-1}) being taken as equal to the heat of formation of hypothetical unstrained infinite polymer from monomer, the heat of dimerisation to unsaturated dimer is 8·85 kcal. mole^{-1}. The heat of trimerisation [8] to saturated trimer is 14·6 kcal. mole^{-1} and so the heat of trimerisation to unsaturated trimer is 9·7 kcal. mole^{-1}. The contribution of the unsaturated fraction 236—350 (59%) to the total heat of polymerisation is therefore 5·3 kcal. mole^{-1}.


(I)


(II)


(III)


(IV)

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[10] Hukki, *Acta Chem. Scand.*, 1949, **3**, 279.

The formation of the C–O bond will have an important influence on the heat of polymerisation to the esterified polymers. Values of 79, 80, 98·2, and 145 kcal. mole^{-1} may be taken for the C–O, C–C, C–H, and C=C bond energies respectively,[11] and rupture of the O–H bond in trichloroacetic acid yields [12] 3·2 kcal. mole^{-1}. The heat of dimerisation to a simple straight-chain esterified dimer (III) is largely the heat change associated with the conversion of 2 C=C and 1 O–H bonds into 3 C–C, 1 C–H, and 1 C–O bond, and if 4 kcal. mole^{-1} are allowed for loss of resonance stabilisation, it is 58 kcal. mole^{-1} which is much too high to reconcile with the experimental result even though the calculation is approximate. The corresponding value for linear esterified trimer is 41 kcal. mole^{-1}, 3 kcal. being allowed for steric strain. Polymers having this type of structure (III) cannot be formed in this reaction.

The stannic chloride-catalysed polymerisation of α-methylstyrene has been reported to yield cyclised polymers having a terminal substituted phenylindane structure,[13] and this structure (IV) has been assigned to the saturated dimer.[14] Infrared analysis of poly-α-methylstyrene formed by trichloroacetic acid catalysis [1] indicated the presence of trichloroacetic groups and the possibility of the occurrence of CH groups and *ortho*-disubstitution. A feasible structure of the saturated esterfied dimer is therefore (IV) with the trichloroacetate group substituted on the methylene group. Its formation from monomer and acid involves conversion of 2 C=C, 1 C–H, and 1 O–H bond into 4 C–C and 1 C–O bond, and so the heat of dimerisation is ~4·0 kcal. mole^{-1}. Heats of polymerisation to the corresponding trimer, tetramer, and pentamer are 7·6, 8·9, and 9·7 kcal. mole^{-1} respectively. The contribution of the esterified fraction 350—800 (39%), if it has this type of structure, to the total heat of polymerisation is ~2·3 kcal. mole^{-1}, the trimer–pentamer mixtures being treated as a tetramer. Together with the calculated contribution from the unsaturated fraction, this gives a calculated heat of polymerisation of 7·6 kcal. mole^{-1}, which is comparable with the experimental value when the approximate nature of the calculation is considered. This provides further support for the occurrence of the terminal substituted phenylindane structure in the saturated polymers.

Ceiling Temperature for Polymerisation.—The variation of the degree of polymerisation (n) with temperature and monomer concentration ([M]) can be derived from the kinetic definition of n in terms of chain propagation and termination as

$$\ln 1/n = E_n/\boldsymbol{R}T + \ln 1/[\mathrm{M}] + \text{Const.}$$

where E_n is the "activation energy for degree of polymerisation," normally given by $E_n = \sum E_p - \sum E_t$ where $\sum E_p$ and $\sum E_t$ are the activation energies for all types of propagation and chain-breaking process respectively. McCormick [9] has demonstrated the linearity of ln $(1/n)$ with ln (1/[M]) for α-methylstyrene, and the linearity of ln $(1/n)$ with ln $(1/T)$ is illustrated in Fig. 1 for the trichloroacetic acid-catalysed polymerisations of styrene and α-methylstyrene. The ceiling temperature (T_c) is obtained when ln $(1/n) = 0$ and is 60° for α-methylstyrene, in agreement with values obtained for this monomer in other systems.[9,15]

Entropy of Polymerisation.—Dainton and Ivin's equation [15] $T_c = \Delta H_p/(\Delta S^\circ + \boldsymbol{R} \ln [\mathrm{M}])$ (ΔS° is the standard entropy of polymerisation) gives $\Delta S^\circ = -24{\cdot}8$ cal. deg.$^{-1}$ mole^{-1} for the trichloroacetic acid-catalysed polymerisation of α-methylstyrene, the same value as given by McCormick for the sodium–naphthalene catalysis.[9]

Depropagation.—Depropagation is important [16] for some free-radical [17] and anionic [18]

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[11] Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140.

[12] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, 1936.

[13] Dainton and Tomlinson, *J.*, 1953, 151.

[14] Bergmann, Taubadel, and Weiss, *Ber.*, 1931, **64**, 1493.

[15] Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 331

[16] *Idem, Nature*, 1948, **162**, 705.

[17] *Idem, Proc. Roy. Soc.*, 1952, *A*, **212**, 207.

[18] Swarc, Levy, and Milkovich, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

polymerisations near the ceiling temperature. Even at —40° the anionic polymerisation of α-methylstyrene shows propagation–depropagation equilibrium,[19] but the cationic polymerisation catalysed by the boron trifluoride ether complex has too low an equilibrium concentration of monomer at —20° for depropagation to be important, and it has been concluded that the low degree of polymerisation is due to a slow propagation with a normal rapid termination.[20]

The propagation step in the chloroacetic acid-catalysed polymerisation of styrene can be written [21]

$$(M_n^+C^-)C + M \longrightarrow (M_{n+1}^+C^-)C$$

and the similarity of the kinetics suggests that this applies to α-methylstyrene also. The importance of depropagation for α-methylstyrene is determined by treating this as an equilibrium for which the equilibrium constant at 25° is, from $-\Delta H_p$ and $\Delta S°$,

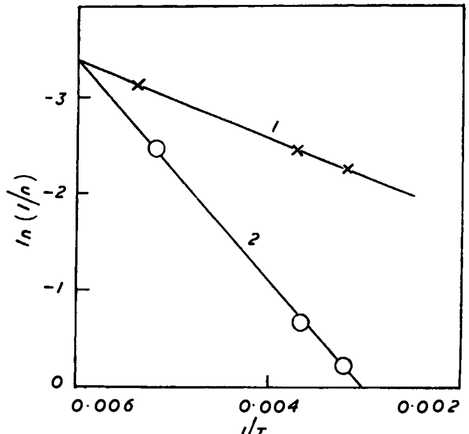
$$K_{pd} = k_p/k_d = [(M_{n+1}^+C^-)C]/\{[(M_n^+C^-)C][M]\} = 4{\cdot}47$$

and the equilibrium monomer concentration ($[M]_e$) for $[(M_{n+1}^+C^-)C] = [(M_n^+C^-)C]$ is 0·224M. The depropagation will be significant for this system. Since the molecular-weight distribution does not change appreciably during polymerisation,[1] $[(M_3^+C^-)C]/[(M_2^+C^-)C]$ is likely to be equal to the ratio of trimer to dimer in the polymer. Assuming that the trimer–pentamer ester mixture is half trimer, we find

$$[(M_3^+C^-)C]/[(M_2^+C^-)C] = 0{\cdot}29 \text{ and } [M]_e = 0{\cdot}065\text{M}$$

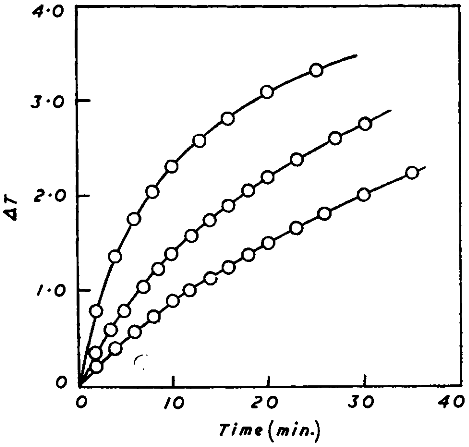
for dimer–trimer propagation–depropagation equilibrium. So although depropagation is important in fixing the ceiling temperature some other process, termination or transfer, is largely responsible for breaking the chains and producing very low polymer.

FIG. 1. *Effect of temperature on degree of polymerisation* (*n*).



1, Styrene; 2, α-methylstyrene.

FIG. 2. *Adiabatic polymerisation catalysed by trichloroacetic acid in ethylene dichloride solution.*



Kinetics by Adiabatic Calorimetry.—The adiabatic calorimeter was used to follow the temperature rise during polymerisation to confirm the kinetic orders established for both styrene and α-methylstyrene. Fig. 2 shows some typical time–temperature curves for α-methylstyrene catalysed by trichloroacetic acid in ethylene dichloride. The initial

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[19] Worsfold and Bywater, *J. Polymer Sci.*, 1957, **26**, 299.

[20] *Idem*, *J. Amer. Chem. Soc.*, 1957, **79**, 4917.

[21] Brown and Mathieson, *J.*, 1957, 3631.

rates of the reactions studied are shown in Table 2 with the appropriate concentration functions. This method fully confirms the kinetic orders of the initial rates already established, *i.e.*,

$$-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t = k_0[\mathrm{M}]_0^{\,2}[\mathrm{C}]_0 \text{ (nitromethane solutions)}$$

$$-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t = k_0[\mathrm{M}]_0^{\,2}[\mathrm{C}]_0^{\,2} \text{ (ethylene dichloride solutions)}$$

$$-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t = k_0[\mathrm{M}]_0^{\,2}[\mathrm{C}]_0^{\,x},\ x = 3{\cdot}51 \text{ (styrene)};\ \ x = 3{\cdot}2 \text{ (}\alpha\text{-methylstyrene)}$$

TABLE 2. *Dependence of initial rates on concentration by the adiabatic method. Trichloroacetic acid catalysis at 20°.*

α-Methylstyrene (no solvent)		α-Methylstyrene in ethylene dichloride		Styrene in nitromethane	
Initial rate (deg. min.$^{-1}$)	$10^3[\mathrm{M}]_0^{\,2}[\mathrm{C}]_0^{\,3}$	Initial rate (deg. min.$^{-1}$)	$[\mathrm{M}]_0^{\,2}[\mathrm{C}]_0^{\,2}$	Initial rate (deg. min.$^{-1}$)	$[\mathrm{M}]_0^{\,2}[\mathrm{C}]_0$
0·100	1·0	0·019	0·65	0·012	0·95
0·104	1·5	0·042	1·02	0·015	1·20
0·108	2·4	0·048	1·35	0·022	1·65
0·115	5·7	0·056	1·90	0·029	2·30
0·131	10	0·092	2·55	—	—
0·141	14	—	—	—	—

Mechanism of the Polymerisations

The results presented here and in the preceding Part[1] indicate that the chloroacetic acid-catalysed polymerisations of α-methylstyrene proceed essentially by the mechanisms established for styrene,[21] with the addition of depropagation, except that the termination occurs by proton expulsion to form unsaturated polymer, some of which reacts with catalyst to form chloroacetate-substituted phenylindane end groups. The relative rates of propagation, termination, and transfer are different for the two monomers. The mechanisms for α-methylstyrene are summarised in Table 3.

TABLE 3. *Mechanism of polymerisation.*

<table>
<tr><th></th><th>No solvent</th><th>Ethylene dichloride solution</th><th>Nitromethane solution</th></tr>
<tr><td>1.</td><td colspan="3">$\longleftarrow\ \mathrm{M} + \mathrm{C} \underset{k_1^{\,1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MC}\ .\ .\ .\ .\ .\ (K_1)\ \longrightarrow$</td></tr>
<tr><td>1*a*.</td><td>$\mathrm{M} + \mathrm{C}_2 \rightleftharpoons \mathrm{MC}_2\ .\ .\ .\ .\ .\ (K_2)$</td><td></td><td></td></tr>
<tr><td>2.</td><td>$\mathrm{M} + \mathrm{CW} \xrightarrow{k_i} \mathrm{M}^+\mathrm{C}^- + \mathrm{W}$</td><td colspan="2">$\longleftarrow\ \mathrm{MC} \xrightarrow{k_i} \mathrm{M}^+\mathrm{C}^-\ \longrightarrow$</td></tr>
<tr><td>2*a*.</td><td>$\mathrm{MC}_2 + \mathrm{CW} \xrightarrow{k_i^{\,1}} \mathrm{M}^+\mathrm{C}^- + \mathrm{C}_2 + \mathrm{W}$</td><td></td><td></td></tr>
<tr><td>3.</td><td colspan="2">$\longleftarrow\ \mathrm{M}^+\mathrm{C}^- + \mathrm{MC} \underset{k_{d_1}}{\overset{k_p}{\rightleftharpoons}} (\mathrm{M}_2{}^+\mathrm{C}^-)\mathrm{C}\ \longrightarrow$</td><td>$\mathrm{M}^+\mathrm{C}^- + \mathrm{M} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \mathrm{M}_2{}^+\mathrm{C}^-$</td></tr>
<tr><td>3*a*.</td><td colspan="2">$(\mathrm{M}_n{}^+\mathrm{C}^-)\mathrm{C} + \mathrm{M} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} (\mathrm{M}_{n+1}{}^+\mathrm{C}^-)\mathrm{C}\ \longrightarrow$</td><td>$\mathrm{M}_n{}^+\mathrm{C}^- + \mathrm{M} \rightleftharpoons \mathrm{M}_{n+1}{}^+\mathrm{C}^-$</td></tr>
<tr><td>4.</td><td colspan="2">$(\mathrm{M}_n{}^+\mathrm{C}^-)\mathrm{C} + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{M}_n + (\mathrm{M}^+\mathrm{C}^-)\mathrm{C}\ \longrightarrow$</td><td>$\mathrm{M}_n{}^+\mathrm{C}^- + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{M}_n + \mathrm{M}^+\mathrm{C}^-$</td></tr>
<tr><td>5.</td><td colspan="2">$(\mathrm{M}_n{}^+\mathrm{C}^-)\mathrm{C} \xrightarrow{k_t} \mathrm{M}_n + \mathrm{C}_2\ \longrightarrow$</td><td>$\mathrm{M}_n{}^+\mathrm{C}^- \xrightarrow{k_t} \mathrm{M}_n + \mathrm{C}$</td></tr>
<tr><td>6.</td><td colspan="3">$\longleftarrow\ \mathrm{M}_n + \mathrm{C} \xrightarrow[k_c^{\,1}]{k_c} \mathrm{M}_n\mathrm{C}\ .\ .\ .\ .\ .\ .\ .\ .\ (K_c)\ \longrightarrow$</td></tr>
</table>

Step 1 is the reversible formation of the monomer–catalyst complex MC, and a second complex MC_2 is formed in absence of solvent (step 1*a*). Initiation (step 2) is the spontaneous conversion of the complex MC into an ion-pair, which in absence of solvent requires cocatalysis by water (W) and may involve MC_2 also (step 2*a*). Propagation–depropagation (step 3*a*) is written differently for the first stage (step 3) to allow for solvation of the ion-pair by catalyst in ethylene dichloride and absence of solvent. The ion-pair is not catalyst-solvated in nitromethane. Steps 4 and 5 are transfer and spontaneous termination and step 6 is the reversible formation of esterified from unsaturated polymer. There is no evidence for non-stationary conditions and the stationary-state assumption is not necessarily invalidated by the low degree of polymerisation when transfer and depropagation reactions are important. However, k_p, k_d, k_{tr}, k_t, and k_c will not be independent of chain-length and in the equations which follow these quantities will represent weighted means of the values for the different chain lengths.

If stationary conditions hold, the stationary concentration of ion-pairs ([G]) is

$$[G] = k_i[MC]/k_t \text{ (solution)}$$

$$[G] = (k_i[M][CW] + k_i^1[MC_2][CW])/k_t \text{ (absence of solvent)}$$

The initial rates of polymerisation are

$$-d[M]_0/dt = k_i[MC](k_p[M]_0[C]_0 - k_d)/k_t \text{ (ethylene dichloride solution)}$$

$$-d[M]_0/dt = k_i[MC](k_p[M]_0 - k_d)/k_t \text{ (nitromethane solution)}$$

$$-d[M]_0/dt = (k_i[M]_0[CW] + k_i^1[MC_2][CW])(k_p[M]_0[C]_0 - k_d)/k_t \text{ (absence of solvent).}$$

Since $k_p = 4{\cdot}47k_d$ and $[M]_0[C]_0 \gg 1$, k_d may be neglected for the initial rate. The observed change in kinetic order with respect to monomer as reaction proceeds[1] suggests a treatment of the formation of the MC complex similar to that for enzyme catalysis.[22] For a stationary concentration [MC]

$$d[MC]/dt = k_1[M]([C] - [MC]) - k_1^1[MC] - k_i[MC] = 0$$

$$[MC] = k_1[M][C]/(k_1[M] + k_1^1 + k_i)$$

and the rate of initiation (V_i) is

$$V_i = k_i[MC] = k_ik_1[M][C]/(k_1[M] + k_1^1 + k_i)$$

When $[C] \gg [MC]$, $V_i = k_ik_1[M][C]/(k_1^1 + k_i)$, and this holds for the initial rate. Hence, in agreement with the experimental kinetic orders

$$-d[M]_0/dt = k_ik_1k_p[M]_0^2[C]_0^2/k_t(k_1^1 + k_i) \text{ (ethylene dichloride solution)}$$

$$-d[M]_0/dt = k_ik_1k_p[M]_0^2[C]_0/k_t(k_1^1 + k_i) \text{ (nitromethane solution)}$$

$$-d[M]_0/dt = k_pK_h[M]_0^2[C]_0[W](k_i + k_i^1[C]_0^3K_2)/k_t \text{ (no solvent)}$$

$$\text{where } K_h = [CW]/[C][W]$$

After the initial stage is over the limiting rate of initiation is $V_i = k_i[C]_0$ if $k_1 \gg (k_1^1 + k_i)$ and so the rate of polymerisation becomes

$$-d[M]/dt = k_ik_p[M][C]^2/k_t \text{ (ethylene dichloride solution)}$$

$$-d[M]/dt = k[M][C][W](k_i + k_i^1[C]^3K_2) \text{ (no solvent)}$$

where k is written for the rate-constant product and steps 2 and 2*a* are considered to proceed analogously to the formation and ionisation of MC. The rate of polymerisation depends on [M] and not $[M]^2$ after the initial stage is over, as observed.[1] For nitromethane solutions, the ionisation of the monomer–catalyst complex is favoured by the high dielectric constant of the medium; [MC] is always very small and never becomes equal

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[22] Michaelis and Menten, *Biochem. Z.*, 1913, **49**, 333.

to $[C]_0$ and the initial kinetics persist throughout the reaction, as observed. This treatment of the initiation applies to styrene as well as to α-methylstyrene.

The initial rate of catalyst consumption ($-d[C]_0/dt$) is determined by the first stage of propagation (step 3) for ethylene dichloride solutions and so shows the same kinetic order ($[M]_0^2[C]_0^2$) and has roughly the same magnitude as the initial rate of polymerisation, as observed.[1] In this solvent then,

$$[M^+C^-] = (k_i + k_{tr}[G])/(k_{tr} + k_{p1})$$

$$-d[C]_0/dt = k_i k_{p1} k_1([M]_0[C]_0 + k_{tr}k_1[M]_0^2[C]_0^2/k_t(k_1^1 + k_i)]/(k_{tr} + k_{p1})(k_1^1 + k_i)$$

$[M]_0[C]_0$ is evidently negligible compared with the term in $[M]_0^2[C]_0^2$ and this agrees with the preponderance of transfer over termination required by the molecular weights (see below) and the small value of $(k_1^1 + k_i)/k_1$ (the " Michaelis constant ") needed to explain the change in kinetic order with respect to monomer. The fall in catalyst consumption and the eventual catalyst regeneration are due to the release of catalyst by termination and transfer, only a part of the released catalyst combining with the polymer. For the reactions in the absence of solvent, initiation depends on [CW] which is small and proportional to [C] when [W] is constant. Hence $-d[C]_0/dt \propto [C]_0$ as observed.

The degree of polymerisation (n) is $n = (V_p - V_d)/(V_t + V_{tr})$ and is independent of [M] and [C] for ethylene dichloride solutions and absence of solvent. Then, since $V_d \ll V_p$, $V_{tr} \gg V_t$, and transfer is the most important polymer-chain-breaking process, and $k_p/k_{tr} = 2{\cdot}7$ at 25° (the corresponding value for styrene[21] is 21). The relatively high negative value of E_n will be due to a large E_{tr}, with a small E_t as for styrene.[23] The increase in n with [C] for nitromethane solutions requires a reduced transfer rate at high [C], or re-activation by the catalyst of terminated unsaturated polymer in preference to cyclisation.

The discussions of the initiation mechanism in terms of the formation of endothermic polarisation complexes with a finite probability of transition to ion-pairs, and of propagation in terms of autocatalysis given for styrene [21] apply equally to α-methylstyrene.

EXPERIMENTAL

Materials were purified as already described.[1] The calorimeter used for the measurement of heat of polymerisation and adiabatic kinetics was that previously employed for the measurement of heats of mixing of hydrocarbons.[24] For the heat of polymerisation experiments, known weights of acid and ethylene dichloride were distilled into glass ampoules which were sealed, and placed in the mixing vessel surrounded by a known mixture of ethylene dichloride and monomer. The procedure was as before [24] except that water at 20° replaced alcohol in the middle Dewar vessel, to increase the thermal equivalent. The temperature rises were kept below 4°. Polymerisation was complete, and the temperature constant, in less than 1 hr. Calibrations were carried out before and after polymerisation to determine the thermal equivalent of the system. Cooling corrections were negligible but the temperature was measured every minute for 15 min. before and after each polymerisation and calibration. The calibration results in Table 1 are the averages of the two determinations. The change in thermal equivalent on polymerisation was negligible. Comparison of experiments at different monomer concentrations indicated that the heat of dilution is negligible compared with that of polymerisation. The calorimetric apparatus was far more precise than necessary, having been designed for the measurement of very small heat changes. The adiabatic kinetic experiments were carried out in the same way except that the reactions were slower and the temperature was measured every 2 min. during the reaction.

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[23] Brown and Mathieson, *J.*, 1957, 3612.
[24] Brown, Mathieson, and Thynne, *J.*, 1955, 4141.