

The Kinetics of Ionic Polymerisations. Part VI. The Copolymerisation of isoButyl Vinyl Ether and 2-Chloroethyl Vinyl Ether.*

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The copolymerisation of *isobutyl vinyl ether* and 2-chloroethyl vinyl ether catalysed by iodine obeys Mayo and Walling's copolymerisation equation. The reactivity ratios are respectively 1.90 and 0.70. Third-order kinetics are obeyed with an apparent velocity constant in between those for the two monomers, but nearer the slower one (2-chloroethyl vinyl ether). An attempt has been made to describe the effect of monomer concentration on rate in terms of the true velocity constants for the separate monomers and the individual formation constants K_c for the inactive iodine-monomer complexes. The results suggest that the K_c value of the *isobutyl vinyl ether* is diminished in the presence of 2-chloroethyl vinyl ether. This may be a dielectric-constant effect. Evidence for this view is also found in the absence of a maximum in the curve of rate against total monomer concentration.

COPOLYMERISATION has been reviewed by Mayo and Walling (*Chem. Reviews*, 1950, **46**, 191) and it appears that quantitative information for carbonium ion copolymerisation is sparse compared with that available for radical intermediates. There are no data for the "reactivity ratios" of the vinyl ethers, and here we make a fairly complete investigation of one monomer pair, catalysed by iodine in the solvent diethyl ether. There is also considerable interest in comparison of kinetics of the copolymerisation with those to be expected from the polymerisation of the individual monomers.

EXPERIMENTAL

The polymerisations were followed in the usual dilatometer (see preceding papers) at 25°. The solvent used was diethyl ether, and the iodine catalyst was used at a concentration of 4.37 mmole/l. in all cases. The materials were all purified as previously described (Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425). The rate of reaction was determined on the basis of the volume contraction, calculated from the density of the mixed monomer system, and the isolated polymer. The monomer contents of the copolymers were determined from commercial halogen microanalyses. Thus density and halogen content were determined for all polymers, and cryoscopic molecular weights in one or two cases.

RESULTS

Effect of Monomer Concentration on Rate.—A number of runs were made in which the total monomer concentration was varied, the molar ratio constant being kept at 43.9 mole % of *isobutyl vinyl ether* to 56.1 mole % of 2-chloroethyl vinyl ether. The catalyst concentration was 4.37 mmole/l. The results are shown in Fig. 1.

It is apparent that the reaction is of first order in monomer up to 4 mole/l., and shows no marked falling off. By assuming that a third-order equation holds, $k = \text{velocity}/[M][C]^2$ is found to have the value 131 l.² mole⁻² min.⁻¹.

The polymers varied somewhat in properties, being liquids, sometimes viscous, from yellow to orange and deep brown. The densities were in the range 0.9919 to 1.057, the average value for the six specimens being $d_4^{25} = 1.018$ (a mixture of 43.9 mole % of *isobutyl vinyl ether* and 56.1 mole % of 2-chloroethylvinyl ether has $d_4^{25} = 0.9015$).

Monomer Reactivity Ratios.—If $d[M_2]/d[M_1]$ be the relative rates of incorporation of monomer M_2 (2-chloroethyl vinyl ether) and monomer M_1 (*isobutyl vinyl ether*) in the polymer, for a ratio of monomer concentrations of $[M_1]/[M_2]$, then the reactivity ratio, r_2 , is related to the reactivity ratio, r_1 (Mayo and Walling, *loc. cit.*), by the differential equation

$$r_2 = \frac{[M_1]}{[M_2]} \cdot \frac{d[M_2]}{d[M_1]} + \left(\frac{[M_1]}{[M_2]} \right)^2 \frac{d[M_2]}{d[M_1]} \cdot r_1 - \frac{[M_1]}{[M_2]}$$

* Part V, preceding paper.

For appreciable amounts of reaction it is more correct to use the integrated equation (Mayo and Walling, *loc. cit.*). The data in Table 1 have been analysed by both the integral and differential equations, by the usual graphical method of Mayo and Walling, with the results given below. As expected, the integral equation gives a slightly smaller error than the differential equation.

Differential equation,

$$\begin{aligned} r_1 &= 1.95 \pm 0.1 \\ r_2 &= 0.70 \pm 0.1 \end{aligned}$$

Integral equation,

$$\begin{aligned} r_1 &= 1.90 \pm 0.05 \\ r_2 &= 0.70 \pm 0.05 \end{aligned}$$

TABLE 1. Composition (mole %) of monomer (initial) and copolymer.

Monomer, M ₁	20.7	43.9	61.05	70.15	91.25
M ₂	79.3	56.1	38.95	29.85	8.75
Copolymer, M ₁	31.45	61.7	72.8	82.15	95.0
M ₂	68.55	38.3	27.2	17.85	5.0

Monomer Composition and Rate.—The relationship between monomer composition and overall rate was determined for a total monomer concentration of 4.1 mole/l. and catalyst concentration of 4.37 mmole/l. The values for the pure monomer are based on the data in Part III (*J.*, 1952, 4167), that for 2-chloroethyl vinyl ether (M₂) being interpolated, and that for butyl vinyl ether (M₁) being calculated from the equation given in the Appendix to Part V (preceding paper).

$$-\frac{d[M]}{dt} = \frac{k[I_2]^2[M]}{(1 + K_c[M])^2} = \frac{4000[I_2]^2[M]}{(1 + 0.8[M])^2}$$

TABLE 2.

Monomer, mole %, M ₁	0	20.7	20.7	43.9
M ₂	100	79.3	79.3	56.1
Velocity, mole l. ⁻¹ min. ⁻¹	6.7 × 10 ⁻³	2.42 × 10 ⁻³	3.38 × 10 ⁻³	10.26 × 10 ⁻³
Monomer, mole %, M ₁	70.15	91.25	100	
M ₂	29.85	8.75	0	
Velocity, mole l. ⁻¹ min. ⁻¹	17.8 × 10 ⁻³	24.37 × 10 ⁻³	17.00 × 10 ⁻³	

Degree of Polymerisation.—This was determined for two copolymers as 3.5 and 4.5. These values are rather lower than that expected for pure *isobutyl* vinyl ether polymer, of about 10, but similar to that expected for pure 2-chloroethyl vinyl ether polymer, of 4.6.

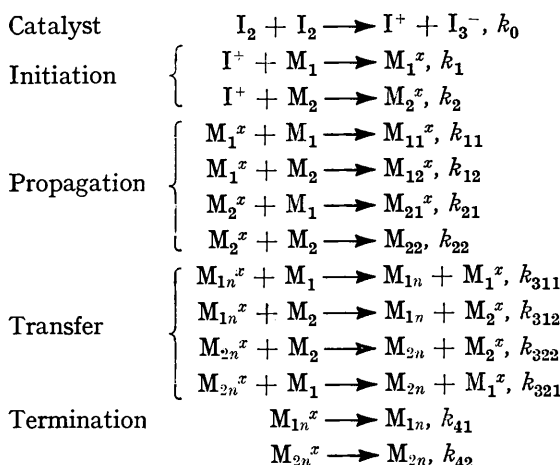
DISCUSSION

The true velocity constants k_t for the pure monomers were 4000 for *isobutyl* vinyl ether and 125 for 2-chloroethyl vinyl ether, and these constants involve the ratio of propagation to termination rates. On the other hand, the reactivity ratios of 1.9 for *isobutyl* vinyl ether and 0.7 for 2-chloroethyl vinyl ether which involve only the propagation rates are relatively much less different. This leads to the conclusion that the termination rate constants must be very different for the two monomers, *i.e.*, much less for the *isobutyl* than for the 2-chloro-ethyl ether.

It is also of considerable interest that the apparent copolymerisation velocity constant of 131 lies much nearer the figure 125 for 2-chloroethyl than 4000 for *isobutyl* vinyl ether. This again leads to conclusions about the termination step, and suggests that the copolymerisation kinetic chains preferentially end on a 2-chloroethyl vinyl ether monomer. The fundamental step may be loss of an I⁺ ion and this would be expected to occur more easily with the 2-chloroethyl monomer than the *isobutyl* vinyl ether monomer, from considerations of the inductive effect of the side-group.

We can discuss the effect of monomer ratio on rate in terms of r_1 , r_2 , $k_{t,1}$ and $k_{t,2}$, if we extend the usual copolymerisation scheme to include inactive complexes. The steps are *

* Our usual numbering of velocity constants is altered so as to agree with that usually used in the field of copolymerisation.



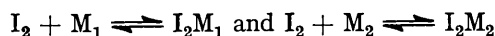
The following data are known :

$$\begin{aligned}
 r_1 &= k_{11}/k_{12} = 1.9 & r_2 &= k_{22}/k_{21} = 0.7 \\
 k_{i,1} &= \frac{k_0 k_{11}}{k_{41}} = 4000 & k_{i,2} &= \frac{k_0 k_{22}}{k_{42}} = 125 \text{ (Appendix, preceding paper)}
 \end{aligned}$$

Stationary concentrations of all intermediates being assumed, we can show that

$$\begin{aligned}
 -\frac{d([\text{M}_1] + [\text{M}_2])}{dt} &= \frac{(r_1[\text{M}_1]^2 + 2[\text{M}_1][\text{M}_2] + r_2[\text{M}_2]^2)}{r_1 \frac{k_{41}}{k_0 k_{11}} [\text{M}_1] + r_2 \frac{k_{42}}{k_0 k_{22}} [\text{M}_2]} [\text{I}_2]_f^2 \\
 &= \frac{(1.9[\text{M}_1]^2 + 2[\text{M}_1][\text{M}_2] + 0.7[\text{M}_2]^2)}{0.475[\text{M}_1] + 5.6[\text{M}_2]} 10^3 \cdot [\text{I}_2]_f^2 \\
 &= 10^3 A \cdot [\text{I}_2]_f^2 \dots \dots \dots (1)
 \end{aligned}$$

Now it can easily be shown, if K_{c1} and K_{c2} are the equilibrium constants for formation of inactive iodine-monomer complexes :



that
$$[\text{I}_2]_f = \frac{[\text{I}_2]}{1 + [\text{M}_1]K_{c1} + [\text{M}_2]K_{c2}} = \frac{4.37 \times 10^{-3}}{1 + 0.8[\text{M}_1] + 0.05[\text{M}_2]} \dots \dots (2)$$

Values of $[\text{I}_2]_f$ calculated from equation (2) are substituted in equation (1) to allow calculation of overall velocities of polymerisation. The values of $10^3 A$ and $[\text{I}_2]_f$ are listed in Table 3.

TABLE 3. Monomer composition-rate curve. $[\text{I}_2] = 4.37$ mmole/l. $[\text{M}_1] + [\text{M}_2] = 4.1$ mole/l.

Monomer, %		$10^3 A$	$[\text{I}_2]_f^2 \cdot 10^6$	$10^3 \times \text{rate}$		Monomer, %		$10^3 A$	$[\text{I}_2]_f^2 \cdot 10^6$	$10^3 \times \text{rate}$	
$[\text{M}_1]$	$[\text{M}_2]$			Calc.	Obs.	$[\text{M}_1]$	$[\text{M}_2]$			Calc.	Obs.
0	100	0.512	13.1	6.7	6.7	70.15	29.85	2.89	1.69	4.9	17.8
20.7	79.3	0.767	5.66	4.3	{ 3.4 2.4	91.25	8.75	7.73	1.18	9.1	24.4
43.9	56.1	1.32	2.92	3.8	10.3	100	0	16.4	1.04	17.0	17.0

The theory reproduces the minimum in the curve, but puts it at about 40% instead of about 22% of *isobutyl vinyl ether*. Beyond the minimum, the experimental results rise much more rapidly than those given by the theory. We attribute this to a failure of equation (2), which is based on the idea of two independent equilibria. It seems possible that the addition of 2-chloroethyl vinyl ether to the system *isobutyl vinyl ether-iodine* changes the equilibrium constant K_{c1} in the direction of a decrease, *i.e.*, making the *isobutyl vinyl ether-iodine* complex less stable. This may be a dielectric-constant effect as

we should expect the chloro-derivative to have a different dielectric constant from the other ethers. There is additional evidence for this theory in Fig. 1. Here we see that 56 mole % of 2-chloroethyl vinyl ether has suppressed the maximum velocity that was found for isobutyl vinyl ether at a monomer concentration of 0.8, which we take to mean that it has

FIG. 1. The rate of copolymerisation as a function of total initial concentration of monomers. The arrow denotes the concentration at which the curve for pure isobutyl vinyl ether monomer reaches a maximum, but no maximum appears in the copolymerisation.

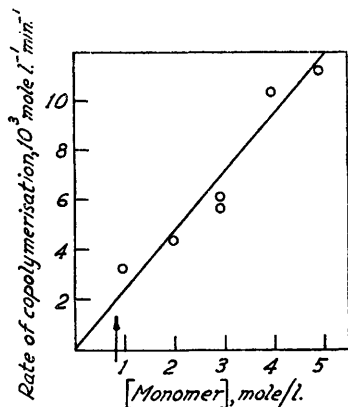
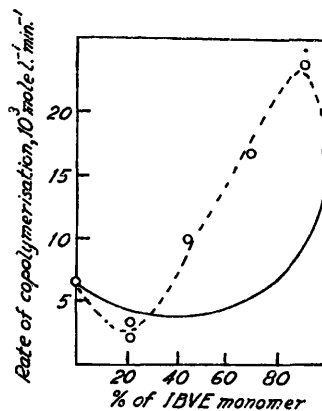


FIG. 2. Rate of copolymerisation at varying ratios of isobutyl vinyl ether to 2-chloroethyl vinyl ether monomer. The broken line links the experimental points, while the full line is calculated from the theory.



decreased the stability of the isobutyl vinyl ether-iodine complex. The existence of such maxima has been attributed in earlier papers of this series to the formation of stable vinyl ether-iodine complexes.

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