Eur. Polym. J. Vol. 20, No. 2, pp. 119–124, 1984
Printed in Great Britain. All rights reserved

0014-3057/84 $3.00 + 0.00

THE KINETICS OF THE POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY *t*-BUTYLMAGNESIUM BROMIDE IN THF, TOLUENE OR MIXED SOLVENT

P. E. M. ALLEN*, C. MAIR†, D. R. G. WILLIAMS and E. H. WILLIAMS
Department of Physical and Inorganic Chemistry, The University of Adelaide, Box 498, GPO, Adelaide, South Australia 5001

(*Received* 7 *June* 1983)

Abstract—The kinetics of the solution polymerization of methyl methacrylate in THF, toluene and their mixtures were studied between 200 and 300 K using dilatometry (in the systems where it was valid), gravimetric determination and monitoring monomer and polymer concentrations by NMR spectrometry. The reaction followed zero order kinetics at 200 K, first order kinetics at 275 K and mixed order in between. At both the limits and intermediate range, the reaction followed an integrated rate equation consistent with terminationless propagation proceeding through a complex between monomer and the propagating species. Above 275 K, termination and side reactions were evident and the yields of high mol. wt polymer were small. Density–temperature calibrations for monomer in THF, toluene and mixtures were constructed for the range 190–283 K. However for polymerizations in toluene-rich mixtures, where very high mol. wt polymer forms, the contraction did not correlate linearly with conversion.

I. POSTULATED MECHANISM AND KINETIC EQUATIONS

Allen and Bateup [1] established a zeroth *internal* order rate equation for the polymerization of methyl methacrylate (MMA) in mixed tetrahydrofuran (THF) and toluene solvent initiated by *n*-butylmagnesium bromide

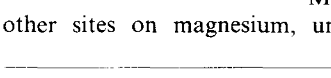
$$v_p = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k\,[\mathrm{I}]_0[\mathrm{M}]_0 \qquad (1)$$

The dependence on initial concentrations, signified by the subscript 0, corresponds to an *external* order, which Laidler says should be called true order [2], of unity with respect to initiator (I) and monomer (M). The rate did not decay with time up to conversions of 40%, corresponding to an internal order of zero.

Equation (1) is significantly different from that obeyed by typical rapid-initiation, terminationless, anionic polymerizations. A pseudoanionic mechanism was postulated in which monomer and the propagating species (P) form a complex (C) prior to the growth step (k_p):

$$\mathrm{P}_n + \mathrm{M} \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_p} \mathrm{P}_{n+1} \qquad (2)$$

It is likely [3, 4] that the propagating species are Mg—C bonds



where the other sites on magnesium, unspecified above, are a halide or butyl group or, in associated species, Mg—C—Mg or Mg—Br→Mg bridging bonds, with coordinated THF or a polymer carbonyl group completing the first coordination shell [3, 4].

Under steady state conditions, the concentrations of the complexed and uncomplexed growth centres are related by

$$(k_{-c} + k_p)[\mathrm{C}] = k_c[\mathrm{P}][\mathrm{M}] \qquad (3)$$

Initiation is rapid, but the efficiency of initiation (f) is low so

$$[\mathrm{P}] + [\mathrm{C}] = f\,[\mathrm{I}]_0 \qquad (4)$$

where $[\mathrm{I}]_0$ is the initial concentration of initiator.

The rate equation corresponding to the mechanism (2) is

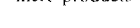
$$v_p = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_c[\mathrm{P}][\mathrm{M}] - k_{-c}[\mathrm{C}] \qquad (5)$$

which under steady state conditions [equations (3) and (4)] becomes

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k'\frac{[\mathrm{M}]}{1 + k''[\mathrm{M}]},$$
$$k' = k_c\{1 - 1/(1 + k_p/k_c)\}f\,[\mathrm{I}]_0,$$
$$k'' = k_c/(k_{-c} + k_p). \qquad (6)$$

Depending on the value of $k''[\mathrm{M}]$, this equation changes from internal zeroth to internal first order.

The initiator efficiency has been shown previously to be dependent on initial monomer concentration $[\mathrm{M}]_0$. The mechanism proposed also involves complex formation [1].


(7)

$$\mathrm{I} + \mathrm{M} \rightleftharpoons \mathrm{I,M} \xrightarrow{k_i,\,+\mathrm{M}} \mathrm{P}_1; \quad \mathrm{I,M} \xrightarrow{k_s} \text{inert products} \qquad (7)$$

---

*To whom enquiries should be addressed.

†Now at ICI Central Research Laboratories, Ascot Vale, Victoria.

Table 1. Limiting cases of equations (6) and (8): the internal order, with respect to [M], and the external order, with respect to $[\mathrm{M}]_0$

Case	$\mathrm{Lim}\left(\frac{[\mathrm{M}]}{1+k''[\mathrm{M}]}\right)$	[M]	Lim (f)	$[\mathrm{M}]_0$
Ia	$(k_p + k_{-c})/k_c$	Zeroth	$k_i[\mathrm{M}]_0/k_s$	First
Ib	$(k_p + k_{-c})/k_c$	Zeroth	1	Zeroth
IIa	[M]	First	1	First
IIb	[M]	First	$k_i[\mathrm{M}]_0/k_s$	Second

so that

$$f = 1/(1 + k_s/k_i[\mathrm{M}]_0) \tag{8}$$

Equations (6) and (8) must both be taken into account in determining the external order with respect to monomer. The external order with respect to initiator is one under all conditions.

Four limiting cases can be identified and are listed with the appropriate conditions in Table 1. Case **Ia** corresponds to equation (1) and case **IIa** is indistinguishable from the rate equation obeyed by a normal rapid-initiation, terminationless polymerization.

The test of the mechanism has rested previously on the limiting case **Ia** being observed in the polymerizations initiated by *n*-BuMgBr, *n*-$\mathrm{Bu_2Mg}$ and *s*-BuMgBr in mixed THF–toluene solution [1] and a demonstration that the internal order with respect to monomer increases to one at higher temperatures and lower initial monomer concentrations [5]. We now extend the tests to *t*-BuMgBr and in particular to the more interesting isotactic polymerizations in toluene-rich media. We apply the more rigid test of fitting the full integrated rate equation

$$\ln[\mathrm{M}] + k''[\mathrm{M}] = C - k't, \tag{9}$$

where $C = \ln[\mathrm{M}]_0 + k''[\mathrm{M}]_0$.

II. EXPERIMENTAL

Procedures for refining reagents and preparing initiator solutions are described elsewhere [5] together with a description of the quick-filling twin-tube dilatometers designed to cope with rapid polymerizations and the programming of a Bruker HX90E NMR spectrometer to accumulate selected resonances of a polymerizing mixture for a predetermined number of scans at predetermined time intervals. Gravimetric determinations of conversion were based on polymer precipitated when the sample was added to a 5-fold excess of methanol.

Concentrations and compositions of initiator solutions are defined in terms of alkylmagnesium group concentration c_R, determined by hydrolysis with excess 0.1 M HCl and back-titration, and MgBr group concentration c_{Br}, by acidification with 6 M nitric acid, addition of 0.1 M $\mathrm{AgNO_3}$ in excess and back-titration with 0.1 M KSCN. Our experiments were carried out at temperatures very different from those at which solutions were prepared so mole fractions χ are more significant parameters than concentrations.

We have previously reported that *t*-BuOMg is undetectable in our initiators. We have recently re-examined stocks, held in vessels sealed under vacuum, by ^{1}H-NMR at 300 MHz and can specify that *t*-BuO contents were $\leqslant 1\%$ of *t*-Bu concentration. Stocks up to 5 years old showed no age-trends so it is likely that the *t*-BuO was formed when the solutions were prepared and not during storage. At 90 MHz we were only able to detect *t*-BuO in solutions prepared by standard bench techniques, but not when the reagents were prepared using high-vacuum techniques to exclude air.

III. RESULTS AND DISCUSSION

1. *The validity of the dilatometric method*

The classical dilatometric method assumes that volumes of mixing are negligible. While this is almost certainly valid for non-polar monomers in non-polar solvents, our system contains a polar monomer, a polar solvent and a non-polar solvent. Furthermore ^{1}H- and ^{13}C-NMR experiments [6] on binary mixtures of toluene with MMA and THF revealed concentration-induced shifts suggestive of dipole-induced dipole interactions between the aromatic and non-aromatic components. Such interactions could lead to significant volumes of mixing.

The apparent densities in borosilicate glass dilatometers of monomer solutions in THF, toluene and equimolar THF–toluene mixtures, ρ_{ms}, were determined over the temperature range 190 to 293 K at 8 monomer mole fractions, $\chi_m \leqslant 0.30$. For pure monomer the data refer to a range 236 to 265 K. The results are expressed in terms of equation (10)

$$\rho_{ms} = A + B\chi_m - (C + D\chi_m)T \quad \mathrm{g/cm^3} \tag{10}$$

the coefficients being given in Table 2. Values of ρ_{ms} for intermediate solvent compositions were estimated by linear interpolation. The coefficients in Table 2 were calculated from linear regressions of experimental data of ρ_{ms} against T at set values of χ_m. Experimental points were randomly disposed about the regression straight lines with correlation coefficients between $r = -0.978$ and -0.999. The standard errors on ρ_{ms} in mid range, 200 to 250 K, lay between 0.0002 g/cm^3 for the more scattered sets, rising to twice these values at 273 K. In practice we found that the combined and smoothed data represented by equation (10) lay within 0.0005 g/cm^3 of experimental values in most of the cases checked. As expected of mixtures whose components have similar molar mass–density ratios, specific volumes correlated linearly with mole fraction just as well. We used the more traditional density correlation. The linearity of the dependence of ρ_{ms} on χ_m at constant T shows the specific interactions apparent in the NMR spectra of solutions of monomers are not strong enough to invalidate the basic assumptions of classical dilatometry.

Table 2. Coefficients of equation (10) for MMA in pure state and in toluene, THF and equimolar toluene–THF solution, $T = 190$–293 K, $\chi_m \leqslant 0.30$

Solvent	A / g/cm^3	B / g/cm^3	$10^3\,C$ / g/cm^3 K	$10^3\,D$ / g/cm^3 K
MMA	1.2700	—	1.1038	—
THF	1.1945	0.0919	1.0332	0.0653
Tol.	1.1287	1.1119	0.8942	0.1280
1:1 THF–Tol.	1.1603	0.0771	0.9682	0.0016

Data on the densities of polymer solutions, ρ_{ps}, are sparse. The usual practice is to calculate values from densities of pure solvent and solid polymer ρ_p, neglecting volumes of mixing. We did not check this assumption directly because some of our isotactic polymers underwent solvent-induced crystallization on precipitation and were difficult to redissolve. We instead checked directly to see if the observed contraction was proportional to conversion. Polymerizing solutions were terminated and the contraction estimated by measuring the mass of toluene required to restore the volume to its original value at the relevant temperature. The contraction so measured was correlated with the conversion, determined gravimetrically. For polymerizations carried out in toluene solutions, the observed contractions were not proportional to conversion. Initiator and monomer solutions were mixed at 250 K and the solutions ($\chi_m = 0.1$) dispensed into similar vessels, polymerized at 250 K and terminated at different reaction times. The contraction–conversion relationship was not linear. The initial slope was often close to that calculated using a ρ_{ps} value calculated from the density of solid polymer $\rho_p = 1.19\ \mathrm{g/cm^3}$ neglecting volumes of mixing, but the slope decreased progressively with conversion until *ca* 85% when contraction effectively ceased while the polymer yield continued to rise.

The phenomenon cannot be attributed to the discrepancy between yields measured in terms of methanol-insoluble polymer and contractions measuring consumption of monomer. Experiments were carried out at low initiator concentrations $[\mathrm{M}]_0/c_R = 100$ where the yields of methanol-soluble polymer and side products are known to be insignificant (see III.3, below). Gross departures from linearity of the contraction–conversion curves were still observed.

The non-linearity seems to be genuinely associated with the accumulation of polymer in the solution and in particular the increasing viscosity. It was frequently noted that, once a solution had become stiff and gel-like, contraction effectively ceased even though the polymer yield continued to increase. Exceptionally high viscosity always developed in polymerizations in toluene even when initial monomer mole fraction was low, e.g. $\chi_m = 0.1$. The polymer produced was 100% isotactic and of very high molar mass ($\bar{M}_w \gg 2 \times 10^6$). In THF solution much lower molar mass polymer was produced with a stereoblock chain configuration. These solutions did not become excessively viscous as they polymerized and the conversions calculated from the contraction, solvent density, solid polymer densities and neglecting volumes of mixing agreed well with those measured gravimetrically.

Viscosity effects have long been known to limit dilatometric studies of high-conversion, radical polymerization [7], but only when high conversion is coupled with high concentration. The limitation is then manifest in the formation of voids and the separation of the gel from the vessel walls, phenomena not observed in our experiments, and the change of meniscus shape to a very deep V-shape, which presents no problem when contractions are determined by our method. On the other hand, the temperature in the interior of the reaction mixture was observed to rise, somewhat irreproducibly, when the solution became very viscous, as Burnett predicted [7]. Temperature rises of 1–4 K could be observed in spherical vessels of 100 cm^3, a volume considerably greater than that of the dilatometers. The greatest temperature rise occurred when monomer and initiator solutions are mixed, as reported earlier [1]. Heating effects cannot account for the whole deviation from linear contraction. The onsets of non-linearity and high viscosity depended on the size and shape of the vessel. Both effects were more prominent in smaller vessels than larger and cylindrical rather than spherical vessels; the relative magnitudes of the heating effect would be the other way round. Burnett [7] also predicted that polymerization in highly viscous solutions must lead to heterogeneity. While our solutions seemed to be homogeneous visibly, microheterogeneity with domains too small to scatter visible light could be the cause of departure from a linear volume–conversion relationship once the solution becomes viscous. Alternatively non-linearity may be an independent consequence of the cause of the high viscosity—the very high molar mass of the polymer which lies well above the range of those from which current theories of the structure of polymer solutions derive.

Dilatometry was thus found to be a dubious kinetic technique for the polymerization in toluene solution: inaccurate for determining external orders and invalid for internal orders of reaction. The cause is not established. The effect seems not to arise from the presence of polar and non-polar components—the doubt which persuaded us to check the validity of such a well-established technique. Instead it arises from an entirely unsuspected cause, which is associated with the very high molar mass of the solute.

2. *Kinetics of polymerization in THF solution*

Dilatometry was found to be valid when THF was the solvent, presumably because abnormally high molar masses did not develop. The coincidence of yields determined dilatometrically and gravimetrically is direct evidence that contraction was proportional to conversion. It confirmed that no burst of very rapid polymerization occurred before the first dilatometer reading could be taken—an effect noted in the anionic polymerization of MMA [8].

At 250 K the external orders of reaction with respect to monomer and initiator (c_R) were both first. The initial rates of four solutions with $\chi_m = 0.025$, 0.05, 0.10 and 0.20 and constant mole fraction of initiator ($\chi_R = 0.001$) gave an order with respect to monomer of 0.89 ± (SE) 0.15. Early curvature of the integrated first-order plot made extrapolation to obtain initial rates uncertain at higher monomer concentrations. The external order with respect to initiator determined at $\chi_m = 0.10$ and $\chi_R = 0.0005$, 0.0010, 0.0015 and 0.0020 was 0.93 ± (SE) 0.19. The accessible range of initiator concentration was set by irreproducibility when monomer–initiator ratios exceeded 200 and precipitation when the initiator concentration exceeded 0.3 M.

The internal order with respect to monomer was one at higher temperatures and low monomer concentration. This is illustrated by the fit of the data obtained at 275 K and $\chi_m = 0.10$ to the integrated first

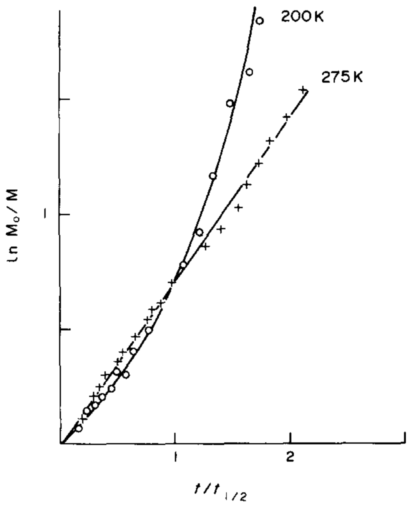


Fig. 1. Conversion curves plotted according to the integrated first order function for solutions in THF of the same batch and concentration ($\chi_m = 0.1$) at 200 K (○) and 275 K (+). The lines are fitted through the half life ($t_{1/2}$) assuming first order kinetics at 275 K and zero order at 200 K. The half life was 10 min at 200 K and 39 min at 275 K.

order rate equation shown in Fig. 1. Under these conditions case **IIa** kinetics prevailed.

At higher monomer concentrations, the data as mentioned above tended to deviate upwards from the integrated first-order plot. The same occurred at lower temperatures. At 250 K and $\chi_m = 0.10$, the upward deviation could be observed at around 15% conversion. At 200 K the first order equation was a complete misfit. The data fitted a zero-order rate law (Fig. 1) corresponding to case **I** kinetics (Table 1).

3. *Extent of side reactions*

The experiments described above were carried out with the initial $(\chi_m/\chi_R)_0$ set at 100. A series of gas chromatographic analyses of hydrolysed polymerization mixtures showed that, when $[M]_0/c_R \gg 100$, no methanol was present. Methanol in the hydrolysed products arises from MeOMg groups formed by attack of initiator on the monomer carbonyl group and termination of the propagating species through carbonyl attack [9]. The identity of conversions calculated from dilatometric and gravimetric measurements also demonstrated the insignificance of side products and methanol-soluble polymer since the former measured monomer consumption and the latter yield of methanol-insoluble polymer. The experimental conditions therefore differed from those of Bateup where side-products were present [9] and where kinetic analysis indicated low efficiencies of initiation [10].

4. *Effects of excess bromide*

The solute prepared in THF did not correspond to the Grignard stoichiometry: χ_{Br}/χ_R lay in the range 1.75 ± 0.05 when filtered at room temperature. The bromide content was further increased by adding $MgBr_2$ in THF (prepared by performing the Grignard synthesis with 1,2-dibromoethane) to initiator solutions led to a reduction in polymerization rates, up to 7-fold in the case of solutions saturated with $MgBr_2$. Bateup [9] also observed this effect with *n*-butyl magnesium initiators and attributed it to a decrease in initiation efficiency.

5. *Polymerizations in mixed THF–toluene solutions*

A limited programme of dilatometric experiments showed that the contraction curves followed much the same course as those observed for solutions in THF alone. Dilatometry was valid only when $\chi_{THF} > 0.5$. When toluene was in excess, rates were inconveniently high and increasing molar mass and isotacticity of the product led to high viscosity.

The dilatometric experiments showed that the rate increased as the mole fraction of THF was decreased. At 250 K, with $\chi_m = 0.1$ $\chi_R = 0.001$ initially, the initial rates of polymerization were 9.0×10^{-3} % sec^{-1} at $\chi_{THF} = 0.75$ and 1.2×10^{-2} % sec^{-1} at $\chi_{THF} = 0.60$. In the absence of toluene ($\chi_{THF} = 0.9$) the rate was 6.3×10^{-3} % sec^{-1}. At 250 K and $\chi_m = 0.1$, the rates may be converted to mol dm^{-3} sec^{-1} units by multiplying by 1.09×10^{-2} in toluene solution, 1.26×10^{-2} in THF and 1.10×10^{-2} in equimolar toluene and THF.

The same decrease in rate with increase in mole fraction of THF was observed in gravimetric experiments as can be seen in Fig. 2 which shows the 1 hr yields of methanol-insoluble polymer. Gelling and high viscosity probably caused the irreproducibility of the yields in toluene-rich solutions.

6. *Kinetics of polymerization in toluene solution*

Toluene solutions of initiator were prepared by dissolving the residues remaining when THF solutions of Grignard solution were evaporated to dryness under high vacuum. The nature of these solutions has been discussed elsewhere [4, 5] together with the residual THF content and the importance of exact specification of initiation conditions. Dilatometry being invalid, these experiments were carried out either gravimetrically or using NMR-spectrometry. In gravimetric experiments, the optimum conditions for the production of isotactic PMMA were duplicated. In the NMR experiments, the conditions were as close to this as practicable.

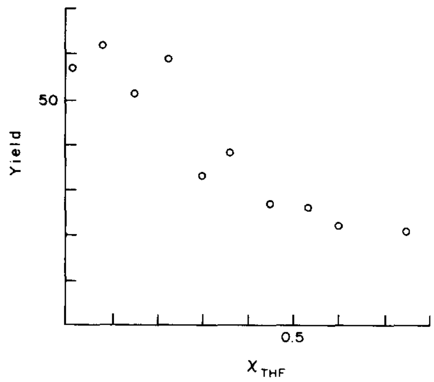


Fig. 2. The effect of increasing mole fraction of THF (χ_{THF}) on rate as shown by the percent yield of methanol-insoluble polymer at 1 hr of solutions of the same batch and concentration ($\chi_m = 0.1$) at 250 K.

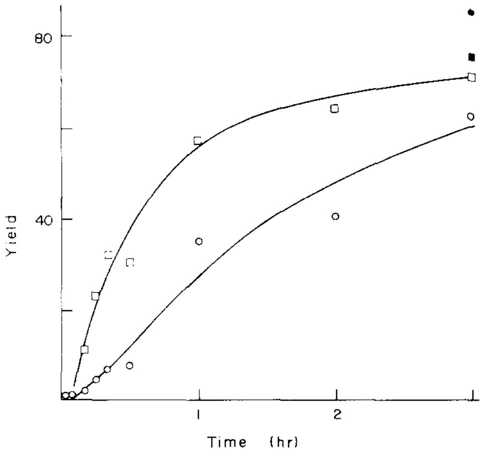


Fig. 3. Percent yield of methanol-insoluble polymer, at different reaction times, of toluene solutions of the same batch and concentration at 250 K: □ $\chi_m = 0.1$, ○ $\chi_m = 0.02$. Also shown are the average 3 hr yields of many preparative runs under these conditions (■, ●).

Batches of initiator used were submitted to thorough but not drastic de-etheration, the residues being warmed but not heated under vacuum. When taken up in toluene, the THF content was somewhat above the minimum amount required to solvate the initiator: $\chi_{THF}/\chi_R = 1$, [4]; in these experiments this ratio lay between 5 and 6. The solute varied slightly from the Grignard stoichiometry: $\chi_{Br}/\chi_R = 1.25 \pm 0.10$.

Gravimetric experiments were carried out in double vessels separated by a Young high-vacuum tap with an extended piston. Reagents were dispensed on a high-vacuum apparatus from stock capsules. Greaseless vacuum taps were used throughout. The mole fractions were determined by weighing the assembly after each charge. The lower vessel was charged first with monomer and solvent and the extended tap closed. The upper vessel was then charged with initiator solution and any further solvent needed. The assembly was brought to the selected temperature and the initiator solution discharged into the monomer solution by opening the extended piston-tap. The order-of-addition effect noted earlier [4] is not significant when large volumes of initiator and monomer solutions, already brought to polymerization temperature, are mixed in this manner. Figure 3 shows the yield of methanol-insoluble polymer as a function of time. Many preparative runs were carried out at $\chi_m = 0.1$, $\chi_R = 0.001$ 250 K. The average yield at 1 hr was 55% and for 3 hr runs 75%. At $\chi_m = 0.02$, the average 3 hr yield was 85%. These results cannot be reliably analysed to obtain internal orders of reactions because of poor reproducibility of the yields at higher conversions when the solutions become viscous.

Gravimetric experiments confirmed that yields and rates declined at higher temperatures, until at ambient no methanol-insoluble polymer formed (Table 3). It also demonstrated that yields and rates depended on monomer–initiator ratio at constant monomer concentration.

The determination of the internal order of the reaction in toluene was made using ^{1}H-NMR to follow the declining concentration of monomer. Details of the data handling procedure developed to make this possible and other experimental details have been described [5]. Examples of the plots of the resonances of interest, stacked according to reaction time, of two preliminary, though typical, experiments have also been published [3,4,5]. It is important to note that, when mixing of initiator and monomer solutions is carried out within the confines of an NMR tube as they melt, the order of addition is important [5]. The procedure has been described in detail [4, 5]. It should also be noted that, in order to minimize viscosity-broadening of the ^{1}H-NMR resonances, initial monomer mole fractions had to be reduced to $\chi_m = 0.02$. Poor reproducibility at the low initiator mole fractions necessary to maintain $\chi_m/\chi_R \gg 100$ forced us to work at higher ratios, usually 10, where side products and methanol-soluble polymer could not be assumed to be suppressed. No evidence of a proton peak from MeOMg groups was apparent, even though unreacted *t*-BuMg groups and residual, coordinated THF could clearly be seen, led us to believe that side product formation was not extensive.

Table 3. Percent yields of methanol-insoluble polymer at 3 hr obtained in toluene solutions ($\chi_{THF} < 0.005$) at two mole ratios of monomer to initiator when initial mole fraction of monomer was constant $\chi_m = 0.1$

Temperature (K)	200	225	250	275	300
$\chi_m/\chi_R = 100$	95	90	90	35	0
$\chi_m/\chi_R = 10$	90	75	60	15	0

A coordinated THF resonance can be seen on the low fields side of polymer methoxy resonance in the spectra published previously [3, 4, 5], but erroneously assigned to a side product.

As with the polymerizations in THF solution, the rates decayed according to a first order law at 275 K but followed zero order kinetics at 200 K. At intermediate temperatures, analysis of half-lives indicated fractional orders: 0.3–0.5 at 225 K and 0.5–0.75 at 250 K. However closer examination showed that the decay could not be represented by a single fractional order, but fitted well to the mixed order equation 9. This is shown in Fig. 4 where data obtained from a run at 225 K with $\chi_m = 0.02$ is fitted. The sum of the integrated intensities of the two vinyl peaks was taken as proportional to monomer concentration. A first estimate of k'' was obtained from visual examination of plots of ln[M] and [M] against time (see Fig. 4). This value was adjusted till the optimum correlation coefficient of the linear least-squares regression was attained. This occurred at $k'' = 4.69\ \text{dm}^3\,\text{mol}^{-1}$ when $r = -0.9994$ for the equation

$$\begin{aligned}\ln[M] + 4.69[M] = {} & -0.672 \pm (\text{SE})\ 0.014 \\ & - \{8.515 \pm (\text{SE})\ 0.072\}\ 10^4 t/\text{sec} \qquad (11)\end{aligned}$$

The technique is valid over too small a range to support a systematic investigation of the effects of initial monomer concentration. In addition to determinations at $\chi_m = 0.02$ we found $k'' = 1\ \text{dm}^3\,\text{mol}^{-1}$ at $\chi_m = 0.11$ and 225 K.

Analysis of the coefficient k' [equations (6) and (9)] is not possible because the initiation conditions were

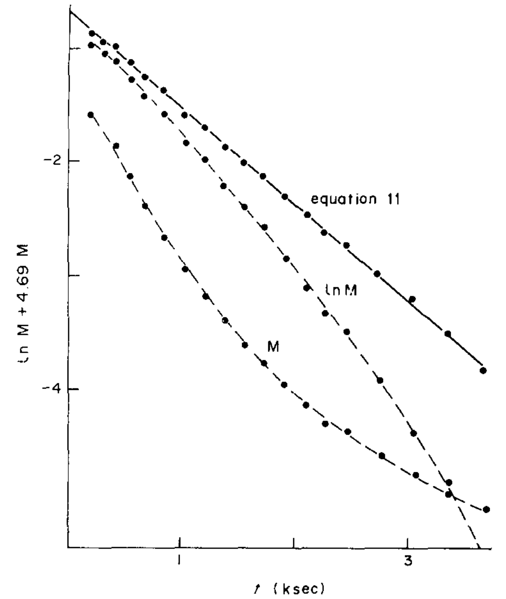


Fig. 4. Monomer decay curves for a typical system in the mixed-order domain ($\chi_m = 0.02$ in toluene at 225 K). The unbroken line represents the linear least regression of the data to equation 11. The broken lines represent ln[M] and [M] (ordinate scales not shown).

insufficiently defined to ensure reproducibility of the efficiency *f*.

The convergence to first order kinetics as the temperature increased was manifest in the decrease of k''. At 250 K it was very small and at 275 K it had vanished altogether.

Increase of temperature above 275 K in large scale experiments led to a decrease in yield of methanol-insoluble polymer until at 300 K (Table 3) none was obtained. The NMR experiment at 300 K indicated rapid initial consumptions of monomer over the first 10 min followed by sudden decelerations with the reactions not proceeding to completion.

IV. CONCLUSIONS

1. The kinetic results in the temperature range 200 to 275 K are consistent with the mechanism (2) in THF (III.2) and for the isotactic polymerization in toluene (III.6). The fit to the integrated rate equation (9) has been obtained not only at the high temperature, low monomer concentration first order and the low temperature, high monomer concentration second order limits, but also in the intermediate mixed order region (III.6).

The dependence of k'' on monomer concentration observed over two concentrations in the NMR experiments may not be significant. Because of the limited concentration range accessible, we did not obtain sufficient data to ascertain the error limits on k''. If the dependence is real, it requires a modification to the mechanism, perhaps to the complex formation stage, but the basic postulates remain valid.

2. The decrease in rate of polymerization at comparable temperature, initiator and monomer concentrations as the proportions of THF in the solvent mixture are increased (III.5), clearly indicates that these are not *true* anionic polymerizations where increasing solvation of the cation leads to an increase in the concentration of free propagating anions and the more reactive types of ion pair. The observed effect is consistent with the proposed mechanism, THF competing with monomer for coordination sites and blocking the formation of the propagating complex C (2). A similar effect was observed in the 4-centre addition reaction between triethyl aluminium and alkenes which is either inhibited or retarded by ethers [11]. If these polymerizations are to be described as ionic at all, they must be specified as *pseudo* anionic.

3. An excess of monomer over initiator $\chi_m/\chi_R \geqslant 100$ is the optimum condition for high yields of methanol-insoluble polymer. Under these conditions, no methanol could be detected in the hydrolysed reaction products provided $T \leqslant 275$ K and the yield of methanol-insoluble polymer corresponded to the monomer consumed, confirming that methanol in the hydrolysed reaction products is an indication of side reactions. The NMR experiments showed that under these conditions the polymerization went effectively to completion, at least when carried out in dilute solutions.

4. At ambient temperatures the negligible yields of methanol-insoluble polymer are partly accounted for by side-reactions, but the NMR reaction traces show that, although most of the monomer is consumed in the first few minutes, there is a slower reaction which continues for up to 1 hr before coming to a stop well short of complete conversion. This suggests that polymerization chains are initiated but at these temperatures are subject to a termination reaction.

5. There is no evidence of a termination-reaction at low temperature ($\leqslant 275$ K).

Acknowledgement—We thank the Australian Research Grants Scheme for their support.

REFERENCES

1. P. E. M. Allen and B. O. Bateup, *J. chem. Soc. Faraday Trans. I* **71**, 2203 (1975).
2. K. J. Laidler, *Reaction Kinetics*, Vol 1, p. 17. Pergamon, Oxford (1963).
3. P. E. M. Allen, M. Fisher, C. Mair and E. H. Williams, *Polym. Prep.* **21**, 65 (1980).
4. P. E. M. Allen, M. C. Fisher, C. Mair and E. H. Williams, *Anionic Polymerization* (Edited by J. E. McGrath), *ACS Symp. Series* **166**, 185 (1981).
5. P. E. M. Allen, C. Mair, M. C. Fisher and E. H. Williams, *J. Macromol. Sci.-Chem.* **A17**, 61 (1982).
6. P. E. M. Allen, unpublished results.
7. G. M. Burnett, *Mechanism of Polymer Reactions*, p. 16. Interscience, New York (1954).
8. P. E. M. Allen, R. P. Chaplin and D. O. Jordan, *Eur. Polym. J.* **8**, 271 (1972).
9. B. O. Bateup and P. E. M. Allen, *Eur. Polym. J.* **13**, 761 (1977).
10. P. E. M. Allen and B. O. Bateup, *Eur. Polym. J.* **14**, 1001 (1978).
11. P. E. M. Allen and R. M. Lough, *J. chem Soc. Faraday Trans. I* **69**, 849 (1973).