Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization Kinetics of n-Alkyl Acrylates

G. E. Scott[a]; E. Senogles[a]
[a] James Cook University of North Queensland, Townsville, Australia

To cite this Article Scott, G. E. and Senogles, E.(1974) 'Polymerization Kinetics of n-Alkyl Acrylates', Journal of Macromolecular Science, Part A, 8: 4, 753 — 773

To link to this Article: DOI: 10.1080/00222337408066396

URL: http://dx.doi.org/10.1080/00222337408066396

J. MACROMOL. SCI.—CHEM., A8(4), pp. 753-773 (1974)

Polymerization Kinetics of n-Alkyl Acrylates

G. E. SCOTT and E. SENOGLES

James Cook University of North Queensland
Townsville, Australia

ABSTRACT

The polymerization kinetics of C_4, C_8, and C_{12} n-alkyl acrylates are characterized by monomer orders of 1.5 or greater and in the case of the C_8 and C_{12} esters an initiator exponent of less than 0.5. Various explanations for the high monomer exponent have been considered including mechanisms based on intramolecular degradative transfer or the presence of a dimeric monomer species. Initiator exponents of less than 0.5 are explained in terms of a chain length dependence of the diffusion-controlled termination constant. Rotating sector curves have been obtained for the acrylates, and this data for n-butyl acrylate yields a value of 1.4×10^6 dm^3/(mole)(sec) for the termination constant.

INTRODUCTION

In a previous publication the polymerization kinetics of n-lauryl acrylate were reported [1]. At 40°C, in both ethyl acetate and n-heptane, the polymerization rate is given by $R_p = K[M]^{1.6(5)}[I]^{0.4(5)}$. The rate was shown to be dependent on the initial viscosity of the polymerization mixture, indicating that the termination constant is diffusion controlled. However, the observed dependence, $R_p \propto (\text{viscosity})^{0.2}$, is insufficient to account for the high monomer order in terms of viscosity variations with monomer-solvent composition. Other possible explanations based on mechanisms involving primary radical termination, radical cage effects, degradative chain transfer, or radical complexing also appear inappropriate [1]. With other acrylate monomers, e.g., ethyl [2] and n-butyl [1], monomer orders of 1.5 and initiator orders of 0.5 have been found to apply. In the present publication further kinetic studies on the polymerization of n-alkyl acrylates are reported and discussed.

EXPERIMENTAL

Materials

n-Octyl acrylate (Borden Chemical Co.) contains methyl hydroquinone as inhibitor. This was removed by passing the monomer down an activated alumina column in petroleum ether (40 to 60°C) solution. After removing the petroleum ether the monomer was fractionally distilled (bp 110°C/13 Torrs).

n-Lauryl and n-Butyl acrylates were purified as previously described [1].

1-Mercaptododecane (RSH), ethyl acetate, 2-azobisisobutyronitrile (AZDN), and 1,1-diphenyl-2-picrylhydrazyl (DPPH) were purified by conventional means.

Number-average molecular weights were determined using a Hewlett-Packard 501 High Speed Membrane Osmometer.

Polymerizations

Initial photosensitized and thermal-sensitized polymerization rates were measured using conventional dilatometers. Polymerizations to high conversion were carried out in "mushroom-type" dilatometers similar to those used by Burnett [3]. Because significant pure thermal polymerization occurred at higher temperatures, initiated polymerizations were conducted at temperatures of less than 45°C. Comparison of dilatometer contraction rates with polymerization rates determined gravimetrically enabled the former to be expressed in mole/(dm^3)(sec).

For k_t determinations a conventional optical and rotating sector assembly was used with a dark to light period ratio of 3. Rates of initiation were evaluated by measuring polymerization induction periods in the presence of DPPH. With low concentrations of DPPH

($1\text{-}4 \times 10^{-5}$ mole/dm^3) induction periods were proportional to inhibitor concentration.

RESULTS AND DISCUSSION

In Fig. 1 initial polymerization rates of n-octyl acrylate in ethyl acetate solution are shown as a function of monomer concentration.

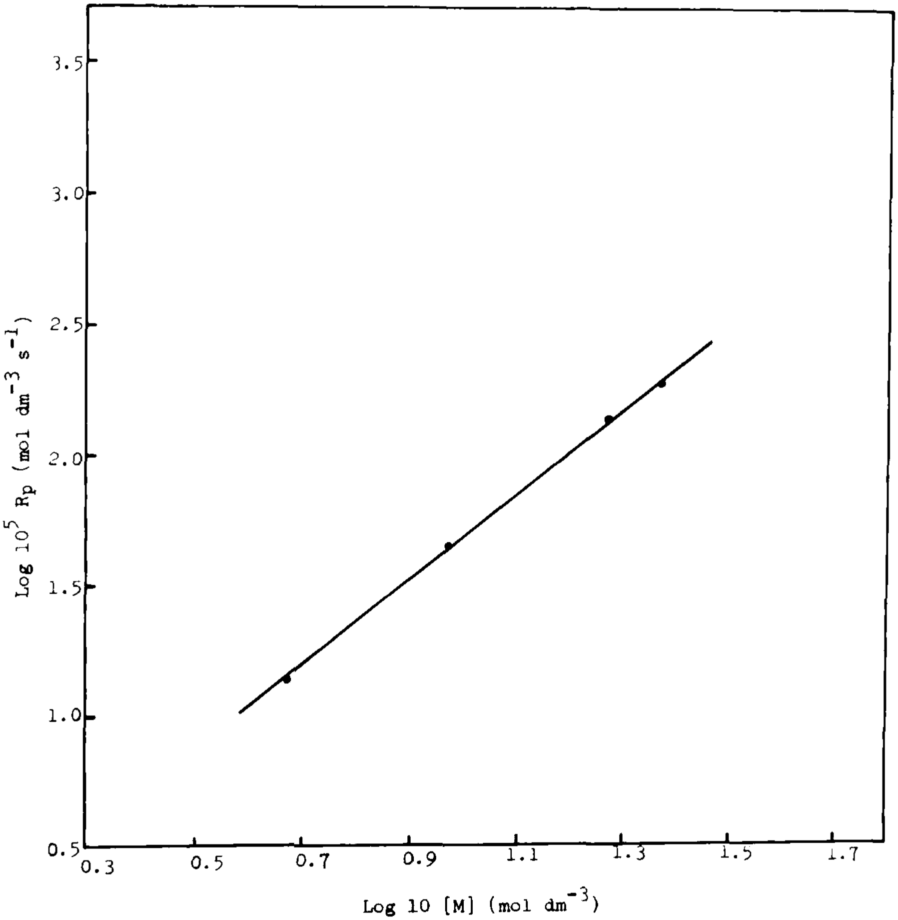


FIG. 1. Dependence of initial polymerization rate, R_p, on the concentration of n-octyl acrylate [M] in ethyl acetate. [AZDN] = 8×10^{-3} mole/dm^3; T = 40°C.

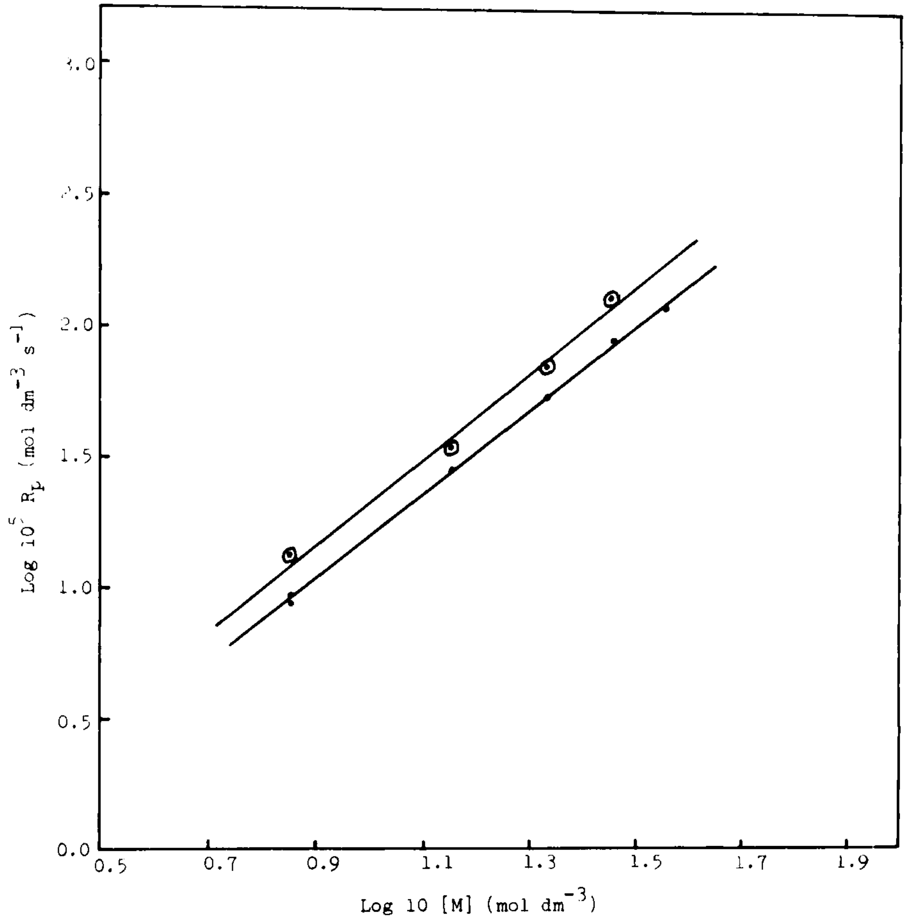


FIG. 2. Dependence of initial polymerization rate, R_p, on the concentration of n-lauryl acrylate [M] in ethyl acetate. [AZDN] = 10^{-3} mole/dm^3; T = 40°C. (⊙) In absence of transfer agent (typical $\overline{M}_n$ = 1-2 × 10^6). (●) In presence of n-dodecanthiol, [RSH]/[M] = 0.10 (typical $\overline{M}_n$ = 17,000).

These are consistent with an order of 1.6, a result similar to that observed with n-lauryl acrylate [1]. Further experiments with the latter monomer (Fig. 2) show that polymerization rates are reduced in the presence of an efficient radical transfer agent, indicating that the diffusion-controlled termination constant is probably inversely dependent on polymer radical size. However, since the monomer order is scarcely affected by the presence of transfer agent at a fixed [RSH]/[M] ratio, it is clear that the high value is not attributable to any kinetic radical size effects.

Photosensitized polymerizations confirm the pattern of kinetic dependencies determined in thermally initiated polymerizations. In Table 1 measured intensity exponents for C_4, C_8, and C_{12} n-alkyl acrylates are given. Figures 3-5 show the corresponding rotating sector results. The curve for n-butyl acrylate shows the expected pattern for a polymerization exhibiting an intensity exponent of 0.5. Using the appropriate theoretical curve for a dark rate to light rate ratio of 0.06 [4] and the measured initiation rates for unsectored conditions (Table 2), k_t for n-butyl acrylate was evaluated as 1.4×10^6 dm^3/(mole)(sec) at 10.0°C. This value differs markedly from previously determined ones of 3.3×10^{10} [5] and 1.8×10^4 dm^3/(mole)(sec) [6] at 25.0°C. The latter value, which was also determined by the rotating sector technique, has subsequently been acknowledged to be unreliable due to possible experimental uncertainties [5]. It is difficult to account for the discrepancy between the present result and that of Bengough and Melville. Despite differences in experimental conditions and technique (Bengough and Melville used a thermocouple method for direct nonstationary state measurement of k_t), such a discrepancy in measured k_t values would not be anticipated. Differences in solution viscosity in the independent measurements might be expected to be the major reason for differing results. However, Benson and North [7] have shown that the termination constant of n-butyl acrylate is surprisingly nonsensitive to viscosity in the range of the latter covered by the measurements. The k_t value determined in the present work is less than values

TABLE 1. Intensity Exponents Measured at 10°C in Ethyl Acetate Solution, [AZDN] = 5×10^{-3} mole/dm^3

Acrylate	[M] (mole/dm^3)	Intensity exponent
n-Butyl	1.375	0.5(0)
n-Octyl	0.934	0.4(4)
n-Lauryl	0.716	0.4(2)
n-Lauryl	1.432	0.4(2)

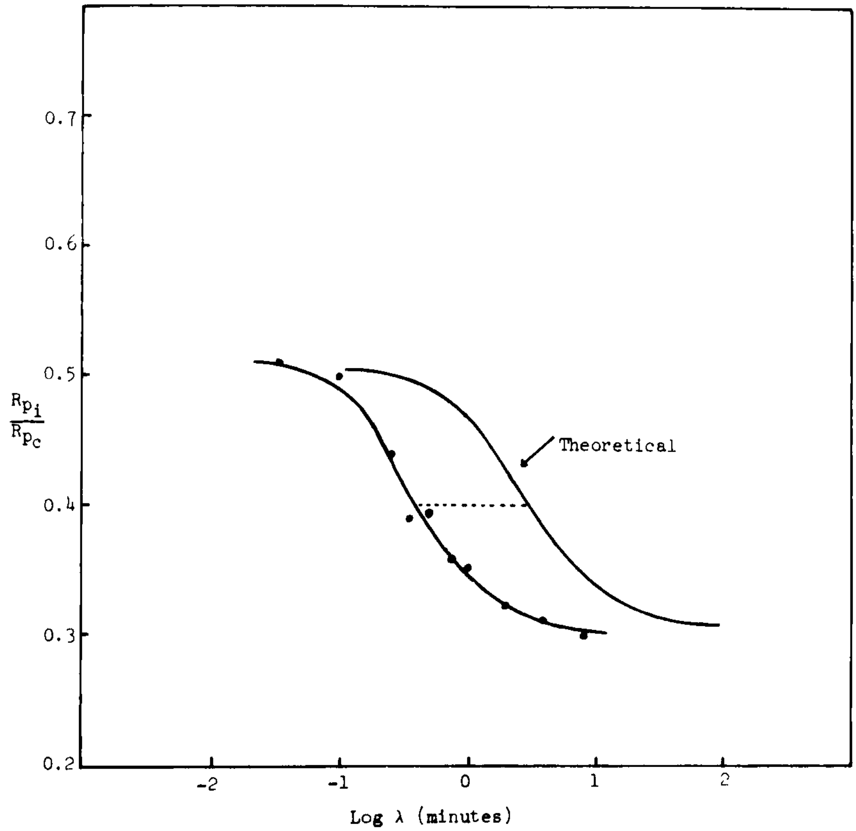


FIG. 3. Rotating sector curve for n-butyl acrylate in ethyl acetate. [M] = 1.375 mole/dm^3; [AZDN] = 5 × 10^{-3} mole/dm^3; T = 10°C. R_{p_i} = Polymerization rate with intermittant radiation. R_{p_c} = Polymerization rate with continuous radiation. λ = flashtime.

reported for methyl acrylate [8], and this is in line with the trend established by Burnett et al. [9] for the corresponding methacrylate series. However, the fall-off in the acrylate series appears to be much more pronounced.

The sector curves for n-octyl and n-lauryl acrylate conform to the pattern expected for polymerizations characterized by an intensity exponent of less than 0.5. Since primary radical termination is expected to be unimportant under the polymerization conditions employed [1], the most likely explanation of the low intensity and initiator

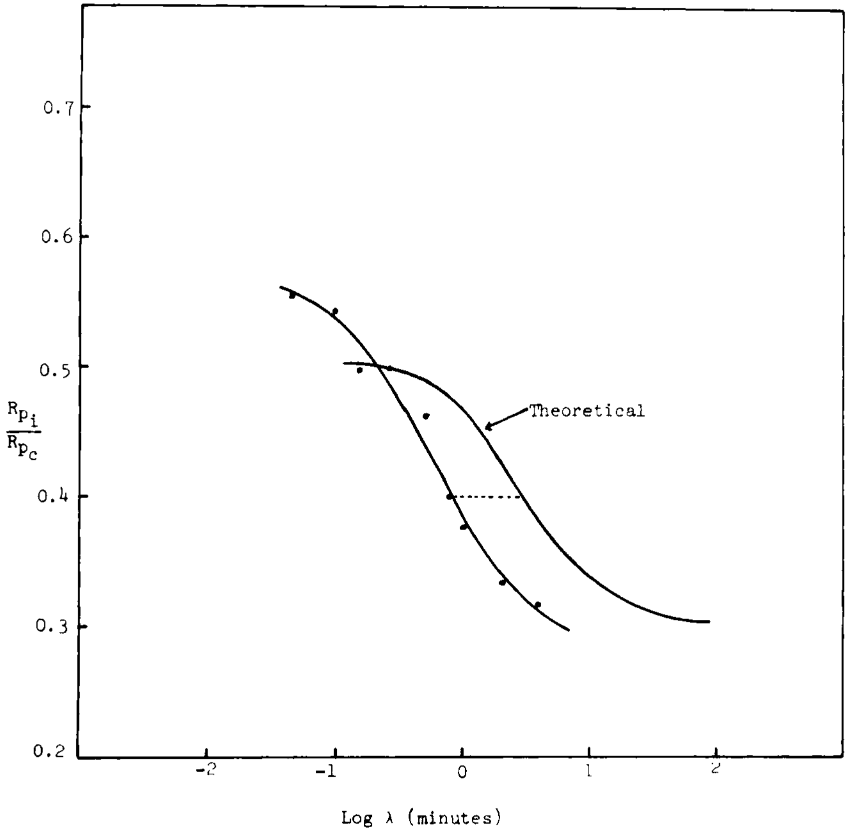


FIG. 4. Rotating sector curve for n-octyl acrylate in ethyl acetate. [M] = 0.934 mole/dm^3; [AZDN] = 5 × 10^{-3} mole/dm^3; T = 10°C.

exponents observed with n-octyl and n-lauryl acrylate is an inverse chain length dependence of k_t. In a theoretical appraisal of the diffusion-controlled termination process Burkhart [10] has predicted k_t values for flexible polymer chains to be almost independent of chain length and inversely proportional to solution viscosity. Both predictions have been confirmed in methyl methacrylate polymerizations [7, 11, 12]. For less flexible polymer radicals Burkhart predicts a weaker dependence of k_t on solution viscosity, as observed in n-lauryl acrylate [1] and some methacrylate polymerizations [13], and an inverse dependence on the square root of radical size. The latter

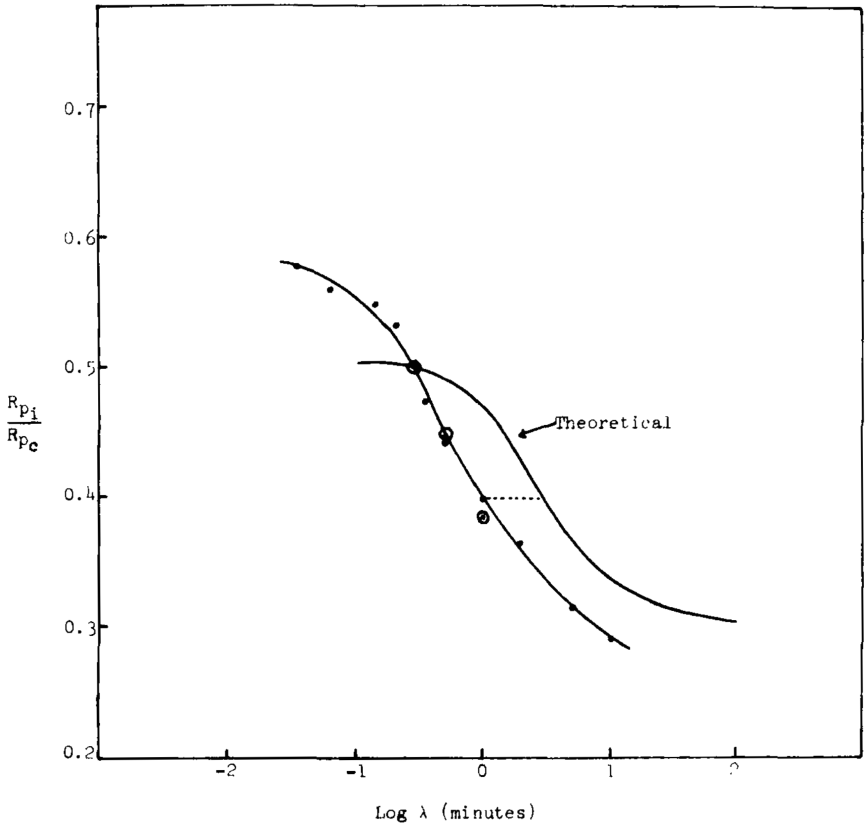


FIG. 5. Rotating sector curve for n-lauryl acrylate in ethyl acetate. (●) $[M]_\circ = 0.895$ mole/dm^3; (◉) $[M] = 1.79$ mole/dm^3; $[AZDN] = 5 \times 10^{-3}$ mole/dm^3; $T = 10°C$.

effect would lead to a slightly reduced initiator exponent. Since rotating sector theory has not been developed to allow for any mechanism leading to an intensity exponent of less than 0.5, no quantitative analysis of the n-octyl and n-lauryl acrylate sector curves was attempted. However, qualitative interpretation suggests average k_t values for these monomers are successively less in magnitude than that measured for n-butyl acrylate. In the absence of a strong viscosity influence on the diffusion-controlled termination step for higher acrylates, this trend probably refelcts a decrease in chain flexibility as the ester group becomes larger.

TABLE 2. Rates of Initiation Corresponding to the Polymerization Conditions of Table 1

Acrylate	R_I [mole/(dm^3)(sec)]
n-Butyl	1.13×10^{-8}
n-Octyl	1.12×10^{-8}
n-Lauryl	1.17×10^{-8}

In previous work the effect of the degree of conversion on the polymerization rates of C_2, C_4, and C_{12} acrylates was reported and discussed [1]. With ethyl acrylate, autoacceleration was observed but with n-lauryl acrylate the polymerization rate decreased continuously from the start of polymerization. With n-butyl acrylate the results were of an intermediate nature, a steady rate being observed up to about 60% conversion despite the fall-off in monomer concentration. In Fig. 6 the corresponding data for n-octyl is given. With this monomer the polymerization rate remains virtually constant up to about 30% conversion and then decreases. These results indicate that autoacceleration effects in the acrylate series become less important as the size of the ester group increases. This reflects both the reduced importance of polymer radical branching [1] and the weak dependence of k_t on solution viscosity observed with the higher acrylates.

The traditional kinetic scheme for radical polymerization predicts a monomer order of 1.0. From the present and other investigations [14] it is clear that monomer orders of 1.5 and greater are common to some acrylate polymerizations. High monomer orders have also been observed in the polymerization of other vinyl monomers [15] and various theories have been advanced to account for these irregularities. Unfortunately, the acrylate results do not readily conform to these theories [1] and we have therefore considered other possible explanations, details of which are discussed below.

Intramolecular Degradative Chain Transfer

Burnett [16] has accounted for high monomer orders by postulating that degradative chain transfer occurs with the polymerization solvent. With this mechanism different monomer orders might be expected with different solvents, since the chemical structure of the latter determines its susceptibility to radical attack. This behavior is not found with the acrylate esters as identical orders for n-lauryl acrylate are observed in ethyl acetate and n-heptane. An extension

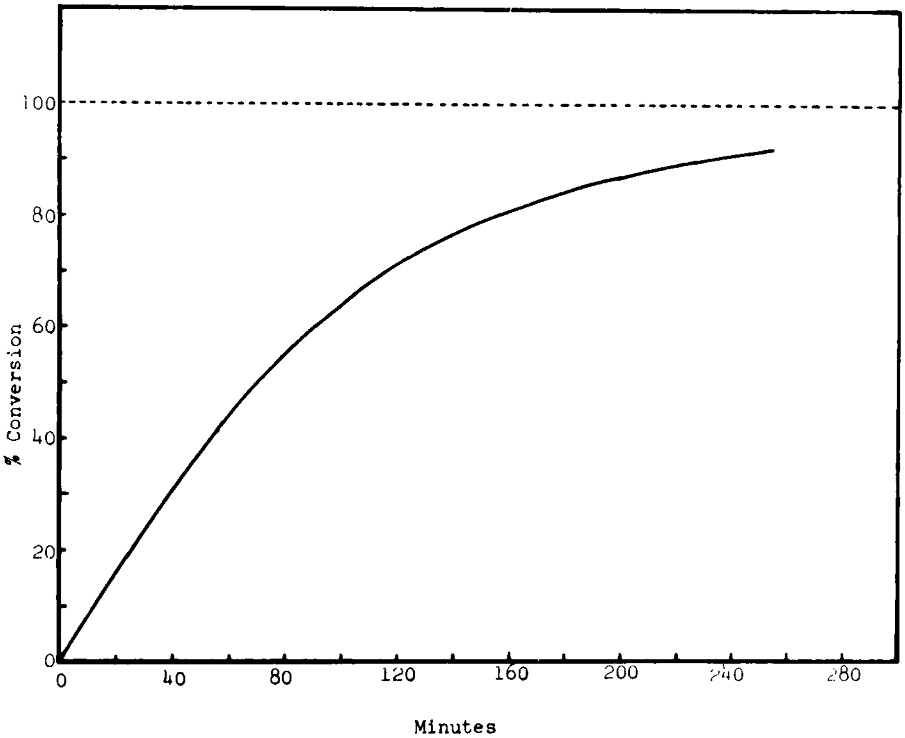
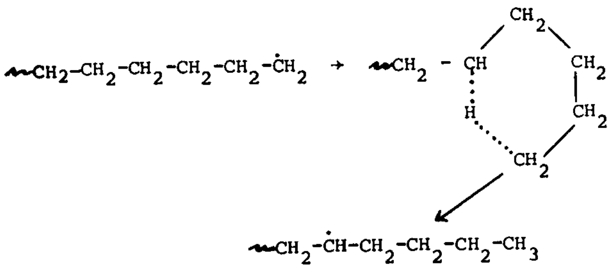


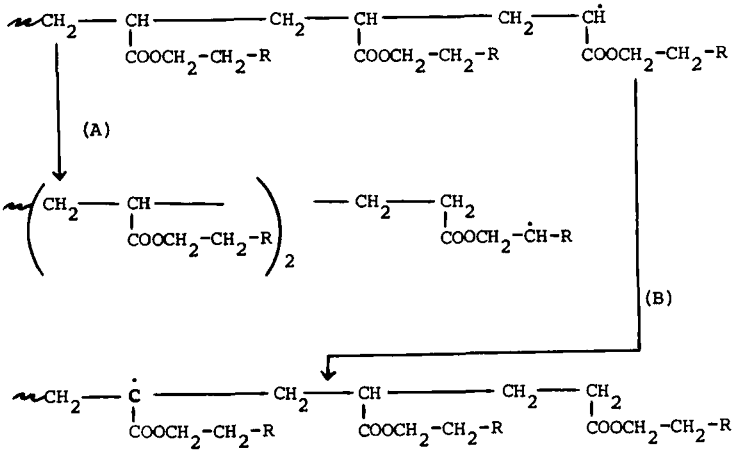
FIG. 6. Conversion vs time for the bulk polymerization of n-octyl acrylate at 35°C. [AZDN] = 3.0×10^{-2} mole/dm^3.

of the Burnett mechanism involving intramolecular degradative chain transfer may, however, apply.

The occurrence of intramolecular radical transfer reactions, termed "backbiting reactions," has been demonstrated in the polymerization of ethylene [17, 18]:



If such processes occur in acrylate polymerizations and lead to the production of a radical of reduced propagation reactivity, then the polymerization rate will be reduced. Intramolecular transfer will be more competitive with normal propagation in dilute solution, since the rate of the latter depends on monomer concentration. Therefore, radical backbiting could lead to reduced fractional rates of polymerization, $R_p/[M]$, with dilution; that is, monomer orders greater than unity. The effect should be independent of the chemical structure of the solvent. Possible radical back-biting reactions for ethyl and higher acrylates are as follows, processes involving a strainless six-membered ring transition state being more likely:



R = H or n-alkyl.

If any of these reactions occur, they can be represented by the following general scheme,

1.	$I \rightarrow 2R^{\cdot}$	k_d
2.	$R^{\cdot} + M \rightarrow P^{\cdot}$	R_I
3.	$P^{\cdot} + M \rightarrow P^{\cdot}$	k_p
4.	$P^{\cdot} \rightarrow P'^{\cdot}$	k_s
5.	$P'^{\cdot} + M \rightarrow P^{\cdot}$	$k_{p'}$
6.	$2P^{\cdot} \rightarrow$ polymer	k_t
7.	$P^{\cdot} + P'^{\cdot} \rightarrow$ polymer	$2k_t$
8.	$2P'^{\cdot} \rightarrow$ polymer	k_t

where P$^\cdot$ and P$'^\cdot$ are normal and "backbitten" polymer radicals, respectively. Since the termination step is diffusion controlled, the same velocity constant can be subscribed to the different termination reactions, although a statistical factor of 2 must be included in the cross-termination process involving chemically unlike radicals. Only if intramolecular transfer occurs with some atom significantly removed from the growing free radical end is this procedure possibly invalid. In this case a long-chain branched radical would be produced which is likely to have a lower diffusion controlled termination constant than a linear or short-chain branched radical.

Applying the usual stationary state procedure to the above mechanism,

$$\frac{d[P^\cdot]}{dt} = 0 = R_I - k_s[P^\cdot] + k_{p'}[P'^\cdot][M] - 2k_t[P^\cdot]^2 - 2k_t[P^\cdot][P'^\cdot] \quad (1)$$

$$\frac{d[P'^\cdot]}{dt} = 0 = k_s[P^\cdot] - k_{p'}[P'^\cdot][M] - 2k_t[P'^\cdot]^2 - 2k_t[P^\cdot][P'^\cdot] \quad (2)$$

Summing Eqs. (1) and (2) leads to

$$[P^\cdot] = \left(\frac{R_I}{2k_t}\right)^{1/2} - [P'^\cdot]$$

Substituting for $[P^\cdot]$ in Eqs. (1) and (2) gives:

$$[P'^\cdot] = \frac{k_s R_I{}^{1/2}}{(2k_t)^{1/2}[k_s + k_{p'}[M] + (2k_t R_I)^{1/2}]}$$

whence

$$[P^\cdot] = \left(\frac{R_I}{2k_t}\right)^{1/2}\left[\frac{k_{p'}[M] + K}{k_s + k_{p'}[M] + K}\right]$$

where

$$K = (2k_t R_I)^{1/2}$$

Assuming intramolecular transfer occurs far less frequently than normal propagation,

$$R_p = k_p[M][P^{\cdot}]$$

Therefore

$$R_p = \frac{k_p R_I^{1/2}[M]}{(2k_t)^{1/2}} \left[\frac{k_{p'}[M] + K}{k_s + k_{p'}[M] + K}\right] \tag{3}$$

Equation (3) can account for monomer orders greater than 1 and initiator orders greater than 0.5, since the magnitude of the bracketed term decreases as both monomer concentration and the initiation rate are lowered. In some circumstances $k_{p'}[M]$ and k_s may be significantly greater than $(2k_tR_I)^{1/2}$ so that Eq. (3) reduces to

$$R_p = \frac{k_p R_I^{1/2}[M]}{(2k_t)^{1/2}} \left[\frac{k_{p'}[M]}{k_s + k_{p'}[M]}\right] \tag{4}$$

If $k_{p'}[M] \gg k_s$, Eq. (4) simplifies to the "normal" polymerization rate equation. This situation is, of course, the same as that occurring in most radical transfer processes, where the derived radical adds monomer rapidly and hence the polymerization rate is unaltered. However, if the magnitude of k_s and $k_{p'}[M]$ are comparable, high monomer orders and initiator orders of 0.5 can occur according to Eq. (4). As stated in the Introduction, such behavior has been observed in ethyl and n-butyl polymerizations. Further complications, such as a chain length dependence of k_t, may result in initiator exponents being reduced slightly below 0.5 as found in the polymerization of n-octyl and n-lauryl acrylates.

Rearrangement of Eq. (4) leads to

$$\frac{[M]}{R_p} = K' + \frac{K'k_s}{k_{p'}[M]} \tag{5}$$

where

$$K' = \frac{(2k_t)^{1/2}}{k_p R_I^{1/2}}$$

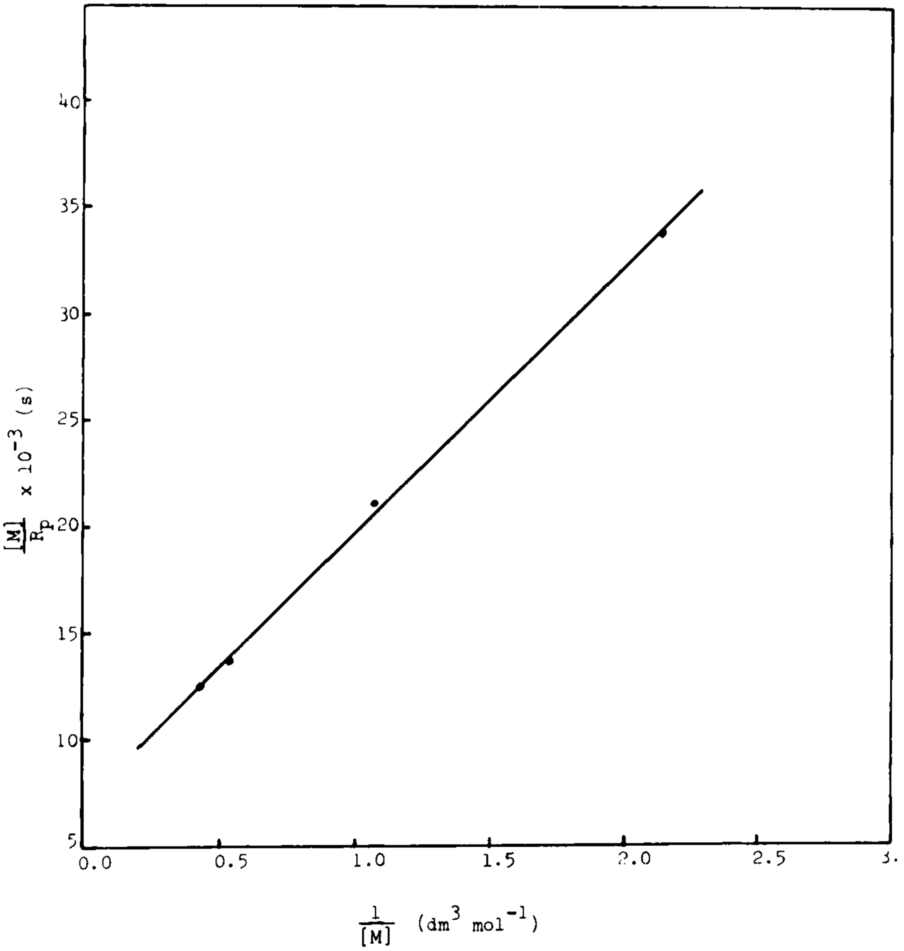


FIG. 7. Data from Fig. 1 plotted according to Eq. (5).

In Fig. 7 the rate data of Fig. 1 is plotted according to Eq. (5). Although a good linear relationship exists, as is also the case with the n-lauryl acrylate data, curvature is readily apparent in the corresponding plot for n-butyl acrylate (Fig. 8). Thus the kinetic data do not strongly support a possible intramolecular degradative transfer mechanism. Speculation on the likelihood of backbiting process (A) occurring could be resolved by hydrolyzing the polymer and seeing if a reduction in molecular weight occurs. Even if this is

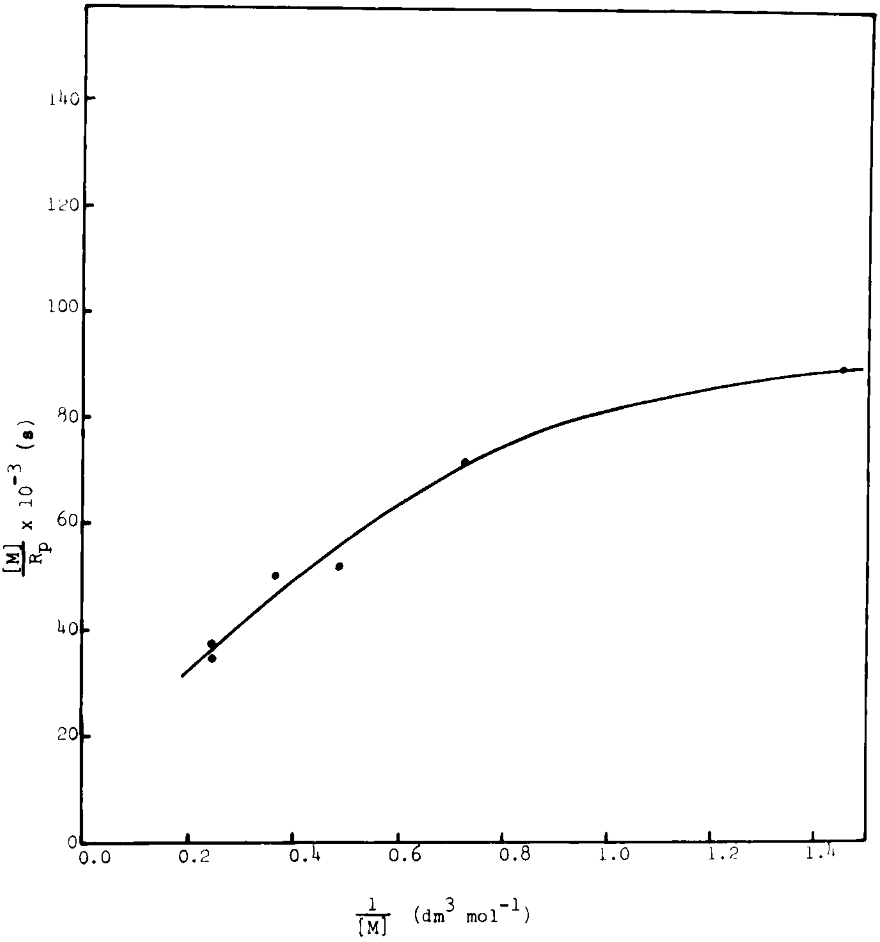
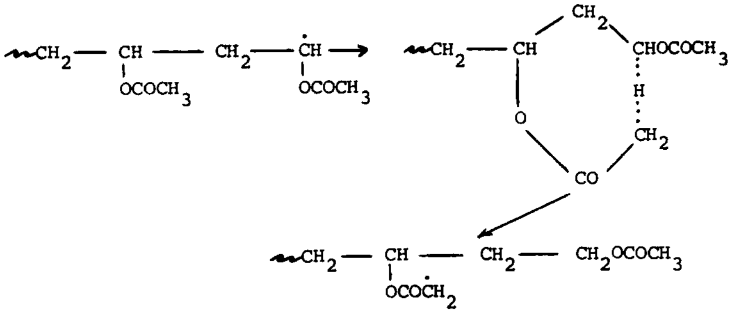


FIG. 8. Data from Fig. 6 (Ref. 1) plotted according to Eq. (5).

the case, no kinetic effect would result unless the derived radical is less reactive to monomer. If this radical is assumed to be of a similar structure to that involved in allyl acetate polymerizations, copolymerization data [19] indicate increased propagation reactivity. On the other hand, radicals resulting from processes such as (B) would certainly be less reactive than the parent radical. However, the occurrence of this reaction cannot be easily demonstrated experimentally. Thus theoretical and experimental evidence is inconclusive for the occurrence of degradative radical backbiting processes in acrylate polymerizations. It is possible, however, that this process is important in the polymerization of other vinyl monomers such as vinyl acetate. In this case there is evidence for backbiting processes such as



occurring [20]. The resulting radical, which would be expected to be more reactive than a polyacrylate radical which it structurally resembles, may nevertheless be less reactive than the highly reactive parent vinyl acetate radical and therefore a kinetic degradative effect may result. However, application of Eq. (5) to the rate data of Burnett [16] for vinyl acetate polymerization did not result in a linear plot.

Dimeric Complex Mechanism

In the analysis of experimental results it was observed that a linear relationship existed when $R_p/[M]$ was plotted against $[M]$ for the n-butyl acrylate—ethyl acetate system. A similar result was obtained when the data of Devalériola [2] was plotted in this manner for the ethyl acrylate—benzene system (Fig. 9). This behavior is indicative of a mixed first-order—second-order reaction with respect to monomer, or, in other words, a rate expression of the form

$$R_p = K'[M] + K''[M]^2$$

applies. Such an expression would hold if the polymerization mechanism involved, as well as the normal reaction steps, the addition of monomer "pairs" to a growing radical chain. Monomer "pairs" can best be regarded as some loose dimeric species or complex formed by the

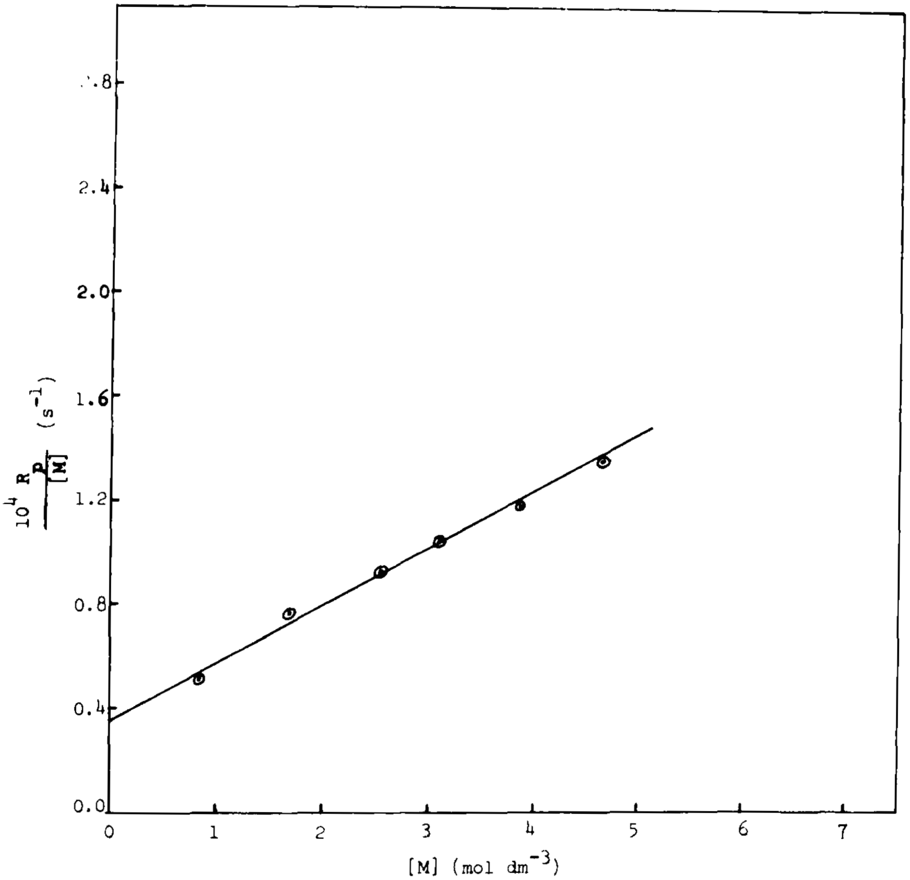


FIG. 9. Rate data of Devaleriola [2] for the polymerization of ethyl acrylate in benzene plotted according to Eq. (6).

association of two monomer molecules. The full kinetic scheme for such a mechanism can be represented as

$$\begin{array}{lcll}
I & \rightarrow & 2R^{\cdot} & \\
R^{\cdot} + M & \rightarrow & P^{\cdot} & R_I \\
P^{\cdot} + M & \rightarrow & P^{\cdot} & k_p \\
M + M & \rightleftharpoons & M::M & K \\
P^{\cdot} + M::M & \rightarrow & P^{\cdot} & k_{p'} \\
2P^{\cdot} & \rightarrow & \text{polymer} & k_t
\end{array}$$

where

$$K = [M::M]/[M]^2$$

Applying kinetic analysis to the above scheme,

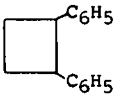
$$\begin{aligned} R_p &= k_p[P^\cdot][M] + k_{p'}[P^\cdot][M::M] \\ &= k_p[P^\cdot][M] + k_{p'}[P^\cdot]K[M]^2 \\ &= \left(\frac{R_I}{2k_t}\right)^{1/2}\left[k_p[M] + k_{p'}K[M]^2\right] \end{aligned}$$

Therefore

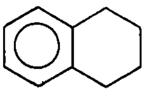
$$\frac{R_P}{[M]} = \left(\frac{R_I}{2k_t}\right)^{1/2}\left[k_p + k_{p'}K[M]\right] \qquad (6)$$

Thus a plot of $R_p/[M]$ vs $[M]$ should be linear, and the slope/intercept = $k_{p'}K/k_p$. The value of this ratio taken from Fig. 9 for ethyl acrylate is 0.63 dm^3/mole. The dimeric complex mechanism is consistent with the initiator exponent observed in this polymerization.

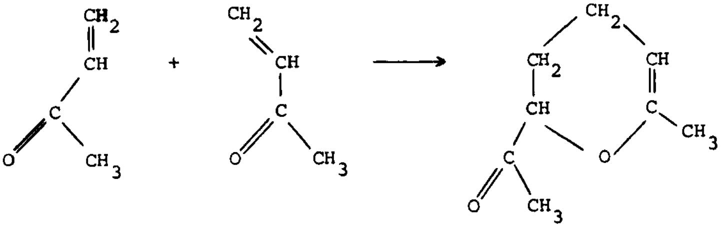
Kinetic data is only of limited value in attempting to establish a reaction mechanism, and therefore some attempt was made to detect a possible dimeric complex in the polymerization mixture. It is well known that many vinyl monomers form stable dimeric adducts under certain conditions. For example, at 150°C, styrene forms a mixture of dimers [21], the most favored having the structures



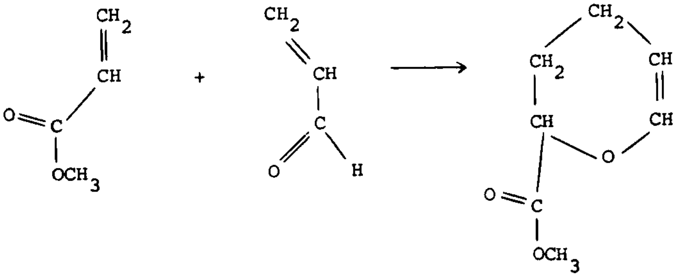
and



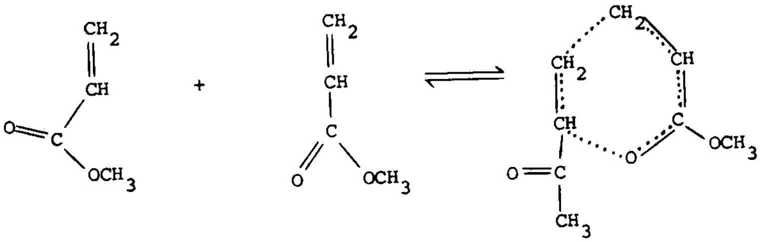
In a similar manner, methyl vinyl ketone [22] dimerizes, producing a derivative of dihydropyran:



Methyl acrylate itself condenses at high temperatures with acrolein, methacrolein, and crotonaldehyde [23]. In the reaction with acrolein the Diels-Alder type mechanism leads to the formation of 2-carbomethoxy-3:4-dihydro-2H-pyran:



Thus some loose association of acrylate monomer pairs could conceivably occur under polymerization conditions:



If such an equilibrium does exist in monomer solution, then deviations would be expected in Beer's law. Examination of the literature on acrylate esters reveals that this is in fact the case. Variations in measured values of the absorption coefficients and wavelengths of maximum absorption for methyl and butyl acrylates have been explained [24] in terms of dimer formation. In similar work ϵ_{max} and λ_{max} have been found [25] to vary with the nature of the solvent for a number of acrylates, although in this case the deviations have been attributed to polarity effects on electronic transition energies.

In an attempt to detect any dimeric complex of the form given above, the NMR spectra of ethyl acrylate and 2,3-dihydropyran were compared. No evidence for complex formation with the acrylate monomers resulted. However, if the equilibrium constant of the association reaction is extremely small and $k_{p'} \gg k_p$, "dimeric" addition in the polymerization could still account for the high monomer orders obtained. K values would be expected to increase at lower temperature, and in the present work there was some indication of an increase in the monomer order under these conditions. Nevertheless, no definite evidence for a polymerization mechanism of the type postulated above is at hand.

In conclusion it can be stated that it has not been possible to unambiguously account for the high monomer exponent observed in acrylate polymerizations. In addition to the mechanisms advanced by other workers, the two introduced above could at least partly account for the observed results. Unfortunately, the sensitivity of kinetic analysis on its own does not allow accurate distinction between the various mechanisms.

REFERENCES

[1] G. E. Scott and E. Senogles, J. Macromol. Sci.—Chem., A4(5), 1105 (1970).

[2] M. Devalériola, Bull. Soc. Roy. Sci. Liege, 30, 367 (1961).

[3] G. M. Burnett, Trans. Faraday Soc., 46, 772 (1950).

[4] K. Yokota, M. Kani, and Y. Ishii, J. Polym. Sci., A-1, 6, 1325 (1968).

[5] W. I. Bengough and H. W. Melville, Proc. Roy. Soc., A, 249, 445 (1959).

[6] H. W. Melville and A. F. Bickel, Trans. Faraday Soc., 45, 1049 (1949).

[7] S. W. Benson and A. M. North, J. Amer. Chem. Soc., 81, 1339 (1959).

[8] J. Brandrup and E. H. Immergut, Polymer Handbook, Wiley, New York, 1966, p. 11-58.

[9] G. M. Burnett, P. Evans, and H. W. Melville, Trans. Faraday Soc., 49, 1096, 1105 (1953).

[10] R. D. Burkhart, J. Polym. Sci., A3, 883 (1965).

[11] A. M. North and G. A. Reed, Trans. Faraday Soc., 57, 859 (1961).

[12] J. P. Fischer, J. Mucke, and G. V. Schulz, Ber. Bunsenges. Phys. Chem., 73, 154 (1969).

[13] A. M. North and G. A. Reed, J. Polym. Sci., A1, 1311 (1963).

[14] D. Mangaraj and S. K. Patra, Private Communication.

[15] G. M. Burnett, Progress in Reaction Kinetics, Vol. 3, Pergamon, London, 1965, pp. 449-470.

[16] G. M. Burnett and L. D. Loan, Trans. Faraday Soc., 51, 219 (1955).

[17] M. J. Roedel, J. Amer. Chem. Soc., 75, 6110 (1953).

[18] A. G. Morrell, Discussions Faraday Soc., 22, 152 (1956).

[19] J. Brandrup and E. H. Immergut, Polymer Handbook, Wiley, New York, 1966, p. 11-155.

[20] H. W. Melville and P. R. Sewell, Makromol. Chem., 47, 154 (1961).

[21] F. R. Mayo, J. Amer. Chem. Soc., 90, 1289-1300 (1968).
[22] K. Alder, H. Offermanns, and E. Rüden, Chem. Ber., 74B, 905 (1941).
[23] C. W. Smith, D. G. Norton, and S. A. Ballard, J. Amer. Chem. Soc., 73, 5270 (1951).
[24] H. E. Ungnade and I. Ortega, Ibid., 73, 1564 (1951).
[25] W. D. Closson, S. F. Brady, and P. J. Orenski, J. Org. Chem., 30, 12, 4026 (1965).

Accepted by editor December 10, 1973
Received for publication December 19, 1973