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Polymerization Kinetics of n-Lauryl Acrylate

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SUMMARY

The polymerization kinetics of n-lauryl acrylate have been investigated in ethyl acetate and n-heptane at 40°C. A high monomer order, 1.6(5), was found in both solvents. Corresponding initiator orders, determined using AZDN and lauroyl peroxide, were slightly less than the usual value of 0.5. Although the chain termination reaction is undoubtedly diffusion controlled from the start of polymerization, diffusion effects dependent on monomer concentration only partly account for the high monomer order. Other possible explanations based on primary radical termination, "cage-effects," degradative chain transfer, and radical complexing are also not applicable. Contrary to observations with lower acrylate esters, autoacceleration effects do not occur in the high conversion polymerization of n-lauryl acrylate. This probably reflects the reduced importance of radical branching reactions with this monomer.

INTRODUCTION

The effect of the nature of the alkyl group on the reactivities of alkyl methacrylate monomers and their corresponding radicals has been investigated in some detail [1-6]. Similar investigations on the acrylate series, however, have been somewhat neglected. Melville and co-workers [1, 7] studied the homopolymerization of various acrylate and methacrylate esters and Table 1 summarizes the information they obtained. It is apparent that with the methacrylate series the propagation constant is virtually independent of the length of the alkyl ester group, whereas the termination constant decreases as the series is ascended. The latter was attributed to steric effects in the bimolecular termination reaction, these effects being minimized in the corresponding radical-molecule reactions. This explanation could not be extended to the acrylate series, however, for in this case k_p and k_t both vary over at least two orders of magnitude. Further work on the methacrylates [3] has confirmed the general pattern of Melville's results but his explanation of the variation of k_t in the series now appears invalid. This conclusion follows both from the experimental investigations of North [8-10] and from the more theoretical arguments of Allen and Patrick [11], who show that the termination constant is diffusion controlled under virtually all conditions. Thus k_t is only controlled by physical factors and has no chemical significance. Although further studies [12, 13] on the polymerization of n-butyl acrylate have cast some doubt on the reliability of the results given in Table 1 for this monomer, Benson and North [8] have shown that k_t for n-butyl acrylate is at least two orders of magnitude less than the well established value for methyl methacrylate. Thus it would appear than an interesting and unuusal radical reactivity pattern may exist in the acrylate series. For this reason a study of the polymerization kinetics of n-lauryl acrylate was undertaken. Of further interest is the extent to which the polymerization process is diffusion controlled, since to date direct investigation of this factor has been essentially limited to methacrylate monomers. In this paper preliminary results obtained on the n-lauryl acrylate system are reported.

Table 1. Radical Reactivities in Acrylate and Methacrylate Polymerizations. Data of Burnett, Evans and Melville [1].

Monomer	Temp. (°C)	k_p (liter/mole/sec)	k_t (liter/mole/sec)
Methyl acrylate	25.0	1580	5.5×10^7
n-Butyl acrylate	25.0	13	1.8×10^4
Methyl methacrylate	23.6	310	6.8×10^7
n-Propyl methacrylate	30.0	467	4.5×10^7
n-Butyl methacrylate	30.0	362	1.0×10^7

EXPERIMENTAL

Materials

n-Lauryl acrylate (Borden Chemical Co., bp 119-121°C/0.8 mm) contains the monomethyl ether of hydroquinone as polymerization inhibitor. This was removed by passing the monomer down an alumina column in petroleum ether (40-60°C) solution. After removing the petroleum ether the monomer was prepolymerized under a nitrogen atmosphere by irradiating with UV light. The resulting mixture was poured into excess methanol and the polymer separated. The lauryl acrylate was recovered from the methanol by cooling below 0°C. Recrystallization was repeated a further two times from methanol. After separating and melting, any remaining methanol (as detected by the IR spectrum) was removed by bubbling dry air through the monomer under vacuum. In subsequent polymerization studies monomer purified by this method gave reproducible kinetic results in which induction periods were absent.

n-Butyl acrylate (Eastman Kodak) was fractionally distilled (bp 50°C/20 mm), prepolymerized by UV irradiation and distilled on the vacuum line from the polymer-monomer mixture.

n-Lauryl propanoate was prepared from fractionated n-dodecanol (BDH) and propanoic acid. The product was fractionally distilled (bp 175°C/20 mm).

Solvents dinonyl phthalate (BDH, GLC quality) and liquid paraffin (BDH for IR spectroscopy) were used without further purification. All other solvents were fractionally distilled.

2-Azobisisobutyronitrile (AZDN) and lauroyl peroxide were purified by recrystallization. All initiator solutions were made up in AR benzene.

Polymerizations

Initial polymerization rates were determined using Pyrex dilatometers of 4.5-8 ml capacity and 1-1.6 mm i.d. capillaries. Polymerizations to high conversion were carried out in "mushroom-type" dilatometers similar to those used by Burnett [14]. Because significant pure thermal polymerization occurred at higher temperatures, initiated polymerizations were conducted at temperatures less than 45°C. Comparison of dilatometer contraction rates with polymerization rates determined gravimetrically enabled the former to be expressed in moles/liter/min.

RESULTS AND DISCUSSION

The dependence of initial polymerization rate on n-lauryl acrylate concentration is shown in Fig. 1. This indicates that the monomer order is 1.6(5) in both ethyl acetate and n-heptane, different polymerization initiators being used in these solvents. Corresponding initiator exponent plots are shown in Fig. 2 from which it can be concluded that the initiator order is 0.4(5). Two effects, primary radical [15] and diffusion-controlled termination, could each theoretically account for the observed deviations from "normal" polymerization kinetics. The former, however, is only likely to be important at low monomer and/or high initiator concentrations, conditions which do not prevail in the above experiments. If the termination

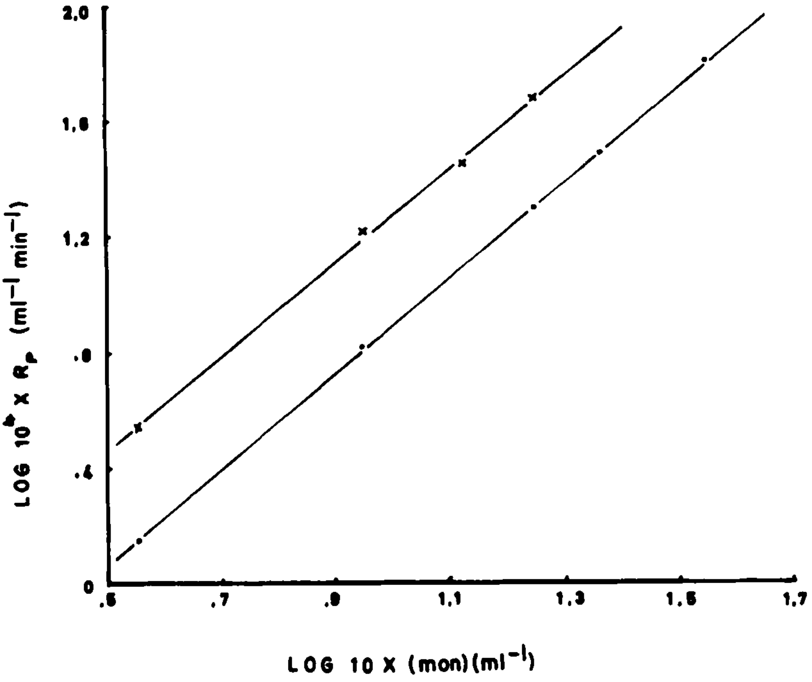

Fig. 1. Log-log plot of initial polymerization rate R_p against the concentration of n-lauryl acrylate, [Mon.]. X: In n-heptane, [lauroyl peroxide] = 1.3×10^{-3} moles liter^{-1}, T = 40°C. ●: In ethyl acetate, [AZDN] = 4.0×10^{-4} moles liter^{-1}. T = 40°C.

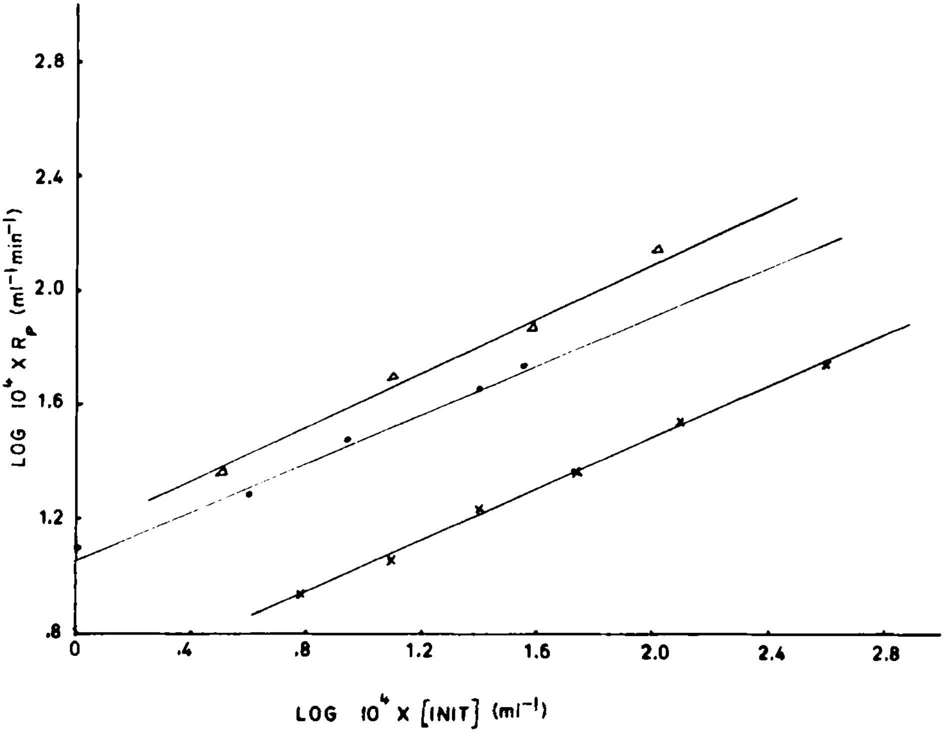

Fig. 2. Log-log plot of R_p against the initiator concentration, [Init.]. Δ: Lauroyl peroxide in n-heptane, [Mon.] = 1.79 moles liter^{-1}, T = 40°C, ●: AZDN in ethyl acetate, [Mon.] = 1.79 moles liter^{-1}, T = 40°C, X: AZDN in ethyl acetate, [Mon.] = 0.895 moles liter^{-1}, T = 40°C.

velocity constant, k_t, is diffusion controlled, its magnitude would be expected to depend on monomer concentration since this affects the initial viscosity of the polymerization system as well as the conformation and average size of the polymeric radicals. Likewise k_t may depend on the initiator concentration since this also controls the size of the polymeric radicals. As a consequence of these effects, monomer orders greater than unity and initiator exponents less than 0.5 could arise since k_t in the normal polymerization rate equation,

$$R_p = \frac{k_p[M] R_I^{\frac{1}{2}}}{2^{\frac{1}{2}} k_t^{\frac{1}{2}}}$$

would be a function of both monomer concentration and the rate of initiation, R_I.

The effect of viscosity on the monomer order has been investigated in two ways. Figure 3 shows the dependence of reaction rate on n-lauryl acrylate concentration using n-lauryl propanoate as the polymerization solvent. In this medium the initial viscosity is practically independent of monomer concentration. Furthermore, the solvating power of the system and, therefore, the conformation of the polymeric radicals, is probably little affected by dilution. The measured monomer order in this case is 1.45-1.50, the corresponding initiator value being 0.44-0.5. In Fig. 4 the initial rate of polymerization is shown as a function of the initial viscosity of the polymerization system. Runs were performed in different viscous solvents of generally similar chemical structure. It will be seen that the polymerization rate increases with the initial viscosity and this indicates the termination step

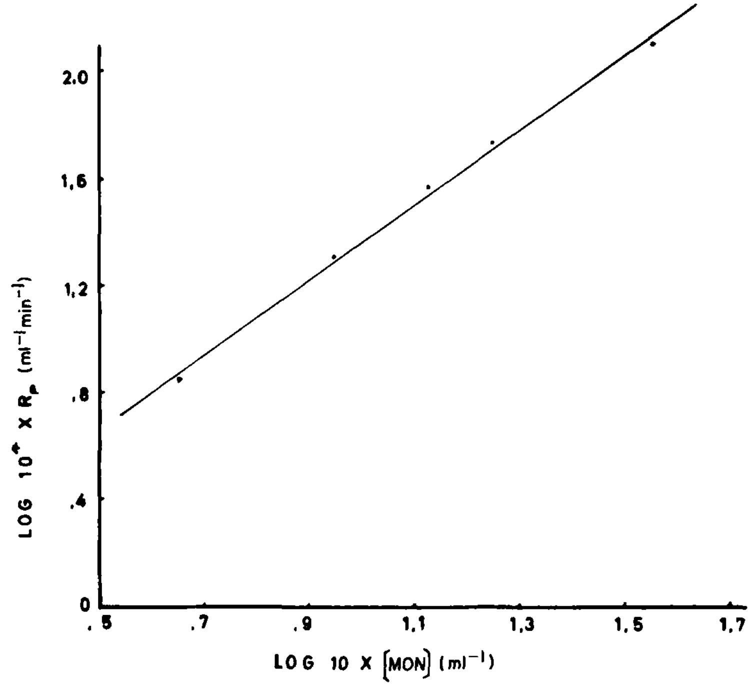

Fig. 3. Log-log plot of R_p against [Mon.] in n-lauryl propanoate, [AZDN] = 1.67 X 10^{-3} moles liter^{-1}, T = 40°C.

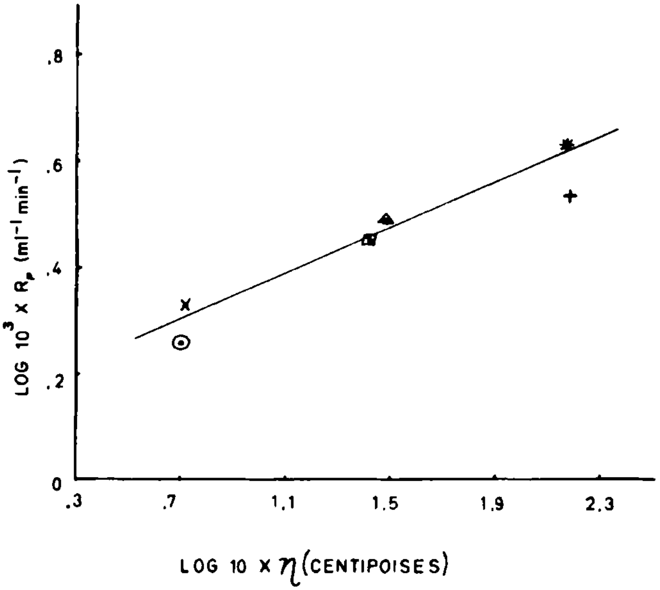

Fig. 4. Log-log plot of R_p against initial viscosity. [Mon.] = 0.716 moles liter^{-1}, [lauroyl peroxide] = 5 X 10^{-3} moles liter^{-1}, T = 40°C, O: In ethyl acetate. X: In n-heptane; *: In liquid paraffin. +: In dinonyl phthalate. Δ: In n-lauryl propanoate. □: In n-heptane-liquid paraffin mixture.

is diffusion controlled. The straight line drawn on Fig. 4 corresponds to a rate dependence on $(\text{viscosity})^{0.2}$, a relationship which is similar to that observed with various higher methacrylate esters [10]. It is probable that deviations from the above relationship observed in polymerizations conducted in ethyl acetate and dinonyl phthalate reflect different solvating effects. Utilizing the results of Fig. 4 and the measured dependence of viscosity on monomer concentration (Fig. 5), the rate measurements of Fig. 1 were corrected to the same initial polymerization viscosity. The resulting amended monomer reaction order was 1.5. These investigations indicate that variations in the diffusion-controlled rate constant, k_t, make only a minor contribution to the high monomer order measured in the polymerization of n-lauryl acrylate. Consequently other explanations must be investigated.

Monomer orders greater than 1 are not an uncommon observation in polymerization solution kinetics, even when dealing with relatively simple monomers, such as vinyl acetate and methyl methacrylate [16]. Initiator

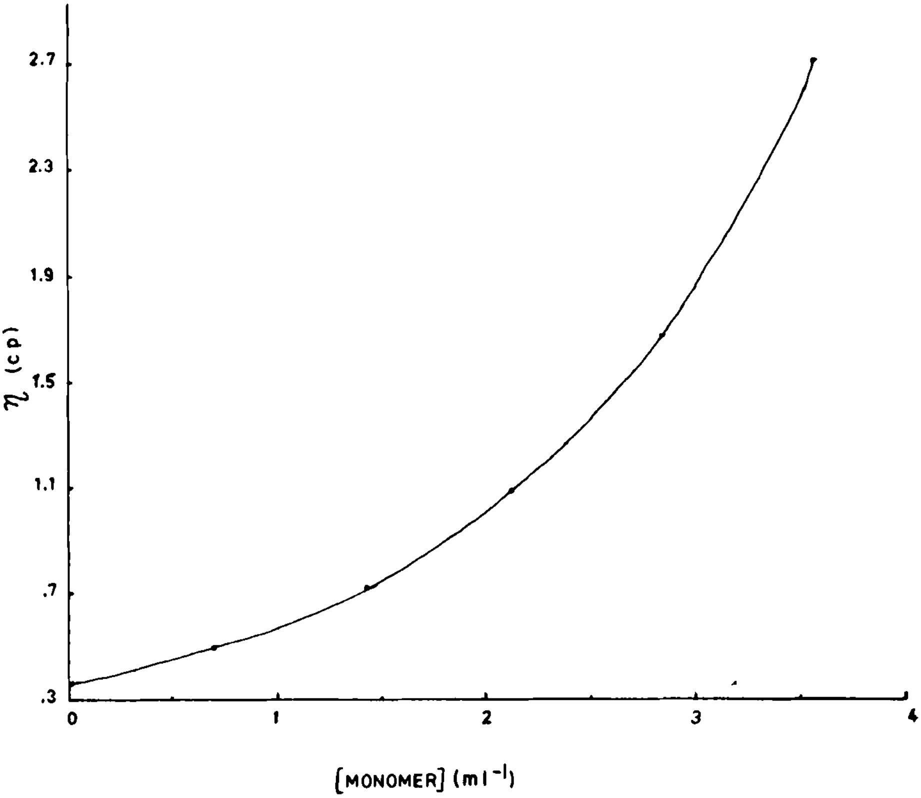

Fig. 5. Plot of initial viscosity (centipoises) against [Mon.] in n-heptane at 40°C.

orders different to 0.5 are, however, less common. Devalériola [17] has measured monomer and initiator exponents of 1.5 and 0.5, respectively, for the polymerization of ethyl acrylate in benzene and the present authors have obtained similar results with n-butyl acrylate in ethyl acetate solution (Figs. 6 and 7). Mangaraj and Patra [18], investigating various other acrylates, report monomer orders between 2 and 2.8, the initiator exponent being in all cases 0.5. It seems reasonable to suggest that a common explanation might apply to the results obtained with these systems and that of n-lauryl acrylate, although in the latter case the initiator exponent is slightly less than 0.5. In addition to primary radical termination, discussed above, three other modified polymerization schemes have been postulated

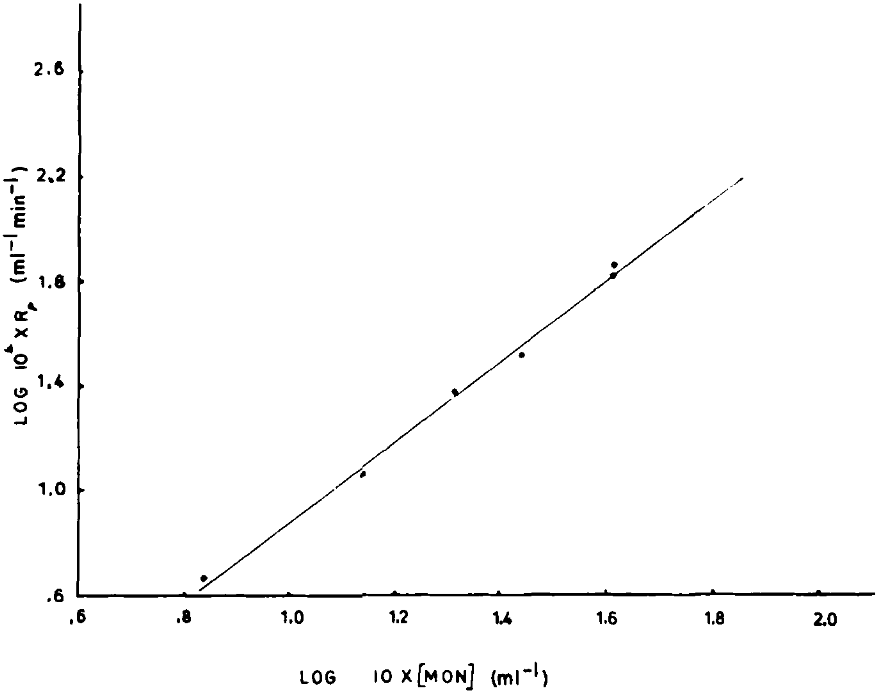

Fig. 6. Log-log plot of R_p against n-butyl acrylate concentration, [M], in ethyl acetate. [AZDN] = 1 × 10^{-3}, T = 40°C.

to account for high monomer orders. These involve the well known "cage-effect" [19], degradative chain transfer [20], and the participation of monomer-radical complexes in the propagation step [21, 22]. As with primary radical termination, cage effects are only to be expected at low monomer concentrations and are therefore unlikely to account for the observed results with acrylate monomers. Transfer to solvent in degradative chain transfer produces a relatively unreactive radical which propagates sluggishly and takes part in the termination process:

$$\begin{array}{lll} P^{\bullet} + M \rightarrow P^{\bullet} & & k_p \\ P^{\bullet} + S \rightarrow P + S^{\bullet} & & k_f \\ S^{\bullet} + M \rightarrow P^{\bullet} & & k_r \\ \left.\begin{array}{l} P^{\bullet} + P^{\bullet} \\ P^{\bullet} + S^{\bullet} \\ S^{\bullet} + S^{\bullet} \end{array}\right\} \rightarrow & \begin{array}{l} \text{Inactive} \\ \text{products} \end{array} & \begin{array}{l} kt_1 \\ kt_2 \\ kt_3 \end{array} \end{array}$$

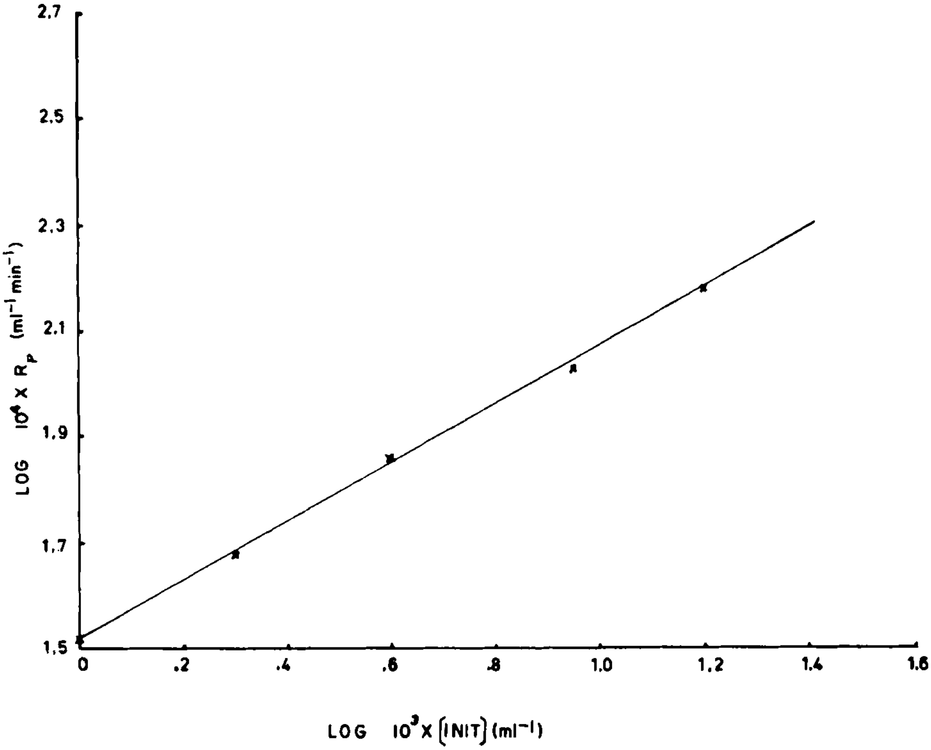

Fig. 7. Log-log plot of R_p against [AZDN] for n-butyl acrylate in ethyl acetate. [M] = 2.75 moles liter^{-1}, T = 40°C.

Although this successfully explains monomer orders greater than unity, it is unlikely to account for the results obtained with n-lauryl acrylate since these polymerizations were conducted in solvents of low transfer constant. Even if limited transfer does occur, different monomer orders might be expected in different solvents and in all cases an initiator exponent greater than 0.5 should result. Henrici-Olivé and Olivé [21, 22] have successfully accounted for the unusual kinetic results obtained when methyl methacrylate is polymerized in bromobenzene by suggesting that the polymer radicals form complexes with both solvent and monomer molecules. They postulate that only monomer-radical complexes can lead to propagation. It is unlikely that radical complexing will occur with solvents like ethyl acetate and heptane, so that this explanation would not account for the n-lauryl

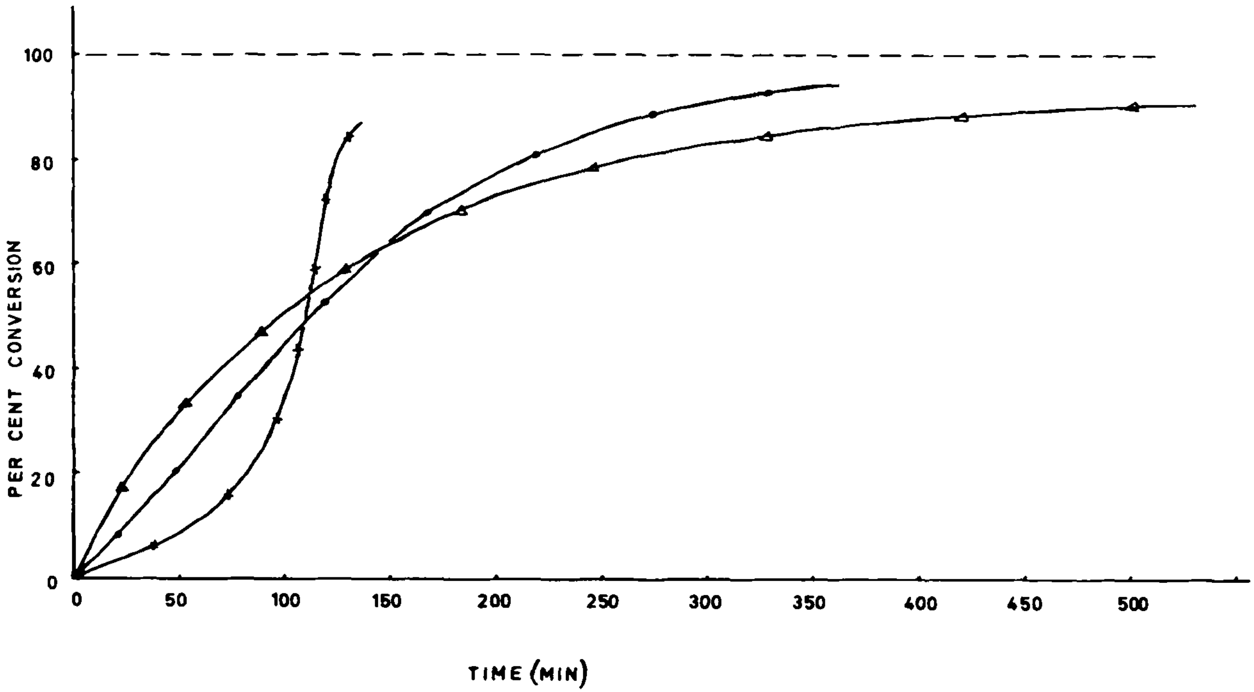

Fig. 8. Conversion-time plots for bulk polymerization of (Δ) n-lauryl acrylate, (●) n-butyl acrylate, and (X) ethyl acrylate (data of Mangaraj and Patra [23]). T = 35°C, [AZDN] = 0.8 X 10^{-2} moles $liter^{-1}$

acrylate results. Furthermore, the results are not consistent with the rate equation derived from the Olivé mechanism. Thus it appears that all previous mechanisms invoked to explain anomalous monomer orders in free radical polymerization systems are not valid for the polymerization of n-lauryl acrylate. This conclusion probably also applies to the other acrylate systems mentioned above. It is hoped that a satisfactory explanation may emerge from further studies being carried out on these systems.

Further aspects of the importance of diffusion effects on the polymerization of n-lauryl acrylate were investigated by studying the reaction rate to high conversion. The experimental data is summarized in Fig. 8 together with corresponding results obtained with n-butyl acrylate and ethyl acrylate. It will be seen that no Trommsdorff effect occurs with the n-lauryl acrylate monomer, the conversion curve being consistent with a monomer order of 1.4. In contrast, marked autoacceleration is observed with ethyl acrylate [23]. The results obtained with n-butyl acrylate are of an intermediate nature, a steady rate being observed up to about 60% conversion despite the fall off in monomer concentration. If polymerization is diffusion controlled from the start of reaction, autoacceleration effects at higher conversion must be attributed to further restrictions on the bimolecular termination step. With lower methacrylate esters this is usually identified with the increasing viscosity of the system. In the case of ethyl and n-butyl acrylate, however, it is probably associated with the increasing production of branched polymer radicals as the reaction proceeds. The existence of branching with these monomers is substantiated by the production of insoluble cross-linked polymer at high conversions. With n-lauryl acrylate branching is much less important, since soluble polymer is obtained at high conversion, and thus no significant change in the rate of the diffusion-controlled termination step occurs as polymerization proceeds.

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