# EFFECT OF THE REACTION TEMPERATURE ON THE POLYMERIZATION OF 2-ETHYLHEXYL ACRYLATE INITIATED BY LITHIUM ESTER ENOLATE–LITHIUM *tert*-BUTOXIDE COMPLEX*

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*Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.*

The effect of reaction temperature in the range from –72 to 0 °C on the course of the anionic polymerization of 2-ethylhexyl acrylate in 9 : 1 (v/v) toluene–THF was studied. In the polymerization, *tert*-butyl 2-lithioisobutyrate and Li *tert*-butoxide were used as initiator and active centre stabilizer, respectively; the alkoxide at two different concentrations. From conversion curves and number-average molecular weights of the polymers, the rate constants of the propagation and autotermination reactions were calculated. The rate constant of autotermination rises more rapidly with temperature than that of propagation. Consequently, at temperatures higher than –60 °C polymerization autoterminates before reaching quantitative monomer conversion. The limiting monomer conversion was higher at the higher alkoxide concentration but did not reach 100%.

The favourable effect of alkali metal *tert*-alkoxides on the anionic polymerization of polar vinyl monomers has been shown in a number of papers[1 – 3]. In recent studies, alkoxides were used for the stabilization of acrylate polymerization systems in which they also restrict the extent of autotermination by the back-biting reaction. In the presence of Li *tert*-butoxide (*t*-BuOLi), 2-ethylhexyl acrylate (EtHA) can be successfully polymerized with *tert*-butyl 2-lithioisobutyrate in a mixed solvent, toluene–THF 9 : 1 (v/v), at low temperature (–60 °C), yielding the product with a narrow molecular weight distribution (MWD)[3]. In a polar solvent, neat THF or a 1 : 1 (v/v) toluene–THF mixture, a cyclization reaction is preferred and the propagation reaction autoterminates at monomer conversions lower than 100%. In these conditions, the molecular weight of poly(EtHA) can be simply controlled stoichiometrically in the range of approximately

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one order of magnitude[4] and the polymerization is almost "ideally living". In a polar solvent, neat THF or a 1 : 1 (v/v) toluene–THF mixture, a cyclization reaction is preferred and the propagation reaction autoterminates at monomer conversions lower than 100%. Using butyllithium (BuLi) as an initiator led to similar results[5]. On the other hand, *tert*-butyl acrylate (*t*-BuA) can be successfully polymerized with the ester enolate in THF in the presence of *t*-BuOLi even at room temperature producing a polymer with a narrow MWD (ref.[6]). A stabilization effect of Li halides (LiCl best) in a combination with organometallic initiators was observed by Teyssié[7,8] in the anionic polymerization of *t*-BuA and MMA. The same system was used for the synthesis of high-molecular-weight poly(*t*-BuA) (ref.[9]) and its block copolymers with other vinyl monomers[10,11]. A model study of the oligomerization of *t*-BuA initiated by the ester enolate showed the difference between the effects of *t*-BuOLi and LiCl (ref.[12]). The former affects mainly the rates of cyclization (more markedly) and propagation while the latter affects favourably MWD of the product and also association phenomena of the initiator and living chains[13], which were shown to influence considerably the width and shape of MWD curves[14]. As shown already in earlier papers[15 - 17], the extent of autotermination in the anionic polymerization of alkyl acrylates depends on the structure of the alkyl group: α-branched alkyl (*tert*-butyl, isopropyl, cyclohexyl) acrylates exhibit the lowest whereas methyl acrylate the highest extent of the back-biting reaction. As the alkyl in EtHA is branched at the β-carbon atom, we were interested in the effect of temperature on its anionic polymerization.

## EXPERIMENTAL

### Materials and Methods

Purification of the monomer and solvents[5] as well as the preparation of the initiator and its components[18] were described previously. All operations were performed in the atmosphere of pure argon.

Polymerization of EtHA was performed in a stirred glass reactor equipped with a dosing cell and a sampling capillary[5]. To the samples withdrawn from the reaction mixture, HCl in THF solution was added and the polymers were isolated by precipitation in a methanol–water mixture (9 : 1 (v/v)). Monomer conversion was determined gravimetrically and by gas chromatography.

SEC measurements of MWD of polymers[4] and GC determination of the residual monomer[19] were described in our previous papers.

### Kinetic Calculations

The rate constants of both propagation and autotermination reactions were calculated on the basis of Scheme 1 (cf. ref.[20])

$$\begin{tikzcd}
I^* + M \arrow[r, "k_i"'] & P_2^* \arrow[r, "M", "k_{p2}"'] & P_3^* \arrow[r, "M", "k_{p3}"'] \arrow[d, "k_{t3}"] & P_4^* \arrow[r, "M", "k_{p4}"'] \arrow[d, "k_{t4}"] & \text{etc.,} \\
 & & P_3^t & P_4^t &
\end{tikzcd}$$

SCHEME 1

where I* represents effective initiator, M monomer, $P_j^*$ living oligomers, $P_j^t$ terminated oligomers, $k_i$, $k_{pj}$, and $k_{tj}$ rate constants of initiation, propagation, and autotermination steps, respectively.

In Scheme 1, the initiation step was assumed to be instantaneous, i.e. $k_i$ equal to infinity. All propagation ($k_{pj}$) and autotermination ($k_{tj}$) rate constants were assumed to be independent of $j$. These assumptions were based on the results of the model study of acrylate oligomerization[12] and are in line with the fact, that the MWD of the polymers is narrow. To simplify the mathematical treatment it was assumed that the living dimer $P_2^*$ autoterminates with the same rate as longer chains; in fact, only trimer or longer chains can undergo the back-biting reaction. The error due to this assumption is negligible. As the $M_n$ values obtained from SEC are higher than theoretical, it can be assumed that only a part ([I*]) of the initiator added ($[I]_0$) is effective in the polymerization. On these assumptions, we obtain for the monomer concentration [M] at reaction time $t$:

$$[M] = ([M]_0 - [I^*]) \exp(-\{1 - \exp(-k_t t)\} k_p [I^*]/k_t) . \qquad (1)$$

The second term in the leftmost parenthesis is a small correction for the monomer consumed in the infinitely fast initiation step. The $M_n$ value is obtained straightforwardly from the monomer consumption assuming that the number of polymer chains equals [I*]. The limiting monomer conversion ($X_{lim}$) after autotermination may be obtained from Eq. (*1*) by setting inner exponential term to zero:

$$X_{lim} = 1 - (1 - [I^*]/[M]_0) \exp(-[I^*] k_p/k_t) . \qquad (2)$$

Equations (*1*) and (*2*) allow to determine some kinetic parameters of the polymerization: the $[M]_0/[I^*]$ ratio is obtainable from the proportionality constant in the conversion–$M_n$ dependence, $k_p[I^*]$ from the initial slope of the semilogarithmic plot of the concentration of unconverted monomer vs time, and the $k_p[I^*]/k_t$ ratio from the limiting conversion at a long reaction time (Eq. (*2*)). Graphical extrapolation to infinite time was uncertain and also the initial slope of the conversion curve could be hardly determined in some runs since considerable conversions were obtained in shortest times. Therefore, the least-square method was used for time dependences of experimental conversions and $M_n$ data. From the resulting values, $k_p$ and the initiator efficiency $[I^*]/[I]_0$ were obtained. In the iteration, the experimental errors of all the log (100 – % conversion) values were assumed to be equal; the same assumption was made for log $M_n$. For each run separately, the ratio of the experimental errors in the conversion and in $M_n$ was selected so as to yield roughly the same ratio of root-mean-square deviations in the log (100 – % conversion) and log $M_n$ values.

## RESULTS AND DISCUSSION

The results of the polymerization experiments performed at various reaction temperatures and with two different concentrations of *t*-BuOLi are summarized in Table I. It is seen that the polymerization proceeds quantitatively only at –72 and –60 °C producing polymers with narrow MWD (runs 1 – 3). An increase in the concentration of the alkoxide (run 3) leads only to a slightly lower polymerization rate (Fig. 1) as expected in view of the results of previous studies[12]. At higher temperatures, i.e. at –40, –20, and 0 °C, polymerizations autoterminated with incomplete monomer conversion dependent on the temperature (see Table I and Fig. 2) and, at the same time, the polymers had broader MWD. In the experiments in which the higher alkoxide concentration was used a higher limiting conversion was reached; the difference is marked when comparing the polymerizations at –20 °C (runs 6, 7). The efficiency of the initiator, estimated from the ratio of the theoretical (9 340 at complete conversion) and experimental (Table I) $M_n$ values is about 40% at –72 and –60 °C and 20 – 25% at –40 °C. At –20 and 0 °C, when a higher concentration of the alkoxide was used molecular weights of the products are relatively low, probably due to a high extent of autotermination. In addition, this phenomenon can be due to a possible direct participation of *t*-BuOLi in the polymerization

TABLE I
Polymerization of 2-ethylhexyl acrylate initiated with *tert*-butyl 2-lithioisobutyrate at –70 to 0 °C in the presence of lithium *tert*-butoxide

| Run[a] | $T$ °C | $Z$[b] | Conversion % | $M_n \cdot 10^{-3}$ | $M_w/M_n$ | $k_p$ l mol$^{-1}$ s$^{-1}$ | $k_t \cdot 10^3$ s$^{-1}$ | $k_p/k_t \cdot 10^{-3}$ l mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | -72 | 3 | 100 | 26.1 | 1.13 | 4.72 | 0.48 | 9.79 |
| 2 | -60 | 3 | 100 | 21.3 | 1.05 | 13.58 | 4.79 | 2.83 |
| 3 | -60 | 10 | 100 | 20.6 | 1.09 | 10.11 | 5.36 | 1.89 |
| 4 | -40 | 3 | 79 | 36.2 | 1.23 | 24.08 | 14.71 | 1.64 |
| 5 | -40 | 10 | 90 | 35.4 | 1.24 | 26.74 | 13.46 | 1.99 |
| 6 | -20 | 3 | 42 | 26.7 | 1.31 | 42.54 | 52.54 | 0.81 |
| 7 | -20 | 10 | 77 | 18.0 | 1.31 | 31.26 | 39.07 | 0.80 |
| 8 | 0 | 10 | 50 | 7.9 | 2.06 | ~50 | ~200 | 0.24 |

[a] Polymerization time 10 min, $[EtHA]_0 = 0.2402$ mol l$^{-1}$, $[t\text{-Bu 2-lithioisobutyrate}]_0 = 0.0048$ mol l$^{-1}$; [b] ratio $[t\text{-BuOLi}]_0/[t\text{-Bu 2-lithioisobutyrate}]_0$.

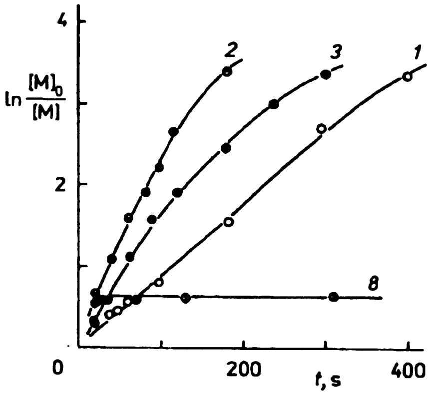


FIG. 1
Plots of ln ([M]$_0$/[M]) vs reaction time. Numbers of the curves correspond to the runs in Table I

because, under these experimental conditions, the addition of a *tert*-alkoxide on the acrylate double bond cannot be excluded. As follows from our previous study[21], at –20 and 0 °C the polymerization of EtHA by the neat alkoxide is not so slow as at lower temperatures. Molecular weight of polymer increases virtually linearly with increasing conversion at –72, –60 and –40 °C thus indicating a negligible extent of chain transfer (see Fig. 3). This fact was already mentioned in our recent paper[3] dealing with the polymerization of EtHA at –60 °C.

If the autotermination is caused mainly by the back-biting reaction (see below) it can be assumed, that two main competing reactions proceed in the polymerization system: chain propagation and cyclization of the last three chain units leading to cyclic ketoester (Scheme 2). Thus, the result of the polymerization depends on the rates of the two basic reaction steps, which are given by Eqs (*3*) and (*4*)

$$r_p = k_p\,[C^*]\,[M] \qquad \text{propagation} \qquad (3)$$

$$r_t = k_t\,[C^*] \qquad \text{autotermination,} \qquad (4)$$

where [C*] represents the concentration of active species.

When the rate of autotermination is much lower than that of propagation, the polymerization proceeds up to a complete monomer conversion without a perceptible de-

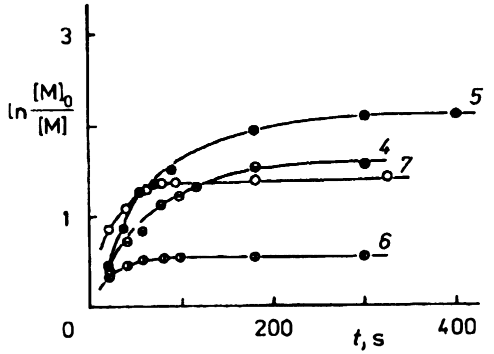


FIG. 2
Plots of ln ([M]$_0$/[M]) vs reaction time. Numbers of the curves correspond to the runs in Table I

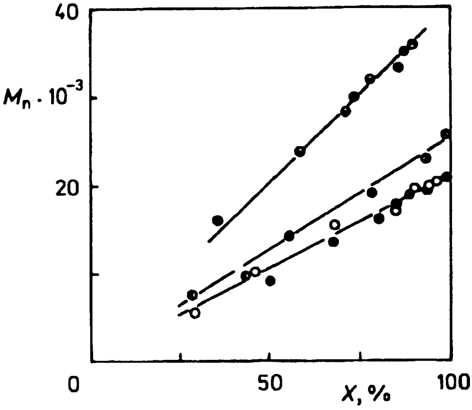
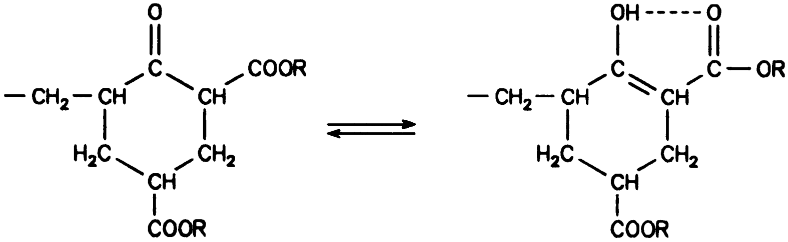


FIG. 3
Dependence of $M_n$ on the monomer conversion. ○ Run 1, ● run 2, ⦶ run 3, ⊖ run 5

crease in number of living centres producing a polymer with a narrow Poisson MWD. On the contrary, when the autotermination is only slightly slower than the propagation, the polymerization autoterminates at a very low monomer conversion producing the polymer having a broad Schulz–Flory MWD with $M_w/M_n$ ratio equal to 2. In real polymerization systems, which are intermediate between these two cases, the value of the limiting conversion depends on the ratio of the rates of propagation and autotermination and on the concentration of the effective initiator, as given by Eq. (*2*). The constants $k_p$ and $k_t$ obtained in the way mentioned above are summarized in Table I. Note that at 0 °C (run 8) the autotermination is so fast that the calculated conversions only rose from 44.2% at the shortest time to the limiting value 44.8%. Hence, the calculated $k_p$ and $k_t$ values are very inaccurate, only their ratio being reliable. It is seen, that the $k_p$ values vary with reaction temperature in the range from 4.72 $l\ mol^{-1}\ s^{-1}$ at −72 °C to 42.54 $l\ mol^{-1}\ s^{-1}$ at −20 °C while $k_t$ values rise with increasing temperature more markedly: from a negligible value (0.48 . $10^{-3}\ s^{-1}$ and zero in two different runs) at −72 °C to 52.54 . $10^{-3}\ s^{-1}$ at −20 °C. A more pronounced temperature dependence of autotermination in comparison with that of propagation is documented also by the temperature dependence of $k_p$, $k_t$ (Fig. 4), and $k_p/k_t$ (Table I).

It should be mentioned, that autotermination involves not only cyclization, but also other possible ways of the chain self-termination (Scheme 2). The product of the backbiting reaction is the cyclic ketoester; in the end form it contains an acidic hydrogen capable of terminating living chains by protonation. In the previous study of *t*-BuA polymerization and oligomerization a difference was found between the rate constants of autotermination calculated either from the curvature of conversion curves or from the absorbance of the products in UV region at 260 nm. Also, the fraction of chains with the ketoester end group was found to be lower than the concentration of all polymer chains, which supports the assumption of the termination by protonation[6]. This step is a bimolecular reaction, so that it does not follow Scheme 1 exactly. A more



SCHEME 2

thorough kinetic study of simultaneous termination by cyclization (rate constant $k_c$) and protonation ($k_b$), assuming a very rapid keto–enol equilibration, showed, that the ratio $r$ of limiting conversions (i.e., of $\ln(([M]_0 - [I^*])/[M])$ values) with and without termination by protonation depends only on the value

$$\rho = c_b\, k_b\, [I^*]/k_c\,, \tag{5}$$

where $c_b$ is the equilibrium fraction of the enol form. The ratio $r$ may be found by solving the equation $\exp(-r\,\rho) + 2\,r\,\rho = 1 + \rho$. Setting $k_t = k_c/r$ the true conversion curves differ from those obtained from Eq. (*1*) by less than 4% of the limiting conversion (Fig. 5). Such a small difference is hardly detectable within the accuracy of our experimental technique and is expected to distort the $k_p$ and the initiator efficiency values by less than 2%. The true conversion curves and those obtained from Eq. (*1*) are shown in Fig. 5, where

$$Y = \{-\ln(1 - X) + \ln(1 - [I^*]/[M]_0)\}\, k_c/(k_p[I^*]) \tag{6}$$

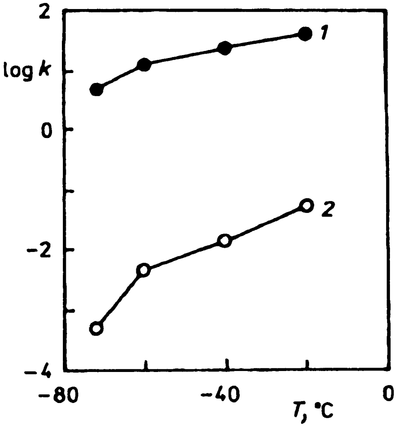


FIG. 4

Dependence of rate constants on reaction temperature: *1* propagation, *2* autotermination

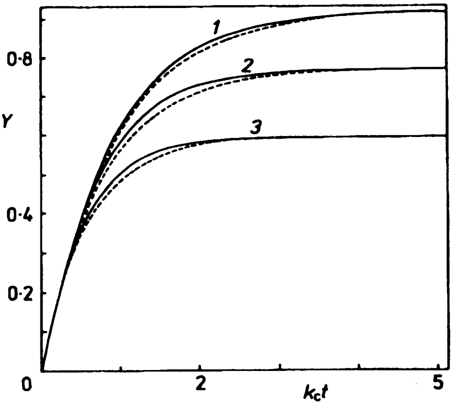


FIG. 5

Conversion curves calculated for the polymerization with cyclization and protonation termination. Broken lines relate to the polymerizations with cyclization only, their termination constants being selected so as obtain the same limiting conversions as with protonation. The numbers of the curves represent the ρ values (Eq. (*5*)): *1* 0.2, *2* 1, *3* 5

($X$ is the monomer conversion) is plotted vs $k_c t$. Axes scaling and a shift on the $y$-axis were used to make the curves universal with respect to $k_p$, $k_c$, and [I*]. Hence, our calculated $k_t$ values involve both $k_c$ and $k_b$ constants. Other possible termination reactions, such as chain-transfer by the α-proton of the monomer or a condensation of the living chain with the carbonyl group of the monomer, can probably be neglected. This assumption is based on the $^{13}$C NMR spectra of the poly(EtHA)[3] prepared under the same conditions as those in this work. No detectable signals of acrylate double bond were found in the spectrum and, moreover, the amount of initial isobutyrate groups in the polymer corresponded to the molecular weight of the polymer determined by SEC.

On the basis of this and recent works it can be concluded, that, by using mixed initiating systems, some of acrylate esters can be successfully polymerized anionically, even though each of the esters needs specific reaction conditions. In contrast to the polymerization of *t*-BuA where, due to the extremely low extent of autotermination, the reaction proceeds quantitatively even at room temperature, 2-ethylhexyl acrylate must be polymerized at low temperatures because of the pronounced temperature dependence of its autotermination reaction. Concerning the influence of alkyl structure on the extent of autotermination, it can be assumed, that the tendency of β-branched EtHA to autotermination is probably somewhere between those of n-alkyl and *tert*-butyl acrylates. Consequently, for an anionic polymerization of n-alkyl acrylates to be successful, the necessity of a very effective stabilization can be expected.

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