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Anionic polymerization of acrylates

9. Lithium 3-methylpentoxide-3, an efficient active-center stabilizer in the anionic polymerization of 2-ethylhexyl and butyl acrylates

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Summary

The article presents preliminary results of the anionic polymerization of 2-ethylhexyl- and butyl acrylates initiated by ester enolate in the presence of Li 3-methylpentoxide-3. Compared with the Li *t*-butoxide which has been widely used earlier, this alkoxide is a more efficient stabilizer of active centers. Under selectively chosen reaction conditions, polymerizations of both monomers proceed quantitatively with a small extent of the self-termination even at -40 and -20 °C producing polymers with narrow MWD's.

Introduction

The controlled polymerization of (meth)acrylic monomers, namely acrylic esters, potentially offers a wide scale of products with variable properties and many technological applications. This is why a great effort has been devoted to its improvement. In the last decade, several methods have been designed for "tailoring" polyacrylates (e.g., GTP and metal-free polymerization). Nevertheless, none of them represents a general way. Most promising seems to be an approach based on the modified anionic polymerization initiated by the complex ("ligated") systems, containing stabilizers, which restrict the extent of side reactions of the active centres. Moreover, with the use of these stabilizers, the acrylate polymerization can be initiated with other "living" polymers (derived from styrene, dienes, etc.) so that a number of block copolymers can be prepared in this way. The stabilizers described up to now are of the type of either μ-binding ligands like LiCl (1) or hindered σ-ligands like alkali alkoxides (2), both types being more effective in low-temperature polymerizations. Moreover, LiCl operates well in the polymerization of *tert*-butyl acrylate (*t*-BuA) and methacrylates only, i.e. of monomers with rather low extent of self-termination. In the polymerization of 2-ethylhexyl- (EtHA) or butyl acrylates (BuA), its stabilizing effect is not high enough to ensure the quantitative and "living" polymerization. Most recently, another type of ligands (dual σ-π binding) has been described (3), based on chelating Li alkoxides beeing efficient at low temperatures.

As shown in our recent papers, the polymerization of EtHA and BuA proceeds with a very low extent of self-termination when stabilized by Li *tert*-butoxide (*t*-BuOLi). However, the reaction conditions have to be tuned selectively with respect to the type of monomer (4,5). It follows from kinetic studies that the self-termination reaction is not fully excluded even at -60 °C and its extent increases distinctly with the increasing reaction temperature which leads to a lower limiting monomer conversion and broader MWD of the product (6). Nevertheless, under appropriate conditions, the livingness of active centers is long enough to allow even the controlled synthesis of block-copolymers (7).

Based on these results, an attempt has been made to design a system with higher stabilizing activity which would be effective even at temperatures higher then -60 °C. This is of high technological importance, because deep cooling brings about a distinct increase in production expenses. In this paper, preliminary results of the study of stabilizing effect of Li 3-methylpentoxide-3 (3-MPOLi) in the polymerization of EtHA and BuA initiated by *t*-butyl 2-lithioisobutyrate (Li-*t*-BIB) are reported.

Experimental

Materials:

Methods of the purification of the monomers and solvents were described earlier (8) as well as the synthesis of Li-t-BIB (9). 3-MPOLi was prepared by the reaction of Li dust with 3-methylpentanol-3 in a mixed medium heptane-THF and purified by crystallization at low temperature (10).

Polymerization:

Experiments were performed under dry argon in the glass batch reactor with temperating cells which has been described elsewhere (8).

Analysis:

Molecular weights of the prepared polymers were measured by SEC as described earlier (8). In the case of poly(BuA), Mark-Houwink-Sakurada constants valid for poly(MMA) were used; for p(EtHA), specific constants are known (11).

Results and Discussion

EtHA was polymerized with various initiator-to-stabilizer ratios at -40 and -20 °C. The results are summarized in Table 1. At -40 °C, the molar ratio of $[\text{Li-}t\text{-BIB}]_0/[\text{3-MPOLi}]_0 = 1{:}2$ is sufficient to suppress the self-termination reaction to such extent that the polymerization proceeded quantitatively within 10 minutes (Run 2) producing polymer with a narrow MWD (M_w/M_n about 1.2).

TABLE 1
Polymerization of 2-Ethylhexyl Acrylate at Various Conditions.[a]

Run	$\frac{[\text{Li-}t\text{-BIB}]_0}{[\text{3-MPOLi}]_0}$	T, °C	Time, s	Conversion, %	M_n	M_w/M_n
1	1 / 1	-40	300	75	14800	1.63
2	1 / 2	-40	600	100	15800	1.16
3	1 / 3	-40	1200	100	27900	1.23
4	1 / 3	-20	600	87	14800	1.71
5	1 / 6	-20	300	99	10000	1.33
6	1 / 10	-20	600	97	14800	1.34

[a] $[\text{EtHA}]_0$ = 0.480 mol/l, $[\text{Li-}t\text{-BIB}]_0$ = 0.0096 mol/l, solvent: toluene-THF 9/1 (v/v)

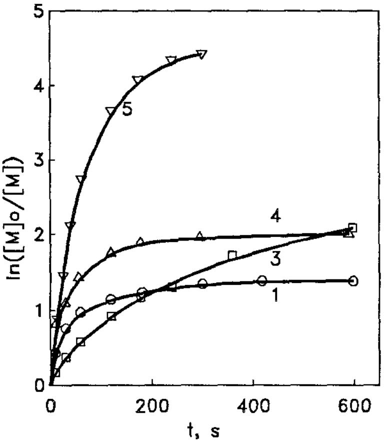


Figure 1. Semilogarithmic conversion plots for 2-ethylhexyl acrylate polymerized at various conditions. The numbers of curves correspond to the runs in Table 1.

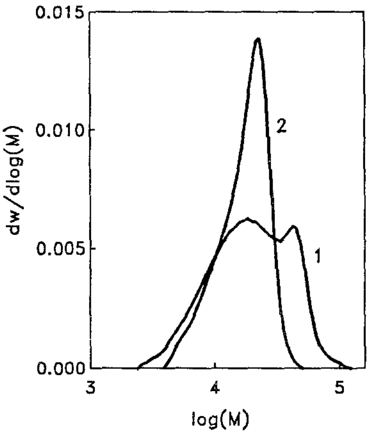


Figure 2. MWD of poly(2-ethylhexyl acrylate) prepared at various 3-MPOLi concentrations. The numbers of curves correspond to the runs in Table 1.

In the initiation by the system $[\text{Li-}t\text{-BIB}]_0/[\text{3-MPOLi}]_0$ = 1:1, the polymerization stops at an uncomplete monomer conversion and the product has rather broadened MWD (Run 1). The MWD of the polymer sample, which was withdrawn from the reaction mixture in the early stage of polymerization (Fig. 2, curve 1) is clearly bimodal. It can be supposed that the observed curve is a superposition of the distributions of "dead" and "living" chains simultaneously present in the reaction mixture. This result is in an agreement with MWD curves of polymers calculated theoretically on the basis of kinetic measurements (12).

The addition of 3-MPOLi lowers the overall polymerization rate even more than that of t-BuOLi. Moreover, with the increasing concentration of 3-MPOLi, the polymerization rate distinctly decreases, which can be seen from Fig. 1, Runs 1 and 3. At the same time, efficiency of the initiator seems to be lower than 1 as in our forthcoming studies and, moreover, dependent on the concentration of 3-MPOLi (see Table 1, Runs 1-3). All these features call for further studies, indeed.

To obtain poly(EtHA) with a moderately narrow MWD at -20 °C, the composition of initiating system has to be changed, because the system with a three-fold excess of the 3-MPOLi does not exhibit sufficient stabilizing efficiency at this temperature (see Run 4). When, however, the polymerization is initiated by the system $[\text{Li-}t\text{-BIB}]_0/[\text{3-MPOLi}]_0 = 1:6$ or 1:10 (see Runs 5 and 6), the monomer is converted virtually quantitatively to the product with a narrow MWD. The illustrative semilogarithmic curves in Fig. 1 indicate various extent of self-termination reaction in dependence on the reaction temperature and composition of the initiating system.

Recently, we have shown that, comparing to EtHA, BuA has the higher tendency to self-termination and, consequently, requires more efficient stabilization of active species to obtain the polymer with narrow MWD. This was achieved using *t*-BuOLi in the six- or tenfold excess at -60 °C. The results of polymerization of BuA initiated by the system Li-*t*-BIB/3-MPOLi of various compositions at temperatures -40 and -20 °C are given in Table 2.

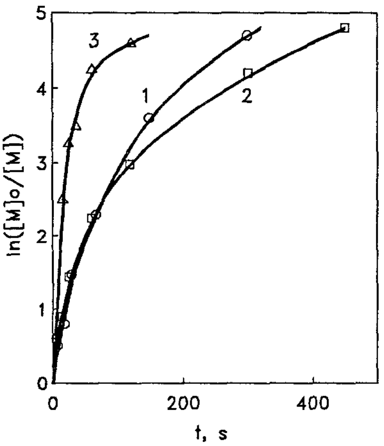
TABLE 2

Polymerization of Butyl Acrylate at Various Conditions.[a]

Run	$\frac{[\text{Li-}t\text{-BIB}]_0}{[\text{3-MPOLi}]_0}$	T, °C	Time, s	Conversion, %	M_n	M_w/M_n
1	1 / 10	-40	600	100	9600	1.19
2	1 / 3	-40	600	99.5	10600	1.28
3	1 / 10	-20	600	99.1	9000	1.32

[a] $[\text{BuA}]_0 = 0.3512$ mol/l, $[\text{Li-}t\text{-BIB}]_0 = 0.00702$ mol/l, solvent: toluene-THF 19/1 (v/v)

At both temperatures, poly(BuA) with rather narrow MWD can be prepared, but the initiating system $[\text{Li-}t\text{-BIB}]_0/[\text{3-MPOLi}]_0 = 1:10$ gives better results, i.e. the quantitative monomer conversion within 10 min and $M_w/M_n = 1.19$. As the polymerization rate of BuA is distinctly higher than that of EtHA, the polymerization of the former monomer remains fast enough even in the presence of 3-MPOLi.



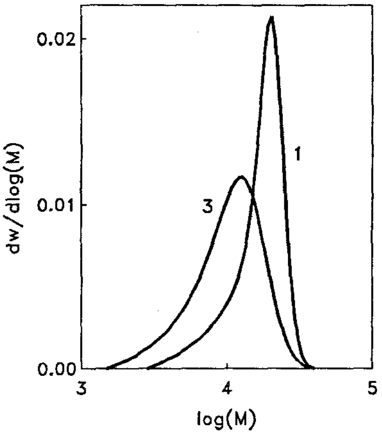


Figure 3. Semilogarithmic conversion plots for butyl acrylate polymerized at various temperatures. The numbers of curves correspond to the runs in Table 2.

Figure 4. MWD of poly(butyl acrylate) prepared at various temperatures. Numbers of the curves correspond to the runs in Table 2.

At -20 °C, the monomer conversion is over 99% within the same time interval and the formed polymer has negligibly broadened MWD. The relevant semilogarithmic curves and MWD of the resulting poly(BuA) are shown in Figs. 3 and 4, respectively.

Conclusion

It can be concluded on the basis of these preliminary results, that the stabilizing capacity of alkoxides is not yet exhausted. It can be justifiably assumed, that the alkoxides with more complicated or bulky alkyl group could be distinctly higher efficient in this sense. The system studied here gives promising results even at temperatures above -60 °C, which is important with respect to potential applications.

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