

## Anionic polymerization of acrylates

### 7. Polymerization of butyl acrylate initiated by the lithium ester enolate/lithium *tert*-butoxide complex

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#### Abstract

The anionic polymerization of butyl acrylate initiated by the complex initiator *tert*-butyl 2-lithioisobutyrate / lithium *tert*-butoxide (mole ratio 1:3 or 1:10) was studied in toluene, tetrahydrofuran and their mixtures (9:1 or 19:1 v/v) at -60°C. The extent of autotermination increases with increasing content of THF; in neat THF the limiting conversion is only ca 70%. In neat toluene, the prepared polymers have broad or even multimodal MWD; conversion curves indicate a slow initiation step.  $M_w/M_n$  ratio of the polymers prepared in THF and in the mixed solvents was 1.7 and 1.12 - 1.35, respectively. In the mixed solvents the molecular weight of the polymers rises virtually linearly with increasing conversion; semilogarithmic kinetic plots indicate that the polymerization proceeds in the manner not too far from a living process.

#### Introduction

Controlled polymerization of acrylic esters is still an open problem, which is very intensively studied. In contrast to methacrylates, the anionic polymerization of acrylates is complicated by a high extent of undesirable side reactions either in the initiation or in the propagation step. Relatively good results were achieved using combined (complex) initiators containing stabilizing additives based either on alkali metal halides or alkali metal *tert*-alkoxides. The former (FAYT et al. 1987) affect markedly aggregation processes of the initiator (KUNKEL and MÜLLER 1992) which results in products with narrow molecular weight distribution (MWD) (VARSHNEY et al. 1990, TEYSSIÉ et al. 1990). Polymerization of *tert*-butyl acrylate (*t*-BuA) and methyl methacrylate (MMA) proceeds in the presence of LiCl virtually as a living process. Nevertheless, the effect of halides on the extent of side reactions, in particular autotermination, is not very pronounced and their stabilization effect is not sufficient in the polymerization of acrylates with normal or  $\beta$ -branched alkyl. In this respect, *tert*-alkoxides are more efficient and restrict the extent of back-biting reaction in the polymerization of *t*-BuA and 2-ethylhexyl acrylate (EtHA) so that these monomers can be polymerized quantitatively (JANATA et al. 1992, VLČEK et al. 1992) and *t*-BuA even at room temperature. In comparison with the systems containing halide additives, the alkoxide systems afford products with slightly broader MWD as a consequence of a higher extent of association of the initiator components. Anyway, the

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initiating system composed of *tert*-butyl 2-lithioisobutyrate (Li-*t*BIB; initiator) and Li *tert*-butoxide (*t*-BuOLi; stabilizer) can be successfully used for the preparation of poly(EtHA) with narrow MWD ( $M_w/M_n = 1.05 - 1.15$ ) in the range of molecular weight ( $M_n$ )  $3 \times 10^3 - 5 \times 10^4$  (VLČEK et al. 1993). As an effect of the monomer structure (in particular branching of the alkyl group) on the extent of autotermination can be assumed, we have tested the possibility of polymerizing butyl acrylate (BuA) using the same initiating system and applying the findings obtained in previous studies. Here, the results of the experiments performed in various solvents and with various concentration of the alkoxide are presented.

## Experimental

**Materials:** Preparation of the initiator components (LOCHMANN et al. 1988) as well as purification of the solvents (VLČEK 1990) were described previously. BuA was washed with alkali and distilled water to neutral reaction, dried with  $MgSO_4$  and  $CaH_2$  and twice distilled from  $CaH_2$  at reduced pressure. All manipulations with reaction components were carried out in dry argon.

**Polymerization:** The polymerizations were performed in a stirred batch reactor (VLČEK and KRÍŽ 1992) at the temperature of  $-60^\circ C$ . In the samples of reaction mixture withdrawn during the experiments, the polymerization was terminated by HCl.

**Analysis:** Conversion curves were determined from the content of unreacted monomer in the reaction mixture (GC) and gravimetrically from the amount of the polymer precipitated from the reaction mixture in methanol/water 9/1 (v/v). Molecular weights of the polymers were measured by GPC of the reaction mixtures (calibration with PMMA standards, THF,  $25^\circ C$ ); the Mark-Houwink constants valid for poly(methyl methacrylate)/THF were used. Molecular weights determined in this way are used only for comparison purposes.

## Results and discussion

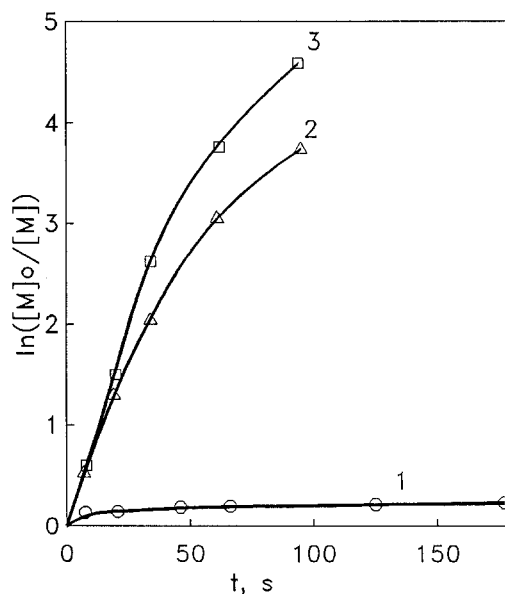
### Effect of alkoxide

The results of the polymerization experiments with various concentrations of *t*-BuOLi are shown in Table 1. The polymerization of BuA initiated with Li-*t*BIB alone converged to the conversion of ca. 23 % and the polymer had a very broad bimodal MWD. The low molecular weight of the resulting polymer can be explained by a high extent of autotermination even at the stage of formation of oligomers. Using the initiating system Li-*t*BIB/*t*-BuOLi 1/3 (mol/mol) the active centres were stabilized to such extent that the conversion exceeded 99 % after 150 s and the formed polymer had  $M_w/M_n = 1.31$ . An increase in the alkoxide concentration to the Li-*t*BIB/*t*-BuOLi ratio 1/10 gives a 99 % conversion even after 90 s and the product has a narrower MWD ( $M_w/M_n = 1.21$ ) which means further restriction of the autotermination. The first-order kinetic plot (Fig. 1) can be considered linear up to higher conversions than that for Li-*t*BIB/*t*-BuOLi 1/3.

TABLE 1  
Effect of *t*-BuOLi concentration on the polymerization of BuA in toluene/THF 9/1 (v/v)

Run	$[\text{Li-}t\text{BIB}]_0 / [\textit{t}\text{-BuOLi}]_0$	Time, s	Conversion, %	$M_n \cdot 10^{-3}$	$M_w/M_n$
1	1/0	8	12.7	2.9	7.84
		600	22.7	3.3	18.8
2	1/3	8	41.1	6.1	1.17
		600	99.6	14.0	1.31
3	1/10	8	45.1	5.8	1.15
		185	100	11.7	1.21

$[\text{BuA}]_0 = 0.351 \text{ mol/l}$ ,  $[\text{Li-}t\text{BIB}]_0 = 0.007 \text{ mol/l}$ ,  $M_{n,\text{theor}} = 6427$



**Figure 1**  
First-order conversion - time plot for polymerization with various composition of initiating system: Li-*t*BIB (1);  $[\text{Li-}t\text{BIB}]/[\textit{t}\text{-BuOLi}]$ : 1/3 (2), 1/10 (3)

### Effect of solvent polarity

It is commonly known that the nature of the solvent used in the anionic polymerization affects to a great extent the process. In the polymerization of EtHA initiated by lithium ester enolate/*tert*-alkoxide complex, the best results were obtained in a reaction medium of low solvation ability (toluene with a small amount of THF). Here, we followed the course of polymerization of BuA in a series of solvents with increasing polarity: toluene - toluene/THF 19/1 (v/v) - toluene/THF 9/1 (v/v) - THF. The results are collected in Table 2.

TABLE 2  
Effect of solvent on the polymerization of BuA initiated with ester enolate/*t*-BuOLi<sup>a</sup>

Run	Solvent	Time, s	Conversion, %	$M_n \cdot 10^{-3}$	$M_w/M_n$
1 <sup>b</sup>	toluene	21	10.5	3.3	3.34 <sup>d</sup>
		600	99.6	11.5	2.67 <sup>d</sup>
2	toluene/THF 19/1	7	51.6	6.5	1.11
		180	100	12.2	1.18
3	toluene/THF 9/1	8	45.1	5.8	1.15
		185	100	11.0	1.23
4	THF	19	24.7	4.3	1.18
		600	67.5	11.8	1.73
5 <sup>c</sup>	toluene/THF 19/1	7	53.9	3.0	1.11
		65	100	5.6	1.12

<sup>a</sup> Initial monomer concentration  $[BuA]_0 = 0.351$  mol/l;  $[BuA]_0/[Li-tBIB]_0/[t-BuOLi]_0 = 50/1/10$ .

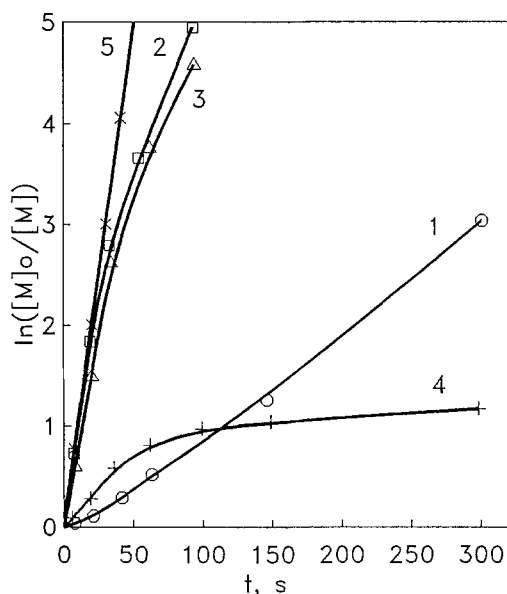
<sup>b</sup> Due to the insolubility of Li-*t*BIB ethyl 2-lithioisobutyrate was used for polymerization in toluene.

<sup>c</sup> Initial monomer concentration  $[BuA]_0 = 0.213$  mol/l;  $[BuA]_0/[Li-tBIB]_0/[t-BuOLi]_0 = 30/1/10$

<sup>d</sup> Polymodal MWD

The first-order kinetic curves are presented in Fig. 2. In neat toluene, a non-linear shape of the kinetic curve can be observed at low conversions of the monomer indicating a slow initiation reaction. The number of active species gradually increases even during the initial stage of the propagation step. Then, from ca. 25% conversion, this dependence is virtually linear up to the conversion higher than 99%, which indicates a low extent of the autotermination reaction. An addition of a small amount of THF to the reaction medium

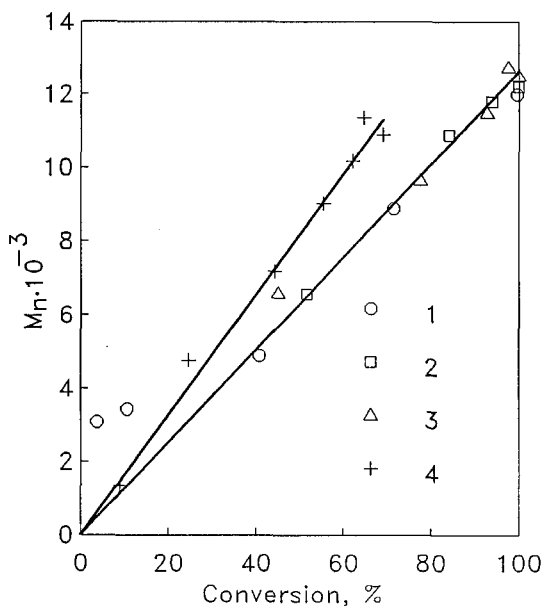
causes a rise in the reaction rate. Quantitative conversion was reached after 180 s (Table 2). However, the deviation of the first-order kinetic curve from linearity indicates that the termination begins to play some role in this system (Fig. 2, run 2). Further rise of solvent polarity (toluene/THF 9/1) slightly lowers the apparent rate constant of polymerization (initial slope of the kinetic curve) along with increasing role of autotermination. In neat THF, the autotermination is so effective, that the polymerization stops even before all the monomer is consumed (limiting conversion ca. 70 %). The dependence of number-average molecular weights on conversion is linear (Fig. 3) and hence any chain transfer reactions can be neglected. The only exception is the reaction in neat toluene where the changes in molecular weights at the beginning of polymerization support the concept of slow initiation step.



**Figure 2**

First-order conversion-time plot for polymerization performed in various solvents. The numbers correspond with the runs in Table 2.

From the kinetic point of view, the reaction medium of low polarity (toluene/THF 19/1) seems to be preferable. Kinetic curves give evidence of significant restriction of side reactions, in particular autotermination. The shape of kinetic curves is almost ideal even if some role of termination is evident not only from kinetic curves but also from GPC - MWD slightly broadens with increasing conversion. In THF, the  $M_w/M_n$  ratio of the polymer is about 1.7.



**Figure 3**

Dependence of number-average molecular weight vs. conversion for polymerizations performed in various solvents (see Table 2, runs 1-4)

If toluene is used, MWD of the polymer is very broad, even multimodal indicating the possible multiplicity of active centers. The polymerization carried out in toluene with a small amount of THF affords polymers with a narrow MWD (Table 2).

When the polymerization is carried out with a lower monomer concentration, the ratio monomer/initiator being lower, it is possible to suppress the role of autotermination virtually completely. In the mixture toluene/THF 19/1 the monomer conversion is 100% in a very short time and the formed poly(BuA) has a narrow MWD with  $M_w/M_n = 1.12$  (Table 2, run 5). During the polymerization, MWD almost does not change and the linear semilogarithmic plot indicates a living behavior of this polymerization system (Fig. 2, run 5). The preliminary results also show that it should be possible to control the molecular weight of poly(BuA) stoichiometrically at least to some extent (Table 2, runs 2,5).

Compared with EtHA, the polymerization of BuA proceeds distinctly faster and shows a higher extent of autotermination. Nevertheless, this undesirable step can be minimized by an excess of the alkoxide stabilizer in the initiating system and by using a reaction medium with rather low solvation ability. Under these conditions, the polymerization course is not too far from the living one producing the polymer with a narrow MWD.

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