Anionic Polymerization of Acrylates. 8. Kinetics of the Anionic Polymerization of Butyl Acrylate Initiated with the Complex Initiator Lithium Ester Enolate/Lithium *tert*-Butoxide

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ABSTRACT: The kinetics of the anionic polymerization of butyl acrylate initiated with the system *tert*-butyl 2-lithioisobutyrate (Li-*t*-BIB)/lithium *tert*-butoxide (*t*-BuOLi) in the mixed solvent toluene/tetrahydrofuran was studied at −70 to −40 °C. At −60 °C, the external reaction order is unity with respect to the concentrations of both the monomer and propagating species. Semilogarithmic conversion curves indicate a certain extent of self-temination at higher degrees of conversion. The termination reaction proceeds formally as a first-order reaction with respect to active centers. Kinetic calculations show that while the rate constant of propagation is concentration-independent, the rate constant of termination increases with the initial concentration of the monomer. The temperature dependence of the polymerization was studied for various solvent compositions and various $[\text{Li-}t\text{-BiB}]_0/[t\text{-BuOLi}]_0$ mole ratios. In toluene/THF = 9/1 (v/v), the rate constant of self-termination grows more steeply with increasing temperature than the rate constant of propagation so that at −40 °C the limiting monomer conversion is approximately 60%. In toluene/THF = 19/1 (v/v), the temperture dependence of the rate constant of self-termination is less distinct than in the former case and the conversion is 90% even at −20 °C. From the GPC measurement it is seen that the autotermination proceeds in all referred experiments and only the relation between concurrent propagation and termination reactions is responsible for the formation of the polymer with a narrow MWD under suitable conditions.

Introduction

The anionic polymerization of acrylates has been intensively studied in recent years. Nevertheless, many aspects of this complicated process are not clear. The course of the polymerization is unfavorably affected by concurrent reactions which restrict the monomer conversion and broaden the molecular weight distribution (MWD) of the polymer. One of the most important undesired reactions is the autotermination due to the intramolecular cyclization of the last three units of the growing chain. A relatively efficient suppression of the autotermination was achieved by stabilizing the active centers based on ester enolates through *tert*-alkoxides.[1-4] As yet, the controlled preparation of polyacrylates with predetermined molecular weights and narrow MWDs has been possible only for monomers with a branched alkyl ester group, namely *tert*-butyl acrylate (*t*-BuA) and 2-ethylhexyl acrylate (EtHA). Recent works in this field show that active centers formed from the monomer bearing a less branched alkyl ester group possess a greater tendency toward autotermination. Thus, *t*-BuA polymerizes[2] quantiatively to the product with a narrow MWD even at room temperature while EtHA requires[5] temperatures below −40 °C. Kinetic studies of the polymerization of *t*-BuA and EtHA indicate the quasi-living character of these reactions under appropriate conditions. It was previously shown that the reaction conditions for preparation of poly(butyl acrylate) (linear alkyl ester group) with a narrow MWD are even more limited; a high excess of alkoxide, low content of THF in mixed solvent, and low concentration of monomer in reaction mixture are required.[6] In this work, our interest turned to the kinetics of the anionic polymerization of butyl acrylate (BuA).

Experimental Part

Materials. Preparation of the initiator components[1] as well as purification of solvents[7] and monomer[6] were described previously. All manipulations with reaction components were carried out in dry argon.

Polymerization. Polymerizations were performed in a stirred batch reactor.[8] In the samples withdrawn from the reaction mixture, the polymerization was terminated by 1 equiv of aqueous HCl. The reaction conditions in detail are described below.

Analysis. Conversion curves were detd. from the content of unreacted monomer in the reaction mixture (GC) and gravimetrically from the amount of the polymer precipitated from the reaction mixture by methanol/water 9/1 (v/v). Molecular weights of polymers were measured by GPC of the reaction mixtures[4] (calibration with PMMA standards, THF, 25 °C); the Mark–Houwink constants valid for poly(methyl methacrylate)/THF were used, and thus the calculated M_n are PMMA equivalent.

Results and Discussion

External Reaction Order. External reaction orders with respect to the monomer and active centers were evaluated for the system *tert*-butyl 2-lithioisobutyrate/lithium *tert*-butoxide (mole ratio $[\text{Li-}t\text{-BiB}]_0/[t\text{-BuOLi}]_0 = 1/10$), toluene/THF = 19/1 (v/v) at the temperature −60 °C. The initial concentration of the monomer was varied in the range 0.098–0.729 mol/L; that of Li-*t*-BIB, in the range 0.0003–0.0117 mol/L. The initial concentration of active centers $[I^*]_0$ was calculated from the plot of the molecular weight of the polymer vs monomer conversion, in accordance with eq 1,

$$[I^*]_0 = \alpha[M]_0/DP_n \tag{1}$$

where $[M]_0$ is the initial concentration of the monomer, α is the conversion, and DP_n is the corresponding polymerization degree. The reaction orders were calculated from the rate equation assumed for the initial stage of polymerization (with instantaneous rate of initiation and negligible extent of termination):

$$v_0 = k_p[I^*]_0^{\,i}[M]_0^{\,m} \tag{2}$$

The initial rate of polymerization was calculated from the

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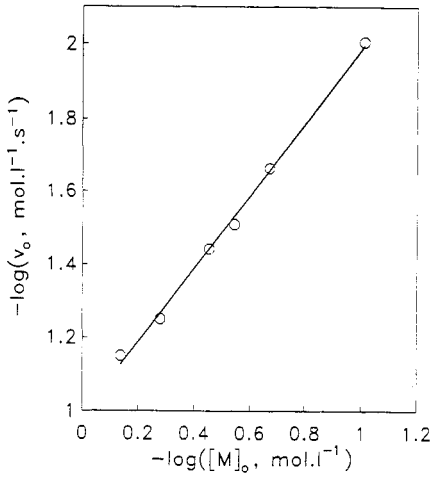

Figure 1. Logarithmic dependence of the initial rate of polymerization on the initial monomer concentration.

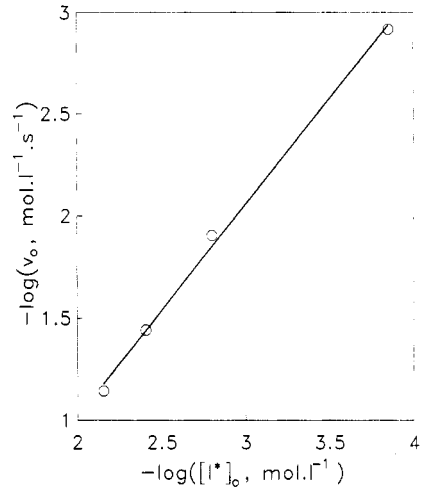

Figure 2. Logarithmic dependence of the initial rate of polymerization on the initial concentration of active centers.

conversion curve extrapolated to zero time. The logarithmic dependences of the initial rate of polymerization on the initial concentrations of monomer and active centers give slopes 0.99 ± 0.03 (Figure 1) and 1.04 ± 0.04 (Figure 2), respectively. The external reaction orders with respect to both the monomer and the active centers can thus be taken to be equal to unity.

Conversion Curves. On the basis of the evaluated reaction orders we can assume that the rate equation (3) is valid.

$$\ln([M]_0/[M]) = k_p[I^*]t \qquad (3)$$

As the semilogarithmic conversion plots are curved in almost all cases (Figure 3), it is clear that the number of active centers decreases during the polymerization, which is manifested by the decrease in the apparent rate constant of propagation. Several termination reactions are possible in the anionic polymerization of acrylates, the autotermination due to the intramolecular cyclization of growing centers being the most significant.[9] Termination, be it intramolecular cyclization of the growing center or another intra- or intermolecular reaction, has been shown to be effectively first-order with respect to active centers.[2,5] The overall equation for polymerization with autotermination is then

$$\ln([M]_0/[M]) = (k_p[I^*]_0/k_t)\{1 - \exp(-k_t t)\} \qquad (4)$$

assuming initiation to be much faster than propagation,

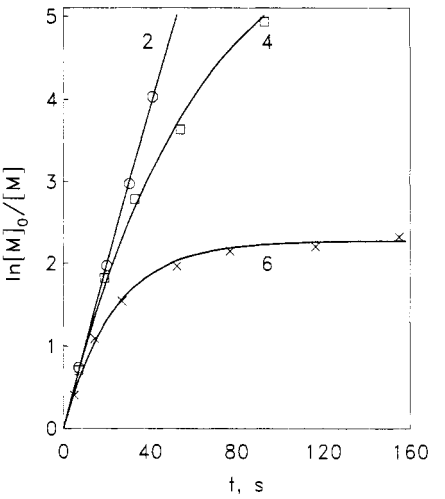

Figure 3. Semilogarithmic conversion plots of the polymerization of butyl acrylate for various initial monomer concentrations. Number of the curves correspond to the runs in Table 1.

which was shown to be the case in all media except neat toluene.[6] The successful fitting of eq 4 to experimental points is shown in Figure 3; the resulting values of the kinetic constants of propagation and termination are listed in Table 1.

Influence of Concentration of Monomer and Initiator. The results of polymerizations using various concentrations of the reaction components are summarized in Table 1. The rate constant of propagation virtually does not depend on the initial monomer concentration while that of autotermination increases with the increasing concentration of BuA by more than 1 order of magnitude (Table 1, runs 1–6). This behavior could be caused by a change in the polarity of the reaction medium due to the addition of a polar monomer or by the competitive termination reaction (1,2-addition to BuA). Both these alternatives were tested simultaneously in experiments where 1 equiv of saturated model compound, ethyl isobutyrate (EtIB), was added with monomer into the reaction mixture. Nevertheless, k_t was virtually not influenced by addition of EtIB so that possibilities mentioned above have not been verified. The dependence of k_t on the initial monomer concentration was observed also in the anionic polymerization of methyl methacrylate. The interpretation of this behavior—formation of deactivating species in the initiation step of polymerization[10]—was not fully supported by experiment. On the basis of the present information, this phenomenon can hardly be explained satisfactorily. At low monomer concentrations, the extent of self-termination is almost negligible (Figure 3, run 2) and, at the same time, the width of the MWD of the polymer virtually does not depend on the monomer conversion (Figure 4). Also, the M_n value of the formed polymer increases linearly with the increasing conversion of the monomer (Figure 5, runs 2 and 4). At higher initial concentrations of BuA (Table 1, runs 5 and 6), the limiting conversion decreases and the monomer is not consumed quantitatively within the reaction time. Plots of M_n vs monomer conversion exhibit some deviations in the range near the limiting conversion (M_n even slightly decreases; see Figure 5, run 6), and the MWD of this polymer becomes broader. From GPC eluograms it follows that, in this case, polymer chains grow not only in the high- but also in the low-molecular-weight region (see Figure 11). The probable reason seems to be generation and operation of a new type of active species being formed either by metal transfer from the growing chain to the unreacted monomer or by the additional polymerization of the residual acrylate by

Table 1. Influence of the Concentration of the Reactants on the Anionic Polymerization of Butyl Acrylate[a]

run	10^3[Li-*t*-BIB]$_0$ (mol·L^{-1})	[BuA]$_0$ (mol·L^{-1})	x_p (%)	$10^{-3}M_n$	M_w/M_n	k_p (L·mol^{-1}·s^{-1})	10^3k_t (s^{-1})	$10^{-3}k_p/k_t$ (L·mol^{-1})
1	7.02	0.0977	100	2.8	1.09	25.15		
2	7.02	0.2135	100	5.9	1.07	21.61	1.5	14.31
3	7.02	0.2855	100	8.1	1.08	24.16	10.0	2.42
4	7.02	0.3512	100	11.3	1.13	26.17	15.3	1.71
5	7.02	0.5268	99.5	13.3	1.64	26.59	19.7	1.35
6	7.02	0.7291	91.5	17.7	2.07	30.06	41.3	0.73
7	0.226	0.3512	12.2	55.6	1.53	24.49	26.2	0.94
8	3.51	0.3512	90	26.5	1.52	22.53	15.4	1.47
9	7.02	0.3512	100	11.3	1.13	26.17	15.3	1.71
10	11.70	0.3512	100	6.6	1.09	29.20	23.7	1.23

[a] [Li-*t*-BIB]$_0$/[*t*-BuOLI]$_0$ = 1/10 (mol/mol), toluene/THF = 19/1 (v/v), reaction temperature −60 °C, reaction time 300 s.

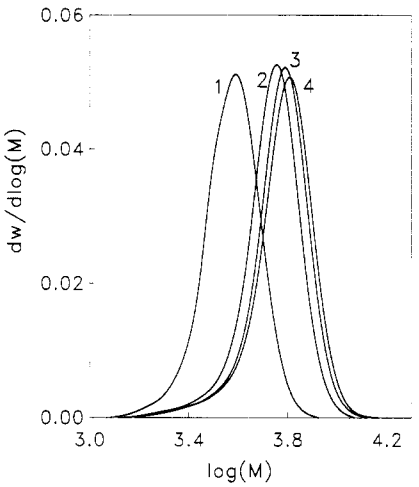

Figure 4. Changes in MWD during the polymerization of butyl acrylate (see Table 1, run 2). Monomer conversion (%)/ polymerization time (s): 1, 53/7; 2, 86/20; 3, 95/30; 4, 100/300.

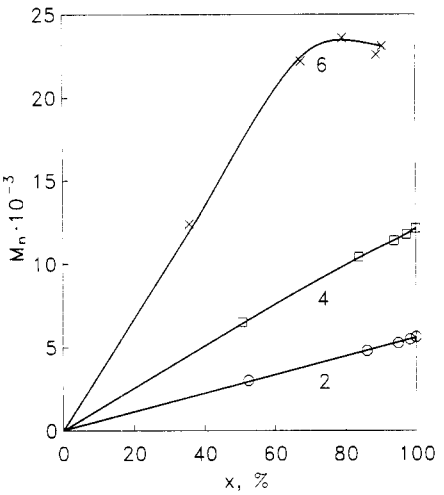

Figure 5. Dependence of the molecular weight of poly(butyl acrylate) on the monomer conversion. Numbers of the curves correspond to the runs in Table 1.

the alkoxide. In fact, both these reactions should affect the MWD of the polymer in similar ways. The problem will be studied later. The dependence of molecular weight on conversion roughly corresponds to theoretical calculations of the kinetics of anionic polymerization with both the spontaneous termination and chain transfer to monomer[11] assuming that the rate constant of transfer is comparable with the rate constant of autotermination.

The variation of the concentration of initiator did not influence significantly the values of the rate constants of propagation and termination (Table 1, runs 7–10). However, the limiting conversion increases and the MWD becomes narrower with the increasing initial concentration of initiator. The relevant semilogarithmic plots are shown

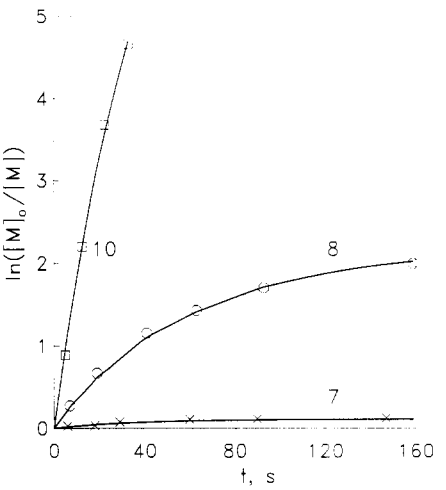

Figure 6. Semilogarithmic conversion plots of the polymerization of butyl acrylate for various initial concentrations of the initiating system. Numbers of the curves correspond to the runs in Table 1.

in Figure 6. On the basis of the semilogarithmic conversion curves it can be said that the kinetic equation (4) satisfactorily describes the polymerization course.

It follows from the data in Table 1 that the limiting monomer conversion and the polydispersity of the formed product depend on the starting composition of the reaction mixture. The best results were obtained in systems in which the ratio [M]$_0$/[I]$_0$ did not exceed 50.

Influence of Reaction Temperature. The temperature dependence of the anionic polymerization of BuA was followed in the range from −70 to −40 (or −20) °C. Similarly to EtHA polymerization,[5] the rate constant of termination is significatly more temperature-dependent than the rate constant of propagation (Table 2, runs 1–4). Thus, the relative extent of termination in comparison to the propagation increases rapidly with increasing temperature, which can be documented by the decrease in the ratio k_p/k_t with increasing temperature. At −40 °C, the monomer conversion is only 90% and the MWD broadens to the value of M_w/M_n = 1.38. Semilogarithmic conversion plots for experiments carried out at various temperatures are shown in Figure 7. At a higher content of polar THF in the reaction medium, the temperature dependence of k_t in comparison with that of k_p is even more distinct than in the system with a lower THF concentration (Table 2, runs 5–7, and Figures 8 and 9). The limiting conversion in this solvent is only 58% at −40 °C, and the M_w/M_n value increases to 1.71.

Variation of the ratio [Li-*t*-BiB]$_0$/[*t*-BuOLi]$_0$ in the initiation complex from 1/10 to 1/3 has no conspicuous effect on the course of the polymerization. The MWD's as well as conversions obtained from the systems with different ratios of the initial components at −40 °C do not

Table 2. Influence of the Reaction Temperature, Solvent, and Initiation System Composition on the Anionic Polymerization of Butyl Acrylate[a]

run	[*t*-BuOLi]$_0$/[Li-*t*-BIB]$_0$	toluene/THF	T (°C)	x_p (%)	$10^{-3} M_n$	M_w/M_n	k_p (L·mol^{-1}·s^{-1})	$10^3 k_t$ (s^{-1})	$10^{-3} k_p/k_t$ (L·mol^{-1})
1	10	19/1	−69.5	100	14.6	1.18	15.71	6.00	2.62
2	10	19/1	−58.8	100	11.3	1.13	26.17	15.3	1.74
3	10	19/1	−40.7	93.2	12.1	1.38	55.55	76.2	0.73
4	10	19/1	−21.8	90	10.0	1.55	52.36	95.6	0.55
5	10	9/1	−70.9	100	13.0	1.21	12.64	3.50	3.61
6	10	9/1	−61.7	100	10.8	1.14	24.84	15.8	1.71
7	10	9/1	−40.3	57.8	18.1	1.71	51.88	99.9	0.52
8	3	9/1	−69.2	100	13.6	1.27	17.40	5.80	3.00
9	3	9/1	−59.8	99.6	13.2	1.22	22.67	13.6	1.78
10	3	9/1	−41.0	70.1	12.8	1.79	41.84	108	0.39

[a] [Li-*t*-BIB]$_0$ = 0.00702 mol·L^{-1}, [BuA]$_0$ = 0.3512 mol·L^{-1}, reaction time 300 s.

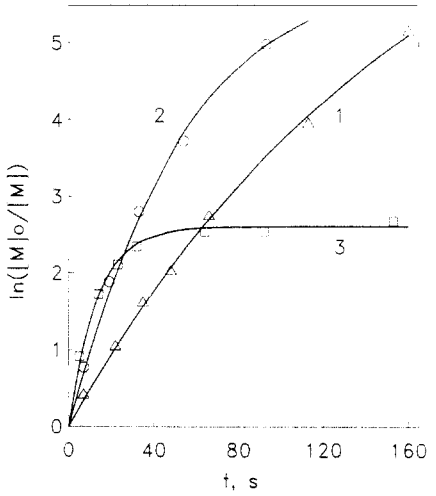

Figure 7. Semilogarithmic conversion plots of the polymerization of butyl acrylate at various temperatures. Numbers of the curves correspond to the runs in Table 2.

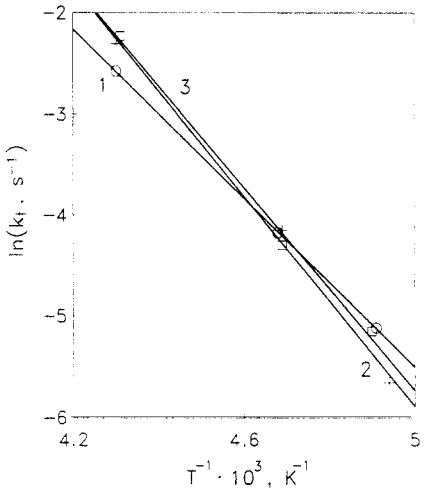

Figure 9. Arrhenius plots of k_t for various compositions of the initiating system and solvent: 1, runs 1–3; 2, runs 5–7; 3, runs 8–10. Reaction conditions are given in Table 2.

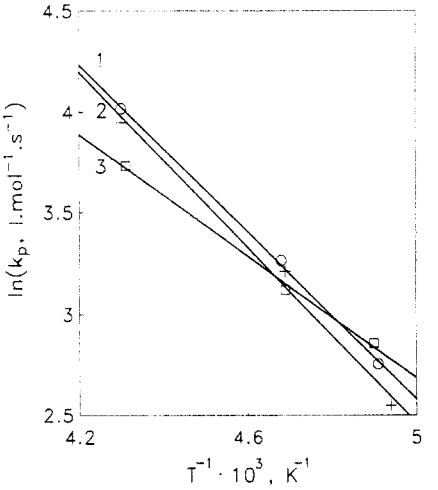

Figure 8. Arrhenius plots of k_p for various compositions of the initiating system and solvent: 1, runs 1–3; 2, runs 5–7; 3, runs 8–10. Reaction conditions are given in Table 2.

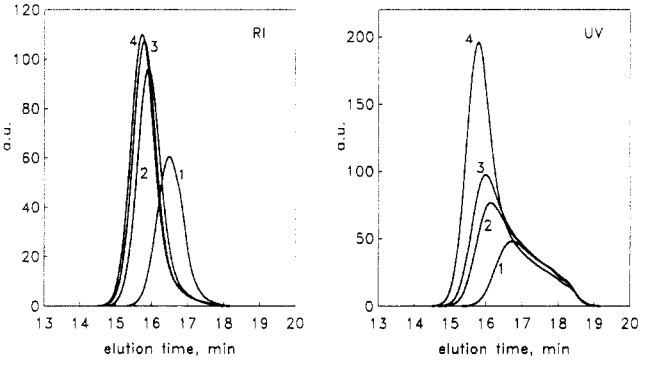

Figure 10. Changes in GPC eluograms (RI and UV detection) during the polymerization of butyl acrylate (see Table 1, run 2). Monomer conversion (%)/polymerization time (s): 1, 53/7; 2, 86/20; 3, 100/90; 4, 100/300.

differ markedly (cf. Table 2, runs 5–7 and 8–10). Figures 8 and 9 show the Arrhenius plots of the constants of propagation and self-termination.

GPC Measurement. In some cases, the anionic polymerization of BuA appears to be not far from the true living process, i.e. without autotermination (Table 1, runs 1 and 2; Figure 3, run 2; Figure 4). In GPC measurements, both the differential refractometer (RI) and UV detector were used. While the former measures the total concentration of polymer in a fraction, the latter detects autoterminated end groups due to the absorption at 256 nm of the enolized form of cyclic trimers of polyacrylates.[2] Thus, on the basis of GPC eluograms we can follow not only the MWD of the total polymer but also the MWD of the macromolecules terminated by the intramolecular cyclization. In order to be comparable with the RI measurement, the UV detector response was multiplied by the actual M_n at the given elution volume because, unlike RI, the UV detects only the end groups and their relative concentrations. Obviously, in reactions producing a polymer with a narrow MWD, the MWDs from the UV and RI detections differ at lower conversions and become similar with increasing reaction time. On the other hand, in reactions with a higher extent of termination, the MWD of the terminated polymer is similar to that of the total polymer even at early stages of polymerization (before the limiting conversion of the monomer is reached). GPC eluograms for polymerizations with a small and high extent of autotermination are shown in Figures 10 and 11, respectively. Theoretical MWD curves have recently been

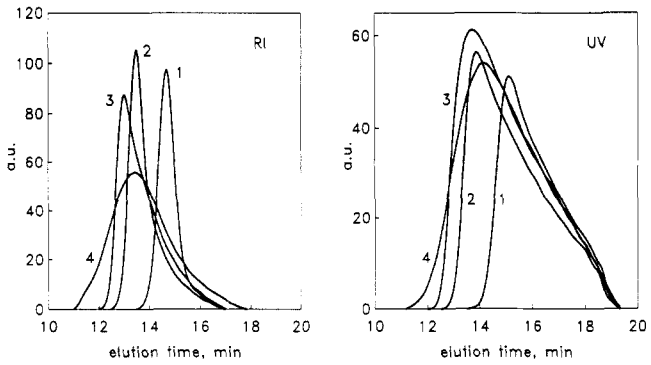

Figure 11. Changes in GPC eluograms (RI and UV detection) during the polymerization of butyl acrylate (see Table 1, run 6). Monomer conversion (%)/polymerization time (s): 1, 36/5; 2, 68/15; 3, 87/53; 4, 92/300.

calculated[12] for terminated and living fractions, and the obtained results are similar to the GPC traces in Figures 10 and 11. In Figure 10, one can see that unlike the response of the RI detector, that of the UV detector, indicating the autoterminated macromolecules, changes even after the quantitative conversion has been reached; i.e. the autotermination proceeds after all the monomer has been consumed, too. In the case of a nonquantitative conversion (Figure 11) the changes in molecular weight are detected by both the UV and RI detection. Thus, the termination reaction proceeds in all cases and it is only the ratio of the rate of propagation to that of termination which is responsible for an apparently living character of the polymerization under optimal conditions.

As we have already assumed in our previous works, anionic polymerization of BuA exhibits a markedly greater tendency toward autotermination by intramolecular cyclization than the polymerization of *t*-BuA and EtHA. Consequently, for instance, controlling the molecular weight of poly(BuA) will be more complicated than that of poly(EtHA). Nevertheless, by using the appropriate initiation system and by careful optimization of reaction conditions, BuA can also be polymerized in an almost living manner, forming tailored products at least to some extent. Obviously, there are many unsolved problems and questions in the controlled polymerization of acrylic monomers which call for further investigation.

References and Notes

(1) Lochmann, L.; Janata, M.; Machová, L.; Vlček, P.; Mitera, J.; Müller, A. H. E. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 29.
(2) Janata, M.; Lochmann, L.; Vlček, P.; Dybal, J.; Müller, A. H. E. *Makromol. Chem.* **1992**, *193*, 101.
(3) Vlček, P.; Lochmann, L.; Otoupalová, J. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 163.
(4) Vlček, P.; Otoupalová, J.; Kříž, J. *Makromol. Chem.* **1993**, *194*, 841.
(5) Vlček, P.; Jakeš, J.; Otoupalová, J. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2565.
(6) Dvořánek, L.; Vlček, P. *Polym. Bull.* **1993**, *31*, 393.
(7) Vlček, P. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2922.
(8) Vlček, P.; Kříž, J. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 1511.
(9) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1990**, *191*, 2253.
(10) Gerner, F. J.; Höcker, H.; Müller, A. H. E.; Schulz, G. V. *Eur. Polym. J.* **1984**, *20*, 349.
(11) Yuan, C.; Yan, D. *Makromol. Chem.* **1986**, *187*, 2641.
(12) Jakeš, J. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2349.