Anionic Polymerization of Acrylates. 10. Synthesis and Characterization of Block Copolymers with Acrylate Blocks

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ABSTRACT: Block copolymers poly(styrene)-*block*-poly(*tert*-butyl acrylate), poly(*tert*-butyl acrylate)-*block*-poly(2-ethylhexyl acrylate), and poly(*tert*-butyl acrylate)-*block*-poly(butyl acrylate) were prepared by a successive anionic polymerization at −60 °C. As initiators, butyllithium/lithium *tert*-butoxide 1:6 (mol/mol) and *tert*-butyl 2-lithioisobutyrate/lithium *tert*-butoxide 1:3 or 1:10 (mol/mol) complexes were used, in the mixed solvent toluene/THF 9:1 or 19:1 (v/v). Products were characterized by SEC, ^{13}C NMR, and DSC. The block character of poly(*tert*-butyl acrylate)-*block*-poly(2-ethylhexyl acrylate) was proved by the extraction test with hexane. Compared to corresponding homopolymers, all the block copolymers exhibit only a slightly broadened MWD, which documents the virtually negligible extent of self-termination under given experimental conditions.

Introduction

In recent years, the importance of block copolymers has markedly grown. These polymer specialties show interesting properties and can be used in a number of applications, such as compatibilization of multicomponent polymer systems,[1] or organized polymer structures in solution,[2] both of which are at present time intensively studied. Some of the block copolymers based on nonpolar vinyl monomers are also commercially available (e.g. Kraton types of Shell). However, there still exists a lack of data on both the preparation and properties of block copolymers of polar vinyl monomers, especially of acrylic and methacrylic esters. The reason can be seen in a rather complicated controlled polymerization of these monomers which is accompanied by a number of undesired side reactions in both initiating and propagating steps.[3] None of the novel polymerization techniques, GTP, metal-free polymerization,[4,5] etc., has solved this problem completely, so that only a few works have appeared, dealing with (meth)acrylate block copolymers.[6–10] In this field, complex initiating systems based on a stabilizing efficiency of ligands[7,11–13] surrounding a living chain end ("ligated polymerization") can be one of the utilizable tools. For instance, the systems containing alkali metal tertiary alkoxides have been applied to a controlled synthesis of some tailored acrylic polymers.[14–16] This method was used now for the preparation of AB type block copolymers composed of styrene and acrylate blocks, and of fully acrylic block copolymers. The last ones, in particular, are so far unmet polymer specialties.

Experimental Section

Preparation of the Copolymers. The copolymers were prepared at −60 °C in a glass batch reactor equipped with an external stirrer and with dosing cells which allow successive dosing of the monomers within a short time interval and at a chosen temperature. The method was described elsewhere.[17]

Poly(styrene)-*block*-poly(*tert*-butyl acrylate) [poly(St-*b*-*t*-BuA)]. Styrene anionic polymerization was initiated by butyllithium (BuLi) in a mixed solvent toluene/THF (9:1 v/v). From the solution of living poly(St) prepared in this way, a small aliquot of the polymer was withdrawn 30 min after starting the polymerization, isolated, and analyzed by SEC. Then, a heptane solution of lithium *tert*-butoxide (*t*-BuOLi) was added to the reaction mixture (the molar ratio $[t\text{-BuOLi}]_0$:$[\text{BuLi}]_0$ was 6:1). Afterward, the toluene solution of *t*-BuA was added and polymerized for 5 min. The reaction was stopped by HCl, and the block copolymer was isolated by precipitation into a methanol/water mixture (9:1 v/v).

Poly(*tert*-butyl acrylate)-*block*-poly(2-ethylhexyl acrylate) [poly(*t*-BuA-*b*-EtHA)] and Poly(*tert*-butyl acrylate)-*block*-poly(butyl acrylate) [poly(*t*-BuA-*b*-BuA)]. In the first step, living poly(*t*-BuA) was prepared in toluene/THF 9:1 or 19:1 (v/v) using the initiation with the *tert*-butyl 2-lithioisobutyrate (Li-tBIB)/*t*-BuOLi complex in the mole ratio 1:3 (*t*-BuA–EtHA copolymerization) or 1:6 or 1:10 (*t*-BuA–BuA copolymerization). The time interval Δt between additions of the first and second monomer was 7–30 min depending on the mole ratio $[t\text{-BuA}]_0$:$[\text{Li-tBIB}]_0$ in the first polymerization step. Immediately before the addition of the second monomer, a small sample of poly(*t*-BuA) was withdrawn and analyzed by SEC. Like poly(St-*b*-*t*-BuA), the copolymers were isolated by precipitation into a methanol/water mixture. Conversion of the monomers was determined by gas chromatography of the reaction mixtures before precipitation or by gravimetry. In all experiments, the monomer conversion was found to be 95–100%.

Characterization. Molar Masses. Molar masses of the polymers and copolymers were determined by the SEC method described earlier[14] with toluene as an internal standard. For data treatment, the Mark–Houwink–Sakurada equation was used with constants valid either for poly(St)/THF, poly(*t*-BuA)/THF,[18] or poly(EtHA)/THF[19] systems. In all cases, reaction mixtures were measured before the precipitation of a polymer.

Extraction Test. The copolymer poly(*t*-BuA-*b*-EtHA) with a higher molar mass (run 3, Table 1) was extracted by hexane, which is a good solvent for poly(EtHA). A 160 mg quantity of the copolymer was dissolved overnight in hexane at room temperature. After sedimentation of the insoluble fraction, the clear solution was carefully separated. Then, both the soluble and insoluble fractions were evaporated to dryness and dried in a vacuum oven. The chemical composition of the crude copolymer and of both fractions was investigated by ^{13}C NMR spectroscopy.

NMR Spectra. ^{13}C NMR spectra (75.5 MHz) of 20% w/w solutions of the copolymers in $CDCl_3$ with hexamethyldisiloxane (HMDS) internal standard were measured on a Bruker ACF 300 spectrometer at 333 K. Continuous WALTZ decoupling was used in order to enhance the sensitivity. At least 10 000 scans with a $\pi/6$ reading pulse and 6 s repetition time were accumulated for each sample.

DSC Measurement. Glass transition temperatures, T_g, were evaluated from the temperature dependences of heat capacities, c_p, measured with a DSC-2 Perkin-Elmer calorim-

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Table 1. Preparation and Characteristics of Acrylate Block Copolymers

					homopolymer			copolymer	
run	monomer; amt, mmol		initiator; amt, mmol	Δt, min	M_n(calc) g/mol	M_n (SEC), g/mol	M_w/M_n	M_n(SEC), g/mol	M_w/M_n
1	St; 39	*t*-BuA; 41	BuLi; 0.78[a]	30	5250	4300	1.23	10 510	1.27
2	*t*-BuA; 39	EtHA; 38	Li-tBIB; 0.78[b]	8	6540	13 620	1.06	30 230	1.08
3	*t*-BuA; 31	EtHA; 38	Li-tBIB; 0.31[b]	30	12 940	26 170	1.06	63 000[d]	1.17
4	*t*-BuA; 40	BuA; 35	Li-tBIB; 1.21[a]	7	4250	8560	1.09	13 850[e]	1.25
5	*t*-BuA; 40	BuA; 41	Li-tBIB; 0.81[c]	20	6540	14 780	1.05	20 300	1.37

[a] Mole ratio $[\text{initiator}]_o$:$[t\text{-BuOLi}]_o$ = 1:6. [b] $[\text{Initiator}]_o$:$[t\text{-BuOLi}]_o$ = 1:3 [c] $[\text{Initiator}]_o$:$[t\text{-BuOLi}]_o$ = 1:10. [d] M_n = 75 600; mole ratio *t*-BuA:EtHA in the copolymer = 0.76:1 (NMR). [e] M_n = 16 300; mole ratio *t*-BuA:BuA in the copolymer = 1.1:1 (NMR).

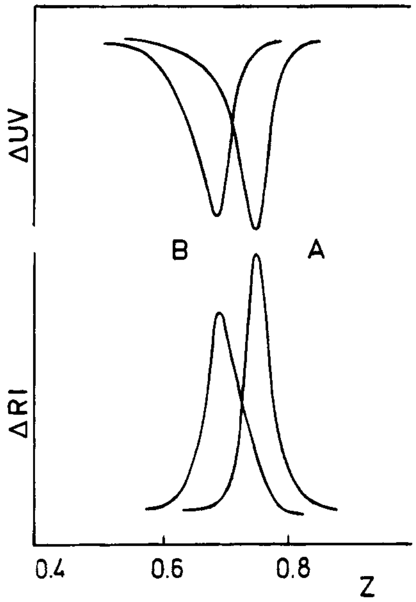


Figure 1. SEC curves of the poly(St) precursor (A) and poly(St-*b*-*t*-BuA) copolymer (B) (Table 1, run 1), RI and UV detection. Z = ratio of the elution times of the polymer and toluene as an internal standard.

eter calibrated by cyclohexane, *n*-decane, *n*-dodecane, hexatriacontane, water, and indium; the Al_2O_3 monocrystal was used as a heat capacity standard. The temperature dependence of c_p was measured in two temperature intervals using a heating rate of 10 K/min. The measurements in the intervals 230–400 and 100–400 K were performed using an ethanol–dry ice bath under a nitrogen gas atmosphere and liquid nitrogen in a helium atmosphere, respectively. For comparison, T_g's of the poly(EtHA)/poly(*t*-BuA) blend (0.572/0.428 w/w) were measured.

Hydrolysis of Copolymers. Poly(St)-*block*-poly(acrylic acid) and poly(acrylic acid)-*block*-poly(EtHA) were prepared by selective hydrolyzis of poly(St-*b*-*t*-BuA) and poly(*t*-BuA-*b*-EtHA), respectively, with aqueous HCl in 1,4-dioxane[20] and isolated by precipitation in hexane or, after neutralization of the acid block, in methanol.

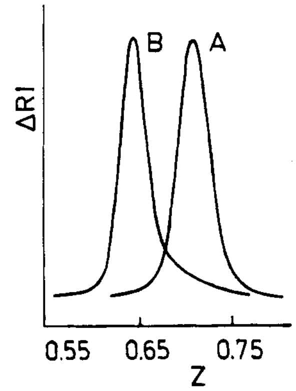


Figure 2. SEC curves of the poly(*t*-BuA) precursor (A) and poly(*t*-BuA-*b*-EtHA) copolymer (B) (Table 1, run 2), RI detection.

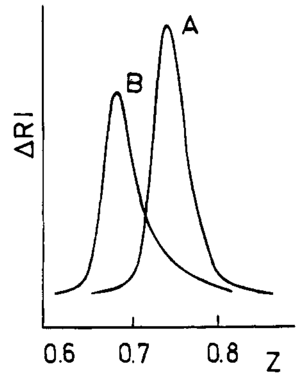


Figure 3. SEC curves of the poly(*t*-BuA) precursor (A) and poly(*t*-BuA-*b*-BuA) copolymer (B) (Table 1, run 4), RI detection.

Table 2. Extraction of poly(*t*-BuA-*b*-EtHA)[a] with Hexane

fraction	amt, % w/w	*t*-BuA units, % mol	EtHA units, % mol
hexane-soluble	95	40.5	59.5
hexane-insoluble	5	82.1	17.9
crude copolymer	100	43.2	56.8

[a] Run 3 in Table 1.

Results and Discussion

The results of the copolymer synthesis and molecular parameters of the copolymers are summarized in Table 1. In all cases, the mole ratio of the monomers in copolymerizations was kept equal to approximately 1. As shown in Table 1, the molar masses of the copolymers are proportionally higher than those of the homopolymer precursors and, at the same time, the molar mass distributions (MWD) of the homopolymers and copolymers do not change distinctly. Figures 1–3 show the SEC traces of the copolymers and the corresponding homopolymer precursors. This means that the extent of self-termination of the living precursors is almost negligible even in the case of poly(*t*-BuA) after an extended time period (runs 3 and 5). At the same time, it can be reasonably assumed that virtually no chain transfer proceeds between the living precursor and second monomer and, also, that the extent of self-termination during the second step is very low. However, as homopolymerization of EtHA and BuA does not proceed under comparable conditions entirely without a back-biting reaction, this process can be assumed to take place also in block copolymerization. This is indicated by "tailing" of MWD's of the poly(*t*-BuA-*b*-EtHA) and poly(*t*-BuA-*b*-BuA) block copolymers toward the lower molar mass region (Figures 2 and 3). This conclusion is corroborated by the results of extraction of poly(*t*-BuA-*b*-EtHA) with hexane, which are shown in Table 2. It is seen that the hexane-insoluble fraction represents an almost negligible part of the crude copolymer (approximately 5%) and, moreover, the fraction contains almost 20% (mol/mol) of poly(EtHA) units.

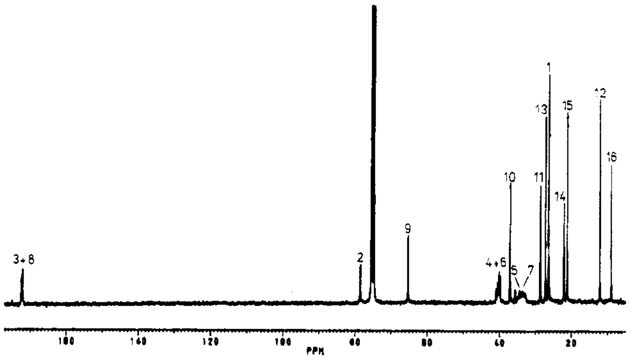
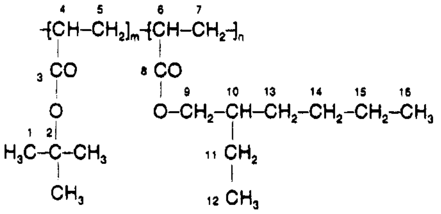


Figure 4. ^{13}C NMR spectrum of the poly(*t*-BuA-*b*-EtHA) copolymer (Table 1, run 3).

Chart 1



It should be mentioned that, owing to its M_w/M_n ratio higher than unity, the copolymer also contains macromolecules, which are composed of long poly(*t*-BuA) blocks and short poly(EtHA) ones and vice versa. These structural inhomogeneities can be, among others, a reason for the insolubility of a minor part of the copolymer in hexane and of the found difference in chemical composition of the crude copolymer and its hexane-soluble, and hexane-insoluble parts. It should be noted here that, to guarantee the "living" character of the second step of copolymerization, the reaction conditions of the precursor preparation have to be chosen with respect to the second monomer (see Table 1). As follows from the previous results, controlled polymerization of BuA[15] requires a reaction medium with a lower polarity and a higher content of the alkoxide in the initiating system than for the polymerization of EtHA.[12]

Figure 4 shows the 75.5 MHz ^{13}C NMR spectrum of a 20% (w/w) poly(*t*-BuA-*b*-EtHA) copolymer solution in $CDCl_3$ measured at 333 K. The signal assignment was done by combination of APT, COSY, and HETCOR NMR spectra and corresponds to Chart 1. Chemical shifts are related to the HMDS internal standard, i.e. 2 ppm shifted with respect to TMS. The spectrum is a superposition of poly(*t*-BuA) and poly(EtHA) spectra, which itself indicates the block structure of the copolymer. Direct NMR proof of the block copolymer structure is possible[21] but needs a copolymer with a lower molar mass. The relative content of *t*-BuA units in the copolymer can easily be determined by comparing the signal intensity of the *t*-Bu methyl carbons at 26.3 ppm with the average intensity of the signals of CH_2 and CH_3 carbons of the 2-ethylhexyl group at 28.6, 27.2, 22.0, 21.1, and 7.0 ppm. Owing to the fact that the nuclear Overhauser enhancement is nearly equal for the compared quantities, such a comparison was also possible under our experimental conditions. Similarly, the chemical composition of poly(*t*-BuA-*b*-BuA) (Table 1, run 4) was determined by NMR spectroscopy. In this connection it should be noted that the M_n values of the copolymers were calculated from SEC eluograms using the constants of the Mark–Houwink–Sakurada equation which are valid for the respective homopolymer from the first step of synthesis, so they do not represent exact values of the number-average molar masses and can be used for comparison only. Nevertheless, they are in good agreement with M_n's calculated from the results of spectroscopic analyses (see Table 1, runs 3 and 4).

Table 3. Glass Transition Temperatures of Poly(EtHA), Poly(*t*-BuA), Their Blend, and Their Block Copolymers

polymer	$10^{-3}M_n$ (SEC), g/mol	M_w/M_n	T_g1, K	T_g2, K	note
poly(*t*-BuA)	19.6	1.06		313.4	
poly(EtHA)	20.6	1.08	200.3		
poly(*t*-BuA)–	19.6	1.06	202.3	304.0	*b*
poly(EtHA) blend	20.6	1.08	195.8	282.7	*c*
copolymer run 2[a]	30.2	1.08	214.1		*c*
			222.4		*d*
			229.4	315.8	*e*
			227.1	323.7	*f*
copolymer run 3[a]	63.0	1.17	207.8		*c*
			201.5	311.8	*d*
			207.8	297.1	*g*

[a] See Table 1. [b] Annealed at room temperature, weight fraction of poly(*t*-BuA) in the blend = 0.428. [c] 400 K, immediately measured from 150 K. [d] 400 K, 3 weeks at room temperature, measured from 150 K. [e] 400 K, 1 h at 260 K, measured from 150 K. [f] 400 K, 1 h at 150 K, measured from 150 K. [g] 400 K, 3 h at 290 K, measured from 150 K.

M_n's of the acrylate polymers, determined by both methods, are approximately two times higher than the theoretical values, calculated from the ratio [monomer]$_0$:[Li-tBIB]$_0$, so that the estimated efficiency of the initiator is about 50%. This fact was already observed in recent studies.[14,15] Our results indicate that the unreacted Li-tBIB is also inactive in the second step of block copolymerization. The reason for this phenomenon is not yet fully clear; it seems to be associated with the aggregation of the initiating complex. The problem is now studied by theoretical means and by NMR.[22–25]

In Table 3, the values of glass transition temperatures of homopolymers poly(*t*-BuA) and poly(EtHA), their blend, and corresponding block copolymers are summarized. The T_g of poly(*t*-BuA) is in very good agreement with the value 313 K, given by van Krevelen.[26]

The blend of poly(*t*-BuA) and poly(EtHA), prepared by solvent evaporation from the solution of both homopolymers in $CHCl_3$, exhibits two glass transition temperatures near the T_g's of the homopolymers. With the blend, two T_g values were observed even after heating to 400 K, cooling to the starting temperature (100 K) at 10 K/min, and immediate repeating of the measurement. The existence of two T_g's is a clear indication of a phase separation of the blend. A higher extent of phase separation into components is observed in a well-relaxed mixture (regime a, Table 3) rather than in the sample treated under regime b (Table 3). This shows a narrowing of the immiscibility region with increasing temperature and slow rate of phase separation.

For block copolymers annealed at room temperature a different behavior was found. The copolymer with the higher molar mass (run 3, Table 1) has two T_g's, while the copolymer with the lower molar mass (run 2) has only one T_g in the same conditions (regime c, Table 3). This means that in the copolymer with the higher molar mass microphase separation of blocks takes place at room temperature. The blocks of the other copolymer (run 2) are not separated, due to their short lengths. Therefore, only one T_g is found. These results are in agreement with Leibler's theoretical results[27] concerning the molar mass effect on microphase separation.

Annealing both the copolymers at subzero temperatures leads in both cases to microphase separation of blocks (regimes d, e, Table 3). The slow evolution of the glass transition region in poly(*t*-BuA) is caused by long relaxation times of this polymer below its T_g. Properties of poly(*t*-BuA-*b*-BuA) copolymers and of copolymers containing poly(acrylic acid) blocks will be studied separately.

Conclusions

It is clearly seen from the data given above, that anionic polymerization initiated by complex ("ligated") systems with a well-chosen stabilizing additive is a very useful tool for the synthesis of block copolymers. In dependence on the initiator type, organometallics or ester enolate, copolymers can be prepared either with nonpolar (nonacrylic)/polar (acrylic) blocks or with two different acrylic blocks.

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