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Anionic Polymerization of Acrylic Monomers. 15. Living Anionic Copolymerization of Mixtures of Methyl Methacrylate and *tert*-Butyl Acrylate As Promoted by Dibenzo-18-Crown-6

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ABSTRACT: Although μ-coordinating ligands such as LiCl are effective in promoting the well-controlled living anionic block copolymerization of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBuA), whichever monomer is first polymerized, it has been previously shown that a copolymerization of mixtures of these two monomers does not proceed as expected, giving poor results in terms of both conversion and molecular weight distribution: that was accounted for by the easy back-biting nucleophilic attack of a highly sensitive methyl ester group by a moderately hindered PtBuA anion. It is now reported that such a situation can be completely modified, when a cation-binding σ-ligand, i.e., dibenzo-18-CE-6, is used in chelating a sodium counterion and surrounding it with a steric barrier, blocking a large enough space area around the ion pair. In fact, a living copolymerization process of mixtures of MMA and tBuA prevails in THF at −78 °C, in the presence of that Na^+/DB-18-CE-6 system. The living copolymer is found, although in a relatively small extent, to be of a statistical type rather than a blocky one or a mixture of two corresponding homopolymers. Furthermore, using the extended Kelen–Tüdös method, the monomer reactivity ratios are determined to be $r_{MMA} = 0.02$ and $r_{tBuA} = 8.81$.

Introduction

Devising a perfectly living system for the (co)polymerization of (meth)acrylic esters has been a long-standing problem in polymer synthesis. Partial answers came from the discoveries of group-transfer polymerization by a DuPont research team,[1] metal-"free" anionic polymerization by Reetz's group,[2] and ligated (ligand-modified) classical carbanion initiators by us[3] and others.[4,5] Only the latter approach, if successful, would provide a general tool allowing us to combine easily other monomers, such as vinylics or cyclic ethers with the (meth)acrylic ones.

Although close-to-perfect living homopolymerization and block copolymerization of methacrylates and acrylates have recently been achieved, living anionic copolymerization of mixtures of these monomers is still a very difficult challenge. For instance, because of a too large difference in the reactivity of the monomers, the group-transfer polymerization (GTP) technique does not allow the random copolymerization of mixtures of acrylates and methacrylates;[5] the same limitation is also met in metal-"free" anionic polymerization.[2]

It has been shown that the use of μ-ligands, such as LiCl, was an efficient pathway to prevent the course of anionic polymerizations to be disturbed by secondary transfer and termination reactions[3] and to displace a slow equilibrium between different propagating species.[6] Using that technique, block copolymers of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBuA) have been synthesized with a predictable molecular weight and a narrow dispersity, whichever monomer is first polymerized.[7] In sharp contrast, however, hopefully copolymerization of these two monomers (statistical or tapered) does not proceed as expected and gives very poor results in terms of conversion, degree of polymerization (DP), and molecular weight distribution (MWD), due to the presence of a selective nucleophilic attack of a highly sensitive methyl ester group by a rather moderately hindered PtBuA anion (i.e., a back-biting termination reaction).[8]

Conversely, the use of some cation-binding σ-ligands, i.e., hindered crown ethers, has brought interesting improvements in living anionic polymerization of (meth)acrylates,[3c] such as some control of the microstructure (e.g., ca. 50–60% syndio-PMMA, whatever the solvent), and possible use of temperatures up to 5 °C. It thus seemed of great interest to further test whether crown ethers were also able to suppress the termination in the course of anionic copolymerization of mixtures of methacrylates (e.g., MMA) and acrylates (e.g., tBuA) and lead to living statistical copolymers. This paper provides a first answer to that challenge, using the Ph_2CHNa/DB-18-CE-6 as a ligated initiator and MMA/tBuA as a representative comonomer pair, since Ph_2CHNa/DB-18-CE-6 was shown to promote living character in anionic homopolymerization of either MMA or tBuA in THF.[3c,9]

Experimental Section

Materials. MMA and tBA obtained from Norsolor (France) were first vacuum distilled from CaH_2 after reflux and stored under a nitrogen atmosphere at −20 °C. Before polymerization, they were added with a 10 wt % $AlEt_3$ solution in hexane until a persistent yellowish green color was observed. They were then redistilled under reduced pressure just prior to use. 2,3,11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (DB-18-CE-6) from Aldrich was recrystallized from petroleum ether. THF was purified by refluxing over a fresh sodium benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). (Diphenylmethyl)sodium (Ph_2CHNa) was prepared at room temperature by reacting diphenylmethane with sodium naphthalenide in THF for 24 h, with a sodium naphthalenide solution resulting from addition of sodium metal to naphthalene in THF at room temperature.

Copolymerization. Anionic copolymerization of mixtures of MMA and tBuA was carried out in a flamed glass reactor under a nitrogen atmosphere. DB-18-CE-6 was first introduced and dried as previously described.[3c] THF and initiator were transferred into the glass reactor by using a rubber septum and a stainless steel capillary or a syringe. The initiator solution was added dropwise to THF containing DB-18-CE-6 ligand until the

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Table 1. Characterization Data for PMMA-*b*-PtBuA Diblock Copolymers Anionically Synthesized in THF at −78 °C Using Ph_2CHNa as an Initiator in the Presence of 2 mol equiv of DB-18-CE-6

no.	initiator ($\times 10^3$ mol)	monomer (mol)		% total conv	for PMMA				for diblock			
		MMA	tBuA		$10^{-3}M_{n,calc}$[a]	$10^{-3}M_{n,SEC}$	M_w/M_n	f[b]	$10^{-3}M_{calc}$[c]	$10^{-3}M_{SEC}$	M_w/M_n	f[b]
1	0.60	0.047	0.034	100	7.8	8.2	1.05	0.96	15.8	16.1	1.10	0.98
2	0.80	0.100	0.040	100	12.5	13.8	1.05	0.91	20.9	21.1	1.05	0.99
3	0.80	0.100	0.083	100	12.5	13.6	1.05	0.92	28.0	28.4	1.10	0.99

[a] $M_{n,calc,PMMA} = W_{MMA}$ (g)/$C_{initiator}$ (mol). [b] Initiator efficiency = $M_{n,calc}/M_{n,SEC}$. [c] $M_{n,calc,block\ copolymer} = M_{n,SEC,PMMA} + W_{tBuA}$ (g)/C_{PMMA} (mol) $= M_{n,SEC,PMMA} + W_{tBuA}$ (g) ($M_{n,SEC,PMMA}/W_{MMA}$ (g)).

Table 2. Characterization Data for PtBuA-*b*-PMMA Diblock Copolymers Anionically Synthesized in THF at −78 °C Using Ph_2CHNa as an Initiator in the Presence of 2 mol equiv of DB-18-CE-6

no.	initiator ($\times 10^3$ mol)	monomers (mol)		% total conv	for PtBuA				for diblock			
		tBuA	MMA		$10^{-3}M_{n,calc}$[a]	$10^{-3}M_{n,SEC}$	M_w/M_n	f[b]	$10^{-3}M_{calc}$[c]	$10^{-3}M_{SEC}$	M_w/M_n	f[b]
1	0.60	0.039	0.038	100	8.3	9.0	1.05	0.92	15.8	15.9	1.10	0.99
2	0.60	0.078	0.038	99.5	16.6	13.8	1.10	0.97	23.6	24.0	1.10	0.98
3	0.15	0.039	0.035	100	33.2	33.9	1.15	0.98	57.6	55.4	1.15	1.04

[a] $M_{n,calc,PtBuA} = W_{tBuA}$ (g)/$C_{initiator}$ (mol). [b] Initiator efficiency = $M_{n,calc}/M_{n,SEC}$. [c] $M_{n,calc,block\ copolymer} = M_{n,SEC,PtBuA} + W_{MMA}$ (g)/C_{PtBuA} (mol) $= M_{n,SEC,PtBuA} + W_{MMA}$ (g) ($M_{n,SEC,PtBuA}/W_{tBuA}$ (g)).

initiator color persisted; ca. 5 drops of a 0.2 M initiator solution to 100 mL of a THF/DB-18-CE-6 solution was generally required to get a persistent color, i.e., a highly pure ligand solution. After adding the desired amount of initiator, the solution was cooled to −78 °C, the required amount of MMA and tBuA introduced as a mixture, and the copolymerization performed from a few seconds to 1 h depending on the desired monomer conversion. It was then stopped by adding acidic methanol, and the copolymer was recovered by precipitation into methanol or into a methanol/water (50/50) mixture. The crude polymer was dried under vacuum at 80 °C for 48 h.

Characterization. SEC was carried out by using a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (10^5, 10^3, 500, and 100 Å) and a Hewlett-Packard 1037A refractive index detector. Polystyrene standards were used for calibration and the number- (M_n) and weight-average (M_w) molecular weights as well as polydispersity of the polymer accordingly calculated. The glass transition temperature was measured by differential scanning calorimetry (DSC) using a DuPont 9000 apparatus, calibrated with indium and mercury. Samples were first heated up to 150 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C min^{-1}. Compositional and structural analyses of the copolymers were performed by means of ^1H and inverse-gated proton-decoupling ^{13}C NMR using a Bruker AM 400 spectrometer.

Determination of monomer reactivity ratios was carried out by using the extended Kelen–Tüdős method.[10]

Results and Discussion

Controlled Block Copolymerization of Methyl Methacrylate (MMA) and *tert*-Butyl Acrylate (tBuA), Using a Ph_2CHNa/DB-18-CE-6 Initiator System in THF at −78 °C. As reminded in the Introduction, the addition of crown ethers, e.g., DB-18-CE-6, is an interesting strategy for a well-controlled homopolymerization of MMA and tBuA in THF at −78 °C. Before facing the challenge of their living statistical copolymerization, it was, however, important to first demonstrate the efficient initiation of tBuA by living MMA anions and vice versa.

Living PMMA or PtBuA anions, prepared as described in the Experimental Section, were accordingly used to initiate tBuA or MMA anionic block polymerizations, respectively. The experimental data summarized in Tables 1 and 2 clearly indicate a well-controlled copolymerization process either from PMMA$^-$Na$^+$/DB-18-CE-6 to PMMA-*b*-PtBuA or from PtBuA$^-$Na$^+$/DB-18-CE-6 to PtBuA-*b*-PMMA: very narrow molecular distribution (1.05–1.15), high initiator efficiency for both the first and second block (>90%), and above all absence of any homo-PtBuA or homo-PMMA in the raw final products (see SEC trace in Figures 1 and 2). These results give a clear indication that there is no problem due to cross-reactivity when the sequential anionic copolymerization of MMA and tBuA is considered.

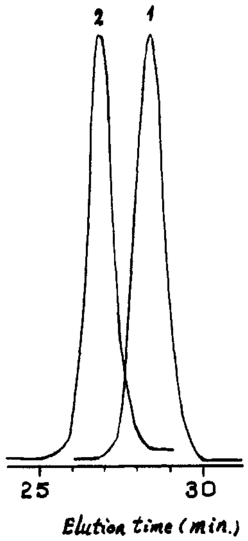

Figure 1. SEC of sample 3 (Table 1). (1) PMMA block: M_n = 13 600, M_w/M_n = 1.05. (2) PMMA-*b*-PtBuA block copolymer: M_n = 28 400, M_w/M_n = 1.10. Prepared in THF at −78 °C using Ph_2CHNa as an initiator in the presence of 2 mol equiv of DB-18-CE-6.

At this point, it is worth mentioning that, in striking contrast to the above-described results, a small amount of homo-PMMA (ca. 5%) always contaminates the PMMA-*b*-PtBuA diblock copolymer when the block copolymerization of tBuA is initiated by living PMMA anions in the presence of a lithium counterion and a μ-type ligand, i.e., LiCl, in THF at −78 °C.[7] It has been accounted for by a partial deactivation of the living macroinitiator upon addition of tBuA monomer, resulting from a back-biting termination reaction between a MMA unit in the antepenultimate position and the PtBuA anion.[8] The present results thus indicate that a DB-18-CE-6 added sodium-containing PtBA anion is able to suppress such a termination reaction.

Living anionic copolymerization of mixtures of MMA and tBuA should expectedly represent a straightforward and valuable extension of the results described in the foregoing section. In that prospect, copolymerization

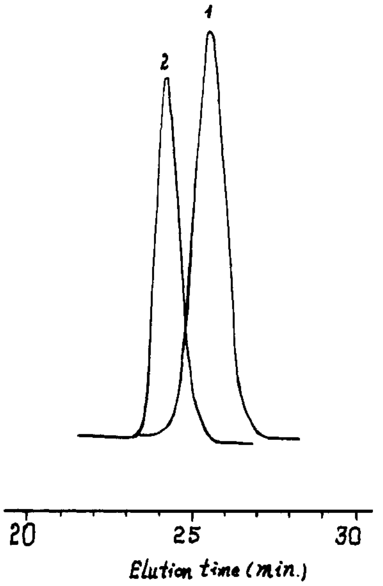

Figure 2. SEC of sample 1 (Table 2). (1) PtBuA block: M_n = 9000, M_w/M_n = 1.05. (2) PtBuA-*b*-PMMA block copolymer: M_n = 15 900, M_w/M_n = 1.10. Prepared in THF at −78 °C using Ph_2CHNa as an initiator in the presence of 2 mol equiv of DB-18-CE-6.

Table 3. Anionic Copolymerization of Mixtures of MMA and tBuA in THF at −78 °C Using Ph_2CHNa as an Initiator in the Presence of 2 mol equiv of DB-18-CE-6

no.	MMA molar fraction in comonomer feed	yield (wt %)	MMA molar fraction in copolymer[a]	M_n calc[b]	M_n SEC	M_w/M_n (SEC)	f[c]
1	1.00	100	1.00	13 400	14 000	1.05	0.96
2	0.90	100	0.90	17 700	19 400	1.10	0.91
3	0.83	100	0.85	17 100	19 000	1.05	0.90
4	0.71	100	0.70	15 200	16 500	1.10	0.92
5	0.52	96.0	0.52	15 200	15 300	1.20	0.99
6	0.28	97.0	0.29	14 400	15 000	1.25	0.93
6[d]	0.20	6.8	0.13	3 000	3 700	2.5	0.81
7	0.07	94.0	0.08	13 800	14 200	1.10	0.97
8	0.00	100	0.00	14 700	16 400	1.13	0.90

[a] ^1H NMR data. [b] $M_{n,calc} = W_{comonomer}$ (g)/$C_{initiator}$ (mol). [c] Initiator efficiency = $M_{n,calc}/M_{n,SEC}$ × yield. [d] In the absence of DB-18-CE-6.

of mixtures of MMA and tBuA was performed under the same experimental conditions as these in the sequential block copolymerization. Table 3 shows indeed that the use of DB-18-CE-6-complexed Ph_2CHNa does promote the beneficial effects on the anionic copolymerization of mixtures of MMA and tBuA in THF at −78 °C. In contrast to the blank carried out in the absence of DB-18-CE-6, in all cases MWD is narrow (1.05–1.25) with a unimodal symmetrical distribution (also see Figure 4), the comonomer conversion is almost quantitative (95–100%), and the initiator efficiency is high (93% as an average): these results might thus indicate a living mechanism in the course of these copolymerizations of mixtures of MMA and tBuA in THF at −78 °C, when Ph_2CHNa is used as an initiator and DB-18-CE-6 as a ligand.

In order to confirm that preliminary conclusion, a series of copolymerizations has been carried out, using various monomer/initiator molar ratios (or theoretical molecular weights, $M_{n,calc}$), a constant additive/initiator molar ratio of 2, and constant initial MMA/tBuA weight ratio of 40/60. Figure 3 compares the experimental molecular weight ($M_{n,SEC}$) and the theoretical value corresponding to the actual monomer conversion (100(MMA + tBuH)/(I) × % conv). A linear plot is observed in a molecular weight range from 5 × 10^3 to 3 × 10^4. The slope of the straight line is 0.96, in good agreement with the initiator efficiency reported in Table 3. Further evidence for a living copolymerization of mixtures of MMA and tBuA initiated by this ligated system is provided by monomer resumption experiments. A first dose of a mixture of MMA and tBuA (0.032 mol) is first polymerized (Ph_2CHNa, 5.96 × 10^{-4} mol; CE/initiator = 2.0) in THF at −78 °C, and 30 min later the same amount of comonomers is added. As a result, SEC traces presented in Figure 4 clearly show that, upon addition of the second dose of comonomers, the SEC peak shifts toward higher molecular weight without any contamination from its first-formed P(MMA-*co*-tBuA). Indeed, M_n of the first copolymer was 6200 (M_w/M_n = 1.10, f = 0.92), and, quite consistently, M_n of the final copolymer was 12 500 (M_w/M_n = 1.10, f = 0.99).

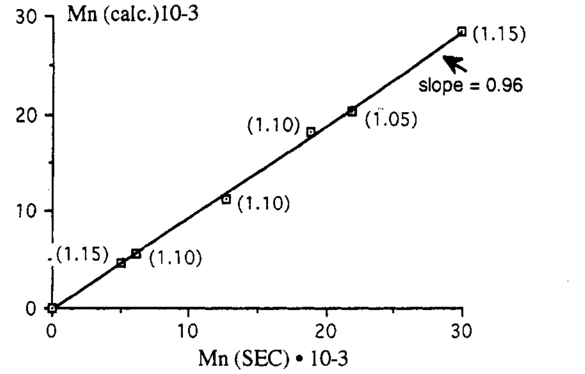

Figure 3. Dependence of experimental M_n as determined by SEC on M_n values calculated from the monomer/initiator ratio and the monomer conversion. Experimental conditions: THF; −78 °C; initiator, (diphenylmethyl)sodium as modified by a 2-fold molar excess of dibenzo-18-CE-6; the ratio of MMA/tBuA, 40/60 (by weight).

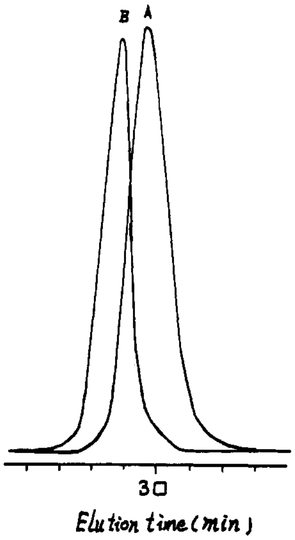

Figure 4. Demonstration of the living character of anionic copolymerizations of mixtures of MMA and tBuA (MMA/tBuA, 40/60 w/w) in THF at −78 °C using PH_2CHNa as an initiator in the presence of 2 mol equiv of DB-18-CE-6. (A) First dose: M_n = 6200, M_w/M_n = 1.10. (B) Second dose: M_n = 12 500, M_w/M_n = 1.10.

Obviously enough, a living anionic copolymerization of mixtures of MMA and tBuA thus prevails in THF at −78 °C in the presence of a sodium counterion and a DB-18-CE-6 ligand. This is again in sharp contrast to the significant discrepancy found for the copolymerization of these comonomers under the same experimental conditions, when a lithium-containing initiator was complexed by LiCl, supporting the idea that the attack of the ester group in PMMA (or PtBuA) by a PtBuA (or PMMA) active species complexed by DB-18-CE-6 is less probable because of the steric hindrance blocking a large enough space area around the sodium-containing ion pairs. In fact, we have reported that the control of livingness in anionic polymerization of MMA and tBuA is limited to THF solutions at low temperature (e.g., −78 °C) when LiCl-added initiator is used,[3b] whereas the living polymerization mechanism remains strictly controlled even in apolar solvents, such as pure toluene and at a temperature as high as 0 °C when DB-18-CE-6 is used as a ligand.[3c]

Characterization of Statistical P(MMA-*co*-tBuA) Copolymer by Means of ^{13}C NMR Spectroscopy and Differential Scanning Calorimetry (DSC). The results described in foregoing sections provide evidence that the products resulting from this living copolymerization of mixtures of MMA and tBuA are not a mixture of two corresponding homopolymers, considering the predicted M_n and composition of the copolymers, as well as the very narrow MWD. However, they do not tell whether these living copolymers are statistical or block ones. In order to answer that question, one has to turn to proton-decoupling ^{13}C NMR spectroscopy, since it is well-known that ^{13}C NMR is very sensitive to the comonomer sequence distribution in copolymers.[11] Moreover, since PMMA-*b*-PtBuA block copolymers have been proved to undergo extensive phase separation,[7] differential scanning calorimetry (DSC) may represent to some extent an alternative tool to distinguish a random P(MMA-*co*-tBuA) copolymer from a blocky one.

Figure 5 illustrates the characteristic resonance of carbonyl groups of PMMA and PtBuA units at 173.5–180.2 ppm, in 100-MHz ^{13}C NMR spectra recorded in $CDCl_3$ at 40 °C, for statistical P(MMA-*co*-tBuA) (Figure 5A), PMMA-*b*-PtBuA (Figure 5B, sample 3 in Table 1), and an equimolar mixture of homo-PMMA and homo-PtBuA (Figure 5C). Comparing parts B and C of Figure 5, it is obvious that the ^{13}C NMR spectrum of the block copolymer is almost identical to the one of a mixture of two corresponding homopolymers. However, the ^{13}C NMR spectrum of P(MMA-*co*-tBuA) displays quite a different pattern. Indeed, one can observe in parts B and C of Figure 5 that the resonances of C=O groups of PMMA and PtBuA segments, in PMMA-*b*-PtBuA block copolymer as well as in the mixture of two corresponding homopolymers, appear at quite different frequencies, the chemical shift of PtBuA (ca. 173.5–174.0 ppm) being at a higher field compared to that of PMMA (176.5–178.2 ppm). However, three sets of new ^{13}C resonances appear between 174.5 and 176.3 ppm in the ^{13}C spectrum of P(MMA-*co*-tBuA) copolymer (as indicated by arrows in Figure 5A). Together with the ones at ca. 173.5–174.0 and 176.5–178.2 ppm, these signals clearly correspond to the different MMA- (M) and tBuA- (A) centered triads.[11] The further splitting in each set might be due to the pentad configuration sequences.[11] A detailed microstructure elucidation of these copolymers is currently being investigated and will be published later.

Up to this point, one may safely state that the living P(MMA-*co*-tBuA) anionically prepared by using a DB-18-CE-6 complexed initiator is not a block copolymer nor a mixture of two corresponding homopolymers. It can be reasonably regarded as an essentially statistical one.

This conclusion is further substantiated by DSC measurements. Figure 6 shows the DSC diagrams of samples which have already been characterized in the above ^{13}C NMR study. In the cases of the PMMA-*b*-PtBuA block copolymer and the mixture of two corresponding homopolymers (Figure 6B, C), two distinct transitions appear at ca. 22 and 102 °C, characteristic of long PtBuA and PMMA segments, respectively. This confirms the previously reported observation that there is an extensive phase separation between PMMA and PtBuA.[7] By contrast, only a very broad weight-averaged T_g is detected for the P(MMA-*co*-tBuA) product (Figure 6A), providing an additional evidence that this is essentially a statistical copolymer.

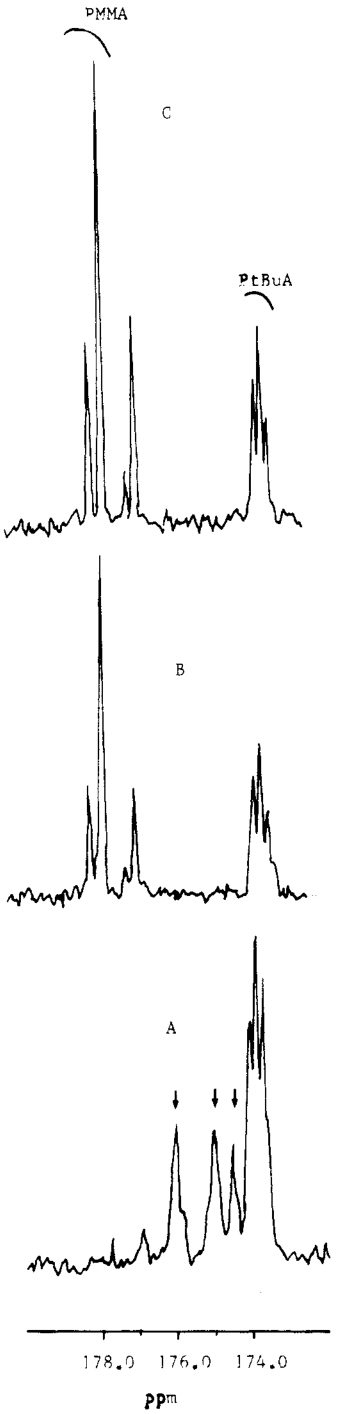

Figure 5. 100-MHz carbon-13 NMR spectra. (A) P(MMA-*co*-tBuA) copolymer (monomer feed composition, 20 wt % tBuA; yield, 10 wt %). (B) PMMA-*b*-PtBuA diblock copolymer (sample 3, Table 1). (C) A mixture of equimolar PMMA and PtBuA. All samples were synthesized in THF at −78 °C using Ph_2CHNa as an initiator in the presence of 2 mol equiv of DB-18-CE-6.

Furthermore, Table 4 lists the observed T_g's of various copolymers with different comonomer fractions. For comparison purposes, the calculated ones in terms of the well-known Fox's equation[12] are also included in Table 4. Clearly enough, only one T_g is detected for all samples, again supporting the idea that they are statistical copoly-

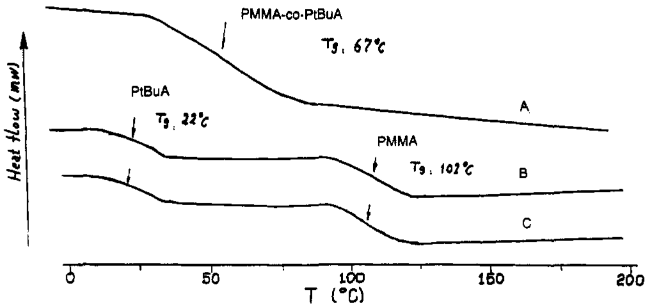

Figure 6. DSC diagrams of different types of PMMA- and PtBuA-based polymers. (A) PMMA-*co*-PtBuA copolymer (sample 4, Table 3). (B) PMMA-*b*-PtBuA diblock copolymer (sample 3, Table 1). (C) A mixture of equimolar PMMA and PtBuA. All samples were synthesized in THF at −78 °C using Ph_2CHNa as an initiator in the presence of 2 mol equiv of DB-18-CE-6.

Table 4. Experimental and Calculated Glass Transition Temperatures (T_g) of Living Copolymers of MMA and tBuA Anionically Synthesized in THF at −78 °C Using Ph_2CHNa as an Initiator in the Presence of 2 mol equiv of DB-18-CE-6

no.	composition of copolymer (wt %) MMA	tBuA	exptl (DSC, K)	calcd (Fox's, K)
1	1.00	0.00	375	
2	0.88	0.12	370	363
3	0.79	0.21	360	354
4	0.66	0.34	340	343
5	0.48	0.52	317	328
6	0.33	0.67	308	317
7	0.06	0.94	303	299
8	0.00	1.00	295	

mers. However, it should be noted that the observed T_g's do not seem to fit the Fox relationship very well. This is not very surprising since it has been repeatedly reported that the dependence of a copolymer glass transition temperature (T_g) on composition cannot in many cases be predicted by simple additive relations such as the Fox equation.[12] In that respect, the effect of the sequential distribution of monomeric units of a copolymer on its T_g cannot be disregarded,[11c,13] and the present data might also well indicate some degree of blockiness (small segments), not a too surprising conclusion considering the vastly different reactivities involved (see the next section).

Monomer Reactivity Ratios. Among several methods available to determine a monomer reactivity ratio, the Finemann–Ross,[14a] Yezrielev–Brokhina–Roskin,[14b] and Kelen–Tüdös[14c] methods are appropriate at low conversions. The Mayo–Lewis[15] and extended Kelen–Tüdös[10] methods consider the drift in the comonomer and copolymer compositions with conversion. In that respect, it has been found that the most reliable method is the extended Kelen–Tüdös one,[16] since one may simply use a linear graphic technique to calculate the reactivity ratio values with a very smaml error up to 60% conversion.[10,16] In addition, for the present living anionic copolymerizations, only data at relatively high conversion could be obtained due to the very high reaction rate. The extended Kelen–Tüdös method was thus used to determine the monomer reactivity ratios.

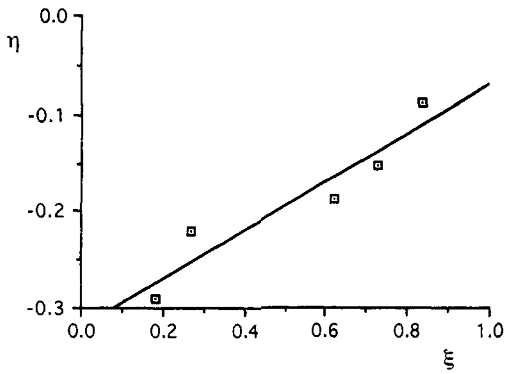

Figure 7. Extended Kelen–Tüdös plot. $\eta = (r_{MMA} + r_{tBuA}/\alpha)\xi - r_{tBuA}/\alpha$.[10]

On the other hand, it was observed that $OC(CH_3)_3$ and OCH_3 resonances do not split while varying the composition of copolymer, leading to sharp peaks at 80.4 and 51.7 ppm, respectively. Therefore, the composition of copolymer samples was determined by direct integration of these two signals. Moreover, the extended Kelen–Tüdös method is expressed by the following equations:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

where

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F)$$

$$\alpha = (F_{\min}F_{\max})^{1/2}$$

$$F = Y/Z^2 \quad \text{and} \quad G = (Y - 1)/Z$$

$$Z = \log(1 - \zeta_1)/\log(1 - \zeta_2)$$

where

$$\zeta_2 = w(\mu + X)/(\mu + Y)$$

$$\zeta_1 = \zeta_2(Y/X)$$

where X and Y represent the molar ratios of monomer 1 to monomer 2 in the comonomer feed and the resulting copolymer, respectively. In addition, w equals the weight conversion of copolymerization, and μ is the ratio of molecular weight of monomer 2 to that of monomer 1.

Table 5 gives the copolymerization data. The extended Kelen–Tüdös plot is also given in Figure 7. The intercepts at $\xi = 0$ and $\xi = 1$ of the ξ versus η plot gives $r_{tBuA} = 8.81 \pm 0.25$ and $r_{MMA} = -0.07 \pm 0.11$, respectively. Since the monomer reactivity ratio cannot be a negative value, the r_{MMA} must be from zero to 0.04, or 0.02 ± 0.02.[17] Nevertheless, these data will confirm that tBuA is much more reactive in anionic copolymerization than MMA, so

Table 5. Kelen–Tüdös Parameters[10] for Anionic Copolymerization of Mixtures of MMA and tBuA[a,b]

no.	f_{MMA}[c]	F_{MMA}[d]	conv (wt %)	X	Y	Z	F	G	ξ	η
1	0.837	0.234	0.10	5.13	0.306	0.0471	138	−14.8	0.831	−0.0892
2	0.751	0.165	0.14	3.01	0.198	0.0520	73.3	−15.4	0.726	−0.152
3	0.662	0.144	0.24	1.96	0.168	0.0612	44.8	−13.6	0.619	−0.188
4	0.459	0.103	0.29	0.848	0.115	0.106	10.2	−8.35	0.270	−0.221
5	0.354	0.0593	0.11	0.548	0.063	0.107	5.49	−8.75	0.183	−0.291

[a] Copolymerization was carried out in THF at −78 °C for a few minutes using 2-DB-18-CE-6/Ph_2CHNa initiator. [b] $2\alpha = 27.5$. [c] MMA molar fraction in monomer feed. [d] MMA molar fraction in copolymer.

much so that the relative reactivity ratio of MMA versus tBuA is scarcely distinguishable from zero.

At this point, it is important to point out that such a large difference in the monomer reactivity ratio might indicate that the early polymer must be close to PtBuA in character and the later be virtually PMMA, so the opportunity for mixed triads would occur only in the intermediate region and to a relatively small extent.

In conclusion, it has been shown here for the first time that a living copolymerization of mixtures of methacrylates (e.g., MMA) and acrylates (e.g., tBuA) can be promoted by using a sodium-containing initiator complexed with a hindered cation-binding ligand, i.e., DB-18-CE-6, in THF, at −78 °C. This gives credit to the efficiency of the ligating technique in producing tailored (meth)acrylate-based materials with various molecular architectures: block copolymers, end functional oligomers, star-shaped polymers, and now statistical copolymers.

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