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Synthesis and Characterization of Poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(methyl methacrylate) Copolymers by Two-Step Controlled Radical Polymerization (ATRP) Catalyzed by $NiBr_2(PPh_3)_2$, 1[†]

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ABSTRACT: Poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(methyl methacrylate) triblock copolymers (MnBM) have been synthesized by the sequential controlled radical polymerization (atom transfer radical polymerization, ATRP) of *n*-butyl acrylate (*n*-BuA) followed by methyl methacrylate (MMA). The polymerization of *n*-BuA has been first initiated by the difunctional (diethyl *meso*-2,5-dibromoadipate) initiator in the presence of the $NiBr_2(PPh_3)_2$ catalyst. After isolation, the α,ω-dibromo poly(*n*-butyl acrylate) chains have been used as macroinitiators for the polymerization of either *n*-BuA or MMA leading to chain extension or to the desired triblock copolymers, respectively. The kinetic study of the two-step process has shown that the initiation of the MMA polymerization by the poly(*n*-BuA) macroinitiator is slow and leads to PMMA outer blocks of broad polydispersity. Differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA) have confirmed the two-phase morphology of the triblocks. Finally, DMA and tensile testing of these copolymers have emphasized poor mechanical properties in possible relation to the broad polydispersity of the PMMA outer blocks.

Introduction

Thermoplastic elastomers (TPE's) have the unique property of being spontaneously and thermoreversibly cross-linked materials.[1] They are basically segmented copolymers that combine major rubbery blocks with minor thermoplastic ones. These blocks have to be immiscible and have to phase separate with formation of thermoplastic microdomains, which act as cross-links for the rubbery matrix. Therefore, heated above T_g of the thermoplastic blocks, TPE's can flow and be reprocessed at will, which is a remarkable superiority with respect to the irreversibly vulcanized elastomers. Glass transition temperatures (T_g) of the hard (thermoplastic) and the soft (rubber) blocks actually fix the upper and the lower service temperatures of the TPE's.

One of the most common TPE's is the poly(styrene)-*block*-poly(butadiene)-*block*-poly(styrene) (SBS) copolymer, which is synthesized by anionic polymerization and available in the marketplace.[1] However, SBS suffers from two major drawbacks. First, the unsaturated polybutadiene block is easily oxidized and is sensitive to UV degradation, unless the double bonds are previously hydrogenated, which increases the final cost. Second, the upper service temperature is limited by T_g of the polystyrene block, which is observed at around 60−70 °C. This situation explains why much effort has been devoted to the replacement of polystyrene by thermoplastics of higher T_g or higher melting temperature and substitution of more stable rubber for polybutadiene.[2] Fully acrylic TPE's might be valuable alternatives for the traditional SBS copolymers. Indeed, the versatility of the (meth)acrylic monomers is such that T_g covers a wide range from ca. −50 to +200 °C. Furthermore, these polymers are not sensitive to UV and oxidation, which does not require the chemical modification of the original triblocks, as is the case for SBS.

Fully acrylic poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(methyl methacrylate) (MnBM) thermoplastic elastomers (TPE's) have already been synthesized by anionic polymerization.[3,4] However, as result of nucleophilic side reactions on the primary ester groups of *n*-BuA, *tert*-butyl acrylate (*t*-BuA) must be first polymerized, followed by transalcoholysis of the poly(*t*-BuA) block in a further step. Yasuda et al. also reported on the synthesis of such MnBM using rare earth metal complexes.[5] However, the drastic experimental conditions required by these two polymerization methods make the synthesis of MnBM copolymers not very attractive. It is the reason why the synthesis has been contemplated by controlled radical polymerization, which is now emerging as a powerful tool for macromolecular engineering.[6] In contrast to the nitroxide-mediated radical polymerization, which is poorly suited to the polymerization of methacrylic monomers (β-proton abstraction by nitroxide radicals),[7] atom transfer radical polymerization (ATRP) is known to impart a good control to the polymerization of styrenic, acrylic, and methacrylic monomers.[8] Therefore, this work aims at synthesizing MnBM's triblocks by ATRP and to evaluate their potential as TPE's.[9]

ATRP is based on a reversible activation−deactivation process of the terminal C−halogen bond of the growing chains by a transition metal complex.[6] The use of complexes of Ru, Cu, Ni, Fe, Rh, and Pd has been

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reported by several research groups.[10] Recently, our laboratory has focused on ATRP of MMA and *n*-BuA catalyzed by $NiBr_2(PPh_3)_2$.[8i] On this occasion, a difunctional initiator, the diethyl *meso*-2,5-dibromoadipate (DEMDBA), has been used with the purpose of synthesizing α,ω-dibromo-poly(*n*-BuA). For the first time in ATRP, the difunctionality of the initiation step has been clearly demonstrated by using a mixture of mono- and difunctional initiators, so leading to the quantitatively predicted bimodality of the SEC chromatograms.[8i]

Since the terminal C−Br bond is relatively stable, α,ω-dibromo-poly(*n*-BuA) can be isolated, dried, and stored while keeping the bromide available at the chain end. So, the C−Br bonds might be reactivated by a freshly added catalyst in the presence of monomer, which opens the way to block copolymers as previously reported by Sawamoto.[11] Difunctional poly(*n*-BuA)'s of different molecular weights have been first synthesized and then used to initiate the polymerization resumption of either *n*-BuA (chain extension) or MMA (triblock formation).

Experimental Section

Materials. $NiBr_2(PPh_3)_2$ (99%) and diethyl *meso*-2,5-dibromoadipate (98%) (DEMDBA) were used as received from Aldrich. Methyl methacrylate and *n*-butyl acrylate (from Aldrich) were dried over CaH_2 and distilled under reduced pressure, in order to remove the stabilizing agents, and stored under N_2 at −20 °C. $NiBr_2(PPh_3)_2$ was stored under nitrogen, although weighed in the air.

Polymerization. In a typical experiment, the initiator, catalyst, and a magnetic stirrer were introduced into a glass flask, which was then capped by a three-way stopcock and purged with nitrogen by repeated vacuum/nitrogen cycles. The monomer was then added under nitrogen with a syringe. The monomer conversion (kinetic experiments) was calculated from the weight of the polymer recovered after elimination of the residual monomer under high vacuum at room temperature, followed by drying at 80 °C for 24 h. The macroinitiator to be used in the synthesis of triblocks was recovered by precipitation in cold methanol.

Resumption of Polymerization. A known amount of previously purified macroinitiator was dissolved in toluene. The required volume of this solution was introduced into a glass reactor and degassed by bubbling nitrogen. The catalyst was then added under a nitrogen flow, followed by the monomer, which was injected with a syringe. The glass reactor was immersed in an oil bath at 85 °C, and the polymerization kinetics was followed by picking up samples from the reactor and weighing the polymer formed and isolated as aforementioned.

Characterization. Molecular weight distribution (MWD) was analyzed by SEC in THF at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. PMMA standards (Polymer Laboratories) were used for calibration. The universal calibration method by Benoit et al.[12] was used to calculate the molecular weight (MW) of poly(*n*-butyl acrylate) according to eq 1, which was derived from the viscometric relationships in eqs 2 and 3.

$$\log M_{\text{Pn-BuA}} = 0.965 \log M_{\text{PMMA}} + 0.139 \qquad (1)$$

$$[\eta] = 1.298 \times 10^{-4} M^{0.688} \text{ (PMMA in THF)}^{13} \qquad (2)$$

$$[\eta] = 7.4 \times 10^{-5} M^{0.75} \text{ (Pn-BA in THF)}^{14} \qquad (3)$$

Before SEC and NMR analysis, polymers were purified by eluting solutions in THF through an Al_2O_3-filled column. ^1H NMR spectra were recorded with a Bruker AM 250 apparatus in $CDCl_3$ with TMS as internal reference at room temperature. DSC analysis was carried out with a Dupont 9000 apparatus under nitrogen (calibration with indium; heating rate: 10 °C/min). Dynamic mechanical analysis (DMA) was performed with a TA apparatus (DMA 983) at a constant frequency of 1 Hz and heating rate of 2.5 °C/min. The samples were cut out from solution cast films.

Table 1. Synthesis of Difunctional Poly(*n*-BuA) Macroinitiators[d]

sample	$[n\text{-BuA}]_0$/ $[\text{DEMDBA}]_0$	convn (%)[a]	M_n(calcd)[b]	M_n(SEC)[c]	M_w/M_n
1a	116	85	15 000	16 500	1.07
1b	780	70	67 000	60 000	1.10
1c	1170	85	127 000	105 000	1.20

[a] After precipitation in cold methanol. [b] M_n(calcd) = ($[n\text{-BuA}]_0/[\text{DEMDBA}]_0$) × convn × 128.17. [c] PMMA standards and universal calibration (eq 3). [d] Conditions: T = 85 °C; reaction time = 24 h; $[n\text{-BuA}]_0$ = 7 M; $[NiBr_2(PPh_3)_2]_0 = [\text{DEMDBA}]_0$ = 60.3 mM, 8.97 mM, 5.98 mM for entries **1a**, **1b**, and **1c**, respectively.

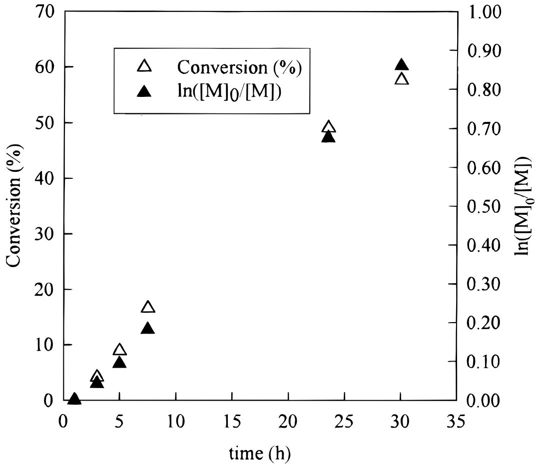


Figure 1. Time dependence of conversion and $\ln([M]_0/[M])$ for the ATRP of *n*-BuA initiated by α,ω-dibromo-poly(*n*-BuA) macroinitiator. Conditions: T = 85 °C; solvent, toluene; $[n\text{-BuA}]_0$ = 3.5 M; [macroinitiator (**1a**)]$_0$ = 4.46 mM; $[NiBr_2(PPh_3)_2]_0$ = 5.17 mM.

Tensile properties were measured with an Adamel Lhomargy tensile tester. Microdumbells (thickness of 1.5 mm and width of 4 mm) were extended at 100 mm/min at room temperature. At least three independent measurements were recorded for each sample.

Films Preparation. Films were prepared by casting copolymer solution (10 wt % in toluene) in a polyethylene dish followed by slow evaporation for 3 or 4 days. They were then dried overnight at 120 °C under high vacuum and slowly cooled.

Results and Discussion

Synthesis of Difunctional Poly(*n*-BuA) Macroinitiators. A key point for the successful synthesis of these macroinitiators is to maintain the monomer conversion below 80−90%. Indeed, termination reactions occur at high conversion (>90%), mainly by coupling of the poly(*n*-BuA) chains.[8i] Although in the case of difunctional polymers, the coupling reaction does not change the end-functionality, the broadening of the MWD may become detrimental. Table 1 lists the main characteristics of the macroinitiators synthesized in this work.

Resumption of ^{n}BuA Polymerization. Figures 1 and 2 show the time dependence of $\ln([M]_0/[M])$ and how the molecular weight and polydispersity depend on the monomer conversion. The concentration of the active species is constant, supported by the quasi linearity of

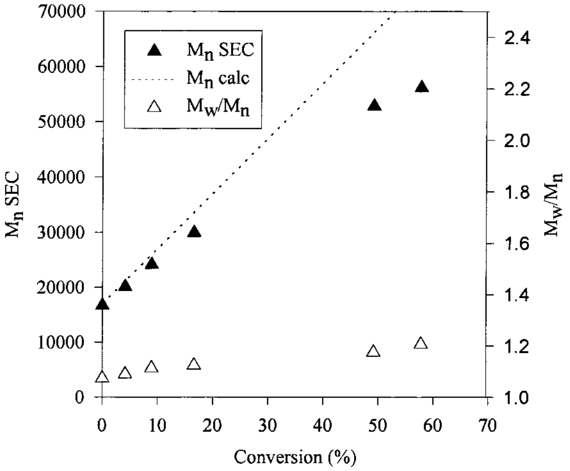


Figure 2. Dependence of M_n and MWD on the *n*-BuA conversion. ATRP initiated by α,ω-dibromo-poly(*n*-BuA) macroinitiator. Conditions: T = 85 °C; solvent, toluene; $[n\text{-BuA}]_0$ = 3.5 M; [macroinitiator (**1a**)]$_0$ = 4.46 mM; $[NiBr_2(PPh_3)_2]_0$ = 5.17 mM.

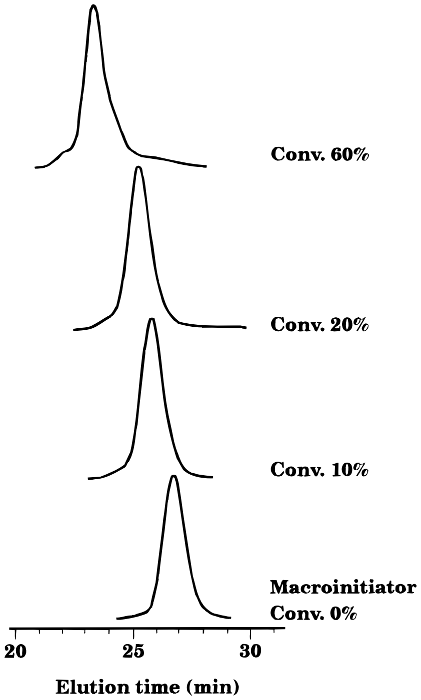


Figure 3. Evolution of the SEC chromatograms with monomer conversion when the polymerization of *n*-BuA is initiated by α,ω-dibromo poly(*n*-BuA) macroinitiator. Conditions: T = 85 °C; solvent, toluene; $[n\text{-BuA}]_0$ = 3.5 M; [macroinitiator (**1a**)]$_0$ = 4.46 mM; $[NiBr_2(PPh_3)_2]_0$ = 5.17 mM.

$\ln([M]_0/[M])$ vs time. The molecular weight increases linearly with conversion, and polydispersity remains narrow. Some transfer reactions combined with possible experimental errors on the amount of macroinitiator used can account for the observed deviation of M_n(SEC) with respect to the calculated values. Figure 3 shows how the SEC chromatogram of poly(*n*-BuA) is completely shifted toward higher molecular weight when the monomer conversion increases. The resumption of the *n*-BuA polymerization by the poly(*n*-BuA) macroinitiator is thus basically quantitative.

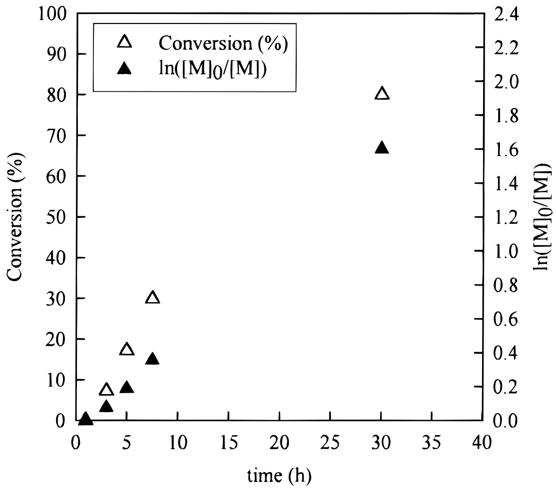


Figure 4. Time dependence of conversion and $\ln([M]_0/[M])$ for the ATRP of MMA initiated by α,ω-dibromo-poly(*n*-BuA) macroinitiator. Conditions: T = 85 °C; solvent, toluene; $[MMA]_0$ = 4.67 M; [macroinitiator (**1a**)]$_0$ = 4.43 mM; $[NiBr_2(PPh_3)_2]_0$ = 5.17 mM.

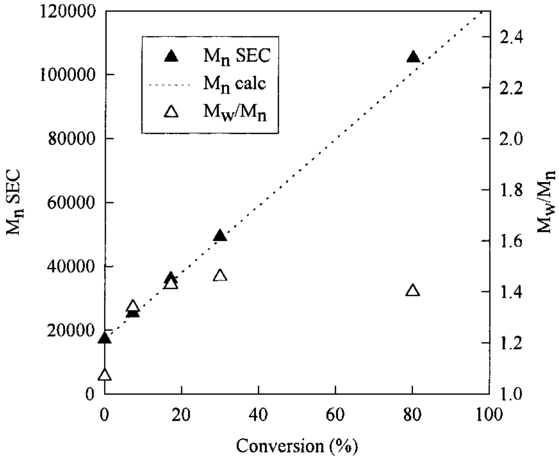


Figure 5. Dependence of M_n and MWD on MMA conversion. ATRP initiated by α,ω-dibromo-poly(*n*-BuA) macroinitiator. Conditions: T = 85 °C; solvent, toluene; $[MMA]_0$ = 4.67 M; [macroinitiator (**1a**)]$_0$ = 4.43 mM; $[NiBr_2(PPh_3)_2]_0$ = 5.17 mM.

Resumption of Polymerization with MMA. In parallel to the resumption of the *n*-BuA polymerization, MMA has been added to poly(*n*-BuA) chains preformed by ATRP. Figure 4 shows the time depence of $\ln([M]_0/[M])$, whereas the evolution of molecular weight and polydispersity with the MMA conversion is shown in Figure 5. In this case, the main criteria for the controlled radical polymerization of MMA are also fulfilled. Nevertheless, a significant increase in the polydispersity (from 1.1 to 1.4) is observed by SEC at low conversion, which indicates that the reinitiation process is slow compared to chain propagation. The evolution of the SEC traces (Figure 6) confirms the slow disappearance of the macroinitiator, which is responsible for bimodality at least until rather high monomer conversion (>30%). This observation is in sharp contrast to the narrow monomodal MWD observed for the resumption of the *n*-BuA polymerization.[15] The difference in the reactivity of the radicals of the methacrylic and the acrylic type and the position of the equilibrium between these radicals and the parent dormant species (Scheme 1) can account for these observations. The initiation step requires indeed the cleavage of the C−Br bond, which is more stable in the case of acrylate compared to methacrylate in relation to the reactivity of the secondary radical derived from the acrylate, which is higher than that one of the tertiary methacrylate radical. Furthermore, the two types of dormant species are not

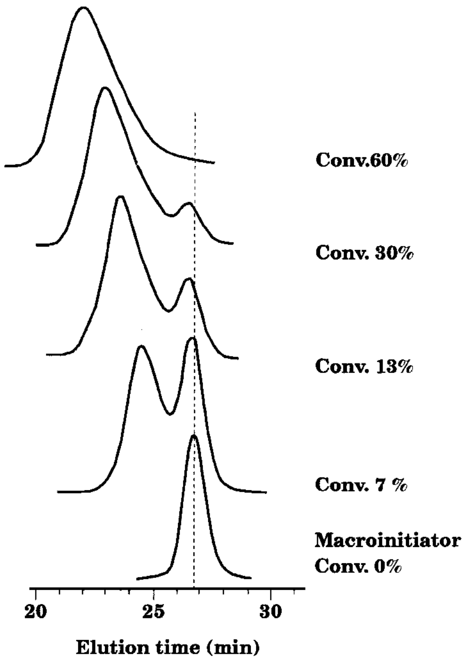
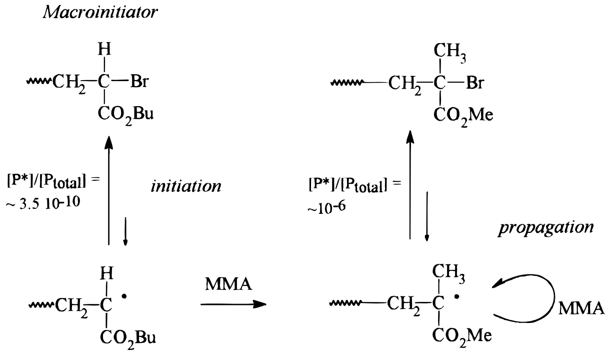


Figure 6. Evolution of the SEC chromatograms with monomer conversion when the polymerization of MMA is initiated by α,ω-dibromo-poly(*n*-BuA) macroinitiator. Conditions: T = 85 °C; solvent,: toluene; $[MMA]_0$ = 4.67 M; [macroinitiator (**1a**)]$_0$ = 4.43 mM; $[NiBr_2(PPh_3)_2]_0$ = 5.17 mM.

Scheme 1



activated to the same extent, the situation being much more favorable for methacrylate for which the molar fraction of active species ([P•]/[P_{total}]) is ca. 300 times larger than for acrylate.[8i] Although the polydispersity is broadened, the reinitiation of MMA by the poly(*n*-BuA) chains seems to be quantitative at high enough conversion (e.g., 80%; Figure 6), since the macroinitiator trace is then no longer observed in the chromatogram. It may thus be concluded that a two-step strategy based on difunctional initiator is well suited to the synthesis of MnBM triblocks.

Synthesis of MnBM Triblock Copolymers. MnBM triblock copolymers have been synthesized by initiating the polymerization of different amounts of MMA by α,ω-dibromo-poly(*n*-BuA) of 60 000 (**1b**, Table 1) and 105 000 (**1c**, Table 1) molecular weights, respectively. Table 2 summarizes the main molecular characteristics of the triblocks that have been accordingly prepared. Although the polydispersity of the PMMA outer blocks is known to be broad (Figure 6), the polydispersity of the final copolymers is rather narrow (<1.3). Figure 7 shows a ^{1}H NMR spectrum typical of MnBM triblock copolymers, which allows the molar composition to be easily determined from the relative intensity of the resonances at 4.04 ppm (CH_2 protons ***a*** of the *n*-Bu substituent) and 3.60 ppm (CH_3 protons ***b*** of the methyl substituent). The MW of the PMMA outer blocks has been calculated from eq 4, which is based on the knowledge of the MW of the poly(*n*-BuA) macroinitiator and the molar composition of the triblock.

$$2\ DP_{\mathrm{PMMA\ outer\ blocks}} = [((\%\ \mathrm{MMA}/100) \times (\mathrm{DP\ macroinitiator}))/(1 - (\%\ \mathrm{MMA}/100))] \quad (4)$$

Since the MnBM copolymers can be synthesized in a controlled way, their physicomechanical properties are worth being investigated.

Characterization of the MnBM Triblocks. The complete shift of the SEC chromatogram of the macroinitiator to higher MW is clearly observed, particularly in the case of samples **2b** and **2c** as the result of long enough PMMA blocks grown from poly(*n*-BuA). This observation confirms the blockiness of the samples analyzed below.

DSC. DSC analysis confirms the phase separation of the constitutive blocks, since T_g of each of them is observed (at −45 °C for the poly(*n*-BuA) block and at 120 °C for PMMA). These transition temperatures agree with the T_g of pure PMMA and poly(*n*-BuA), respectively.

Mechanical Properties. The dynamic mechanical analysis (DMA) of sample **2c** (55 mol % of PMMA) is shown in Figure 8. Two transitions are observed which correspond to T_g's of the poly(*n*-BuA) and PMMA blocks and confirm the two-phase morphology of this triblock copolymer. The storage modulus (G') at 25 °C is found to be 18 MPa, and it becomes too low for being measured accurately by DMA when the PMMA content is decreased (37% in sample **2b**). The ultimate mechanical properties have been measured at 25 °C as shown in Table 3. The stress−strain curve is typical of TPE with a marked increase of stress before break (Figure 9). The maximum elongation at break (ϵ_B) is 545% in the case of sample **2c** which however shows the smallest ultimate tensile strength (σ_B = 0.4 MPa). Conversely, the highest σ_B (7 MPa) is observed for sample **2c**, whose ϵ_B is the smallest (124%). The best compromise is observed for the sample **2b** (14K−60K−14K) with ϵ_B = 385% and σ_B = 5.0 MPa. These data are very much disappointing compared to the classical SBS with ϵ_B up to 800−1000% and σ_B of ca. 30 MPa.[1] Furthermore, anionically prepared MnBM triblocks show better mechanical properties than the parent copolymer prepared by ATRP, ϵ_B and σ_B being typically 700% and 10−15 MPa, respectively.[3] It must be noted that the MnBM copolymers synthesized by Yasuda[5] have low elongation at break, the highest reported value being 263% for the 8K−72K−20K triblock. A more detailed comparison of these MnBM copolymers prepared by ligated anionic polymerization (LAP) and ATRP is the topic of a forthcoming paper.[16] Nevertheless, it may already be suggested that the broad polydispersity of the PMMA outerblocks has something to do with the poor mechanical properties reported in Table 3. Although problems of phase separation for MnBM copolymers prepared by LAP has been pointed out by Monnerie et al.[17] by solid-state NMR, atomic force microscopy (AFM) in the tapping mode with phase detection imaging has confirmed sharp phase separation for MnBM samples (including samples **2b** and **2c** in Table 2).[18] A major reason for the much lower mechanical properties of fully (meth)acrylic triblocks

Table 2. Synthesis of MnBM by ATRP Catalyzed by $NiBr_2(PPh_3)_2$[c]

sample	macroinitiator		MnBM triblock			
	M_n	M_w/M_n	M_n(SEC)[a]	M_w/M_n	% MMA_{NMR} (mol %)	M_n(NMR)[b]
2a	60K (**1b**)	1.10	90K	1.17	24	7.4K−60K−7.4K
2b	60K (**1b**)	1.10	110K	1.18	37	14K−60K−14K
2c	60K (**1b**)	1.10	140K	1.30	55	29K−60K−29K
2d	105K (**1c**)	1.20	140K	1.20	17	8.4K−105K−8.4K
2e	105K (**1c**)	1.20	150K	1.23	22	11.5K−105K−11.5K
2f	105K (**1c**)	1.20	156K	1.25	28	16K−105K−6K

[a] PMMA calibration. [b] Calculated by eq 4. [c] Conditions: Solvent: toluene, $T = 85$ °C, $[\text{macroinitiator}]_0 = 2.1$ mM for **2a,b,c** and 1.1 mM for **2d,e,f**. Reaction time: 24 h. $[NiBr_2(PPh_3)_2]_0 = [\text{macroinitiator}]_0$. $[MMA]_0 = 1.4$ M, 2.2 M, 3.2 M, 0.8 M, 1.2 M, and 1.7 M for **2a**−**f**, respectively.

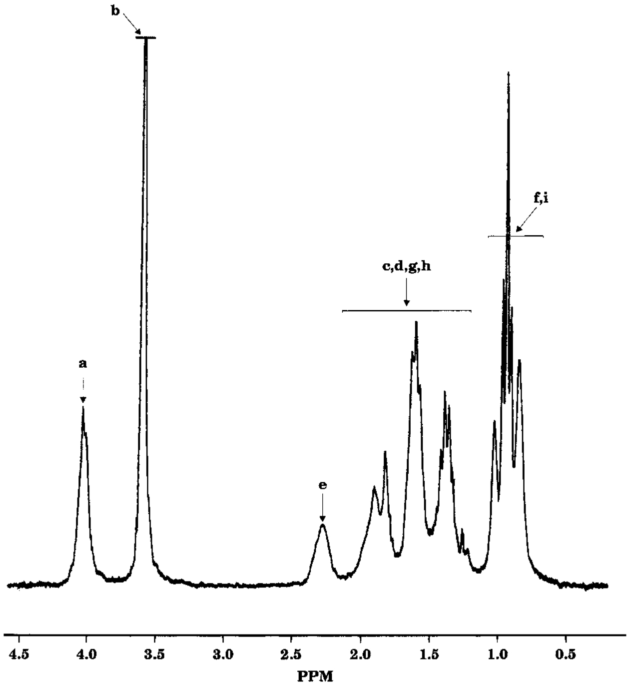


Figure 7. 250 MHz ^1H NMR spectrum of MnBM triblock copolymer (sample **2c**, Table 2).

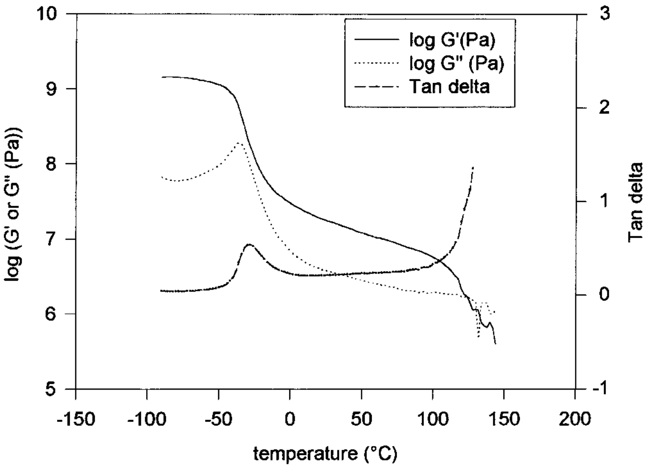


Figure 8. Dynamical mechanical analysis (1 Hz, 5 °C/min) of MnBM containing 55 mol % of MMA (sample **2c**, Table 2).

compared to SBS has to be found in the average molecular weight between chain entanglements of the rubbery block as it is discussed in a forthcoming paper.[19]

Conclusions

MnBM triblock copolymers have been synthesized by ATRP according to a two-step strategy.[20] In the first step, a difunctional initiator is used for the polymerization of *n*-BuA with formation of α,ω-dibromo-poly(*n*-BuA). These telechelic poly(*n*-BuA) chains have proved to be efficient macroinitiators for the polymerization of MMA and the synthesis of the envisioned MnBM triblocks. Nevertheless, the initiation of MMA polyaddition is slow which results in PMMA blocks with rather broad polydispersity and thus in triblocks of as high MWD as the PMMA content is high (Table 2). The phase separation has been confirmed by DSC and DMA analysis. The tensile properties of these MnBM triblocks are poor when compared to anionically prepared MnBM and to SBS. The origin of these poor mechanical properties has something to do, although not only, with the polydispersity of the PMMA outer blocks. Reduction of the MWD of the PMMA outer blocks is now possible as reported by Matyjaszewski et al.,[21] and the effect of this parameter on the mechanical properties is under current analysis.[22] Another important conclusion is that SEC analysis of the triblocks does not provide detailed enough molecular information, particularly in the case of extreme compositions, so that preliminary conclusions might be erroneous.

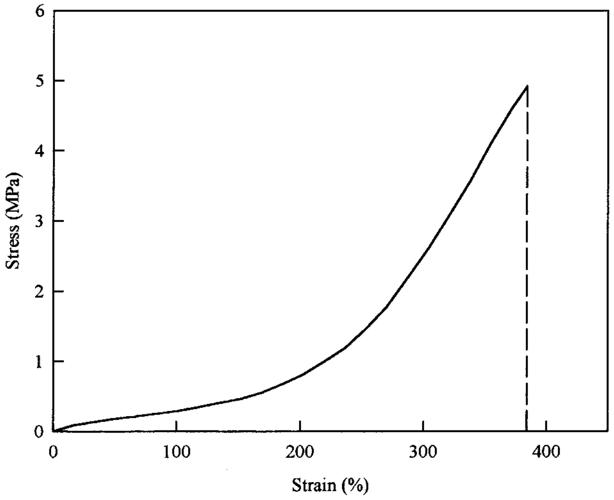


Figure 9. Stress−strain curve for the sample **2b** (Table 2) at room temperature. Strain rate: 10 mm/min.

Table 3. Ultimate Mechanical Properties of the MnBM Triblocks

sample	% MMA_{NMR} (mol %)	M_n(NMR)	ϵ_B (%)	σ_B (MPa)
2a	24	7.4K−60K−7.4K	435	1.2
2b	37	14K−60K−14K	385	5.0
2c	55	29K−60K−29K	125	7.0
2e	22	11.5K−105K−11.5K	545	0.4
2f	28	16K−105K−16K	505	1.8

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