Synthesis and Characterization of ω-Unsaturated Poly(styrene-*b*-*n*-butyl methacrylate) Block Copolymers Using TEMPO-Mediated Controlled Radical Polymerization

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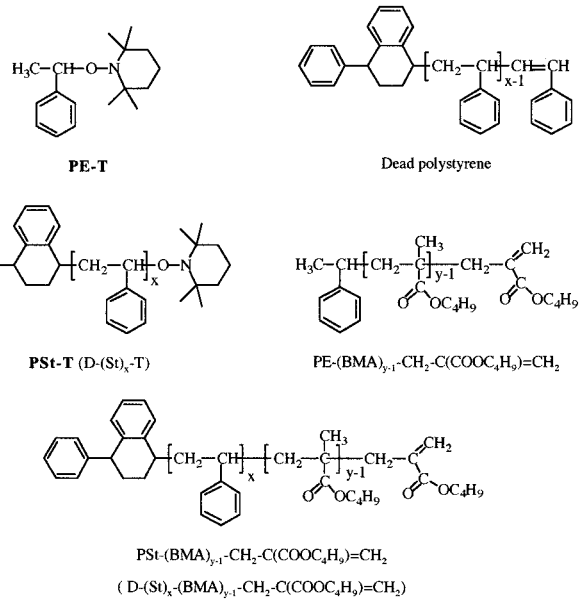
ABSTRACT: *n*-Butyl methacrylate has been polymerized in bulk at 130 °C in the presence of given amounts of a nitroxide stable free radical (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) using either a low molar mass alkoxyamine initiator (2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine) or a TEMPO-capped polystyrene macroinitiator. Complete consumption of both initiators was always observed. In contrast, very low final monomer conversions were found. Proton NMR spectroscopy and MALDI-TOF mass spectrometry were used for investigation of the polymer structure. They showed that the formed poly(*n*-butyl methacrylate) had the attached initiator at one end and that a block copolymer was synthesized when the polystyrene macroinitiator was used. The other terminal functionality of the polymer was not a TEMPO-based alkoxyamine but a methylene unsaturation exclusively. Particularly, no saturated polymer which would also be formed by conventional disproportionation reaction between two propagating radicals could be detected. From this result, it was concluded that the main chain-breaking event is the β-hydrogen transfer from a propagating radical to TEMPO (also called disproportionation reaction). The initial concentration of added TEMPO was shown to directly influence the poly(*n*-butyl methacrylate) block length independently of the initial concentration of alkoxyamine: the larger the concentration of TEMPO, the shorter the block length. The rate constant of disproportionation was calculated to be $k_{dis} = 1.4 \times 10^6$ L mol^{-1} s^{-1} at 130 °C.

Introduction

Nitroxide-mediated "living" free radical polymerization[1,2] enables the synthesis of macromolecules with well-defined architectures, but it is still limited to a few monomers. It is particularly well suited for styrene and styrene derivatives. In contrast, the controlled polymerization of acrylic esters has long been considered as a challenge but can now be achieved using either TEMPO, TEMPO derivatives[3] (in those cases, however, relatively broad molar mass distributions were observed since M_w/M_n was found larger than 1.5), or a phosphonylated nitroxide stable radical,[4] the key parameter being the control of the concentration of free nitroxide during the polymerization process.

In the case of nitroxide-mediated polymerization of methacrylic esters, low monomer conversions were always found because the formed alkoxyamines are totally converted after a short polymerization time into dead polymer chains by a β-hydrogen transfer reaction from the propagating radicals to TEMPO (also called disproportionation reaction). This reaction leads to the corresponding hydroxylamine and to an ω-unsaturated polymer (Schemes 1 and 2).[5] However, except end-group analysis by NMR spectroscopy, no report on a more thorough characterization of the polymers could be found in the literature. "Livingness", in nitroxide-mediated polymerization of methacrylate derivatives, could only be achieved when those monomers were randomly copolymerized with a larger amount of styrenic monomer. This technique was first reported by Hawker[6] and was further applied for the synthesis of poly(styrene-*b*-(styrene-*co*-*n*-butyl methacrylate)) block copolymer.[7]

Scheme 1



The synthesis of block copolymers with polystyrene as a first block and pure poly(methacrylic ester) as a second block was reported in two papers in which a TEMPO-capped polystyrene was used as a macroinitiator. The first case concerned methyl methacrylate polymerization.[8] The authors reported that initiation of this monomer at 125 °C by the TEMPO-capped polystyrene was only observed when reaction was carried out in the presence of camphorsulfonic acid; otherwise, no shift of the size exclusion chromatography peak could

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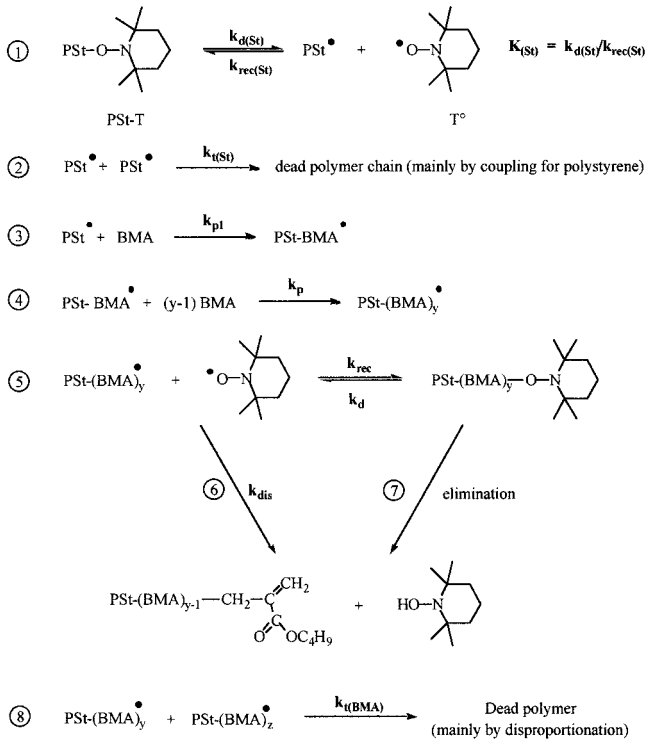
Scheme 2[a–h]



[a] Reaction 1: reversible decomposition of the polystyrene macroinitiator. Equilibrium constant: $K_{(St)} = k_{d(St)}/k_{rec(St)} = [PSt^{\bullet}][T^{\bullet}]/[PSt\text{-}T]$. For polystyrene at 130 °C [ref 17]: $k_{d(St)} = 2.5 \times 10^{-3}$ s^{-1}, $k_{rec(St)} = 1.2 \times 10^{8}$ L mol^{-1} s^{-1}, and $K_{(St)} = 2 \times 10^{-11}$ mol L^{-1}. [b] Reaction 2: irreversible termination between two polystyryl radicals. This reaction can be considered as negligible with respect to the initiation reaction 3. [c] Reaction 3: initiation reaction (reaction of the polystyryl radical with a BMA monomer unit). Rate $= k_{p1}[PSt^{\bullet}][BMA]$; $k_{p1} = 3624$ L mol^{-1} s^{-1} at 130 °C [refs 18, 19] and $k_{p1}[BMA]_0 = 3624 \times 6.3 = 22831$ s^{-1}. Comparison with the rate of reaction 2: rate $= k_{t(St)}[PSt^{\bullet}]^2$ and $k_{t(St)}[PSt^{\bullet}] = k_{t(PSt)} K_{(St)}[PSt\text{-}T]/[T^{\bullet}] < 1$ s^{-1} in the conditions we used with $k_t = 10^9$ L mol^{-1} s^{-1}. [d] Reaction 4: propagation of BMA. $k_p = 3926$ L mol^{-1} s^{-1} at 130 °C [ref 16]. [e] Reaction 5: reversible formation of the TEMPO-based poly(BMA) alkoxyamine. Equilibrium constant: $K = k_d/k_{rec}$. [f] Reaction 6: disproportionation reaction between a poly(BMA) radical and TEMPO. [g] Reaction 7: irreversible decomposition of the TEMPO-based poly(BMA) alkoxyamine. [h] Reaction 8: irreversible termination between propagating poly(BMA) radicals (mainly by disproportionation).

be seen. A bimodal molar mass distribution was obtained and was explained by an incomplete initiation owing to the presence of dead polystyrene chains, the proportion of which increased when styrene conversion in the synthesis of the first block was increased. In the second case, (dimethylamino)ethyl methacrylate was polymerized to provide amphiphilic block copolymers with relatively narrow polydispersities ($M_w/M_n < 1.3$).[9] Total consumption of the polystyrene macroinitiator was reported, but in contrast, monomer conversion was always incomplete, reaching its maximum value in less than 2 h at 125 °C. The poly(methacrylic ester) block length was shown to depend on the macroinitiator initial concentration; the lower the concentration, the longer the block length. Incomplete monomer conversion was explained by irreversible chain termination taking place after the propagation of a limited amount of monomer. However, the authors concluded that a better understanding of the polymerization mechanism was still needed. In both reported cases, polymerization of the methacrylate monomer was not "living".

In the present work, we were interested in the synthesis and characterization of poly(styrene-*b*-methacrylic ester) block copolymers using TEMPO-mediated radical polymerization. Our purpose was to identify the structure of the formed polymer and to understand the parameters that could influence the poly(methacrylate) block length. *n*-Butyl methacrylate (BMA) was chosen as a model monomer and was polymerized in bulk at 130 °C using either a low molar mass alkoxyamine initiator or a self-initiated TEMPO-capped polystyrene macroinitiator. Proton NMR spectroscopy and matrix-assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF MS) were used for investigation of the structure. Effect on the poly(BMA) block length of the initial concentrations of initiator and free TEMPO was also studied.

Experimental Part

Materials. Styrene (St) and *n*-butyl methacrylate (BMA) were distilled under reduced pressure before use. TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl, 98%, from Aldrich) was used without further purification. The 1-phenylethyl TEMPO adduct (PE-T; 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine) was synthesized and purified according to the procedure described by Howell .[10]

Analytical Techniques. Size exclusion chromatography (SEC) was performed using a Waters apparatus working at room temperature with tetrahydrofuran (THF) eluent at a flow rate of 1 mL min^{-1} and equipped with four PL-gel 10μ columns (100, 500, 10^3, and 10^4 Å). A differential refractive index detector was used, and molar masses were derived from a calibration curve based on polystyrene standards.

Proton NMR spectra were recorded with a FT AC200 Bruker apparatus (200 MHz for ^{1}H) in 5 mm diameter tubes, at 25 °C, with $CDCl_3$ as a deuterated solvent and tetramethylsilane as an internal standard.

MALDI-TOF-MS was performed using a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflector modes. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). The polymer solutions (2–5 g L^{-1}) were prepared in THF. The matrices, 1,8-dihydroxy-9[10*H*]-anthracenone (dithranol) or 2,5-dihydroxybenzoic acid (DHB), were also dissolved in THF (10 and 15 g L^{-1} respectively). The polystyrene solution (10 μL) was mixed with 50 μL of the matrix solution. In the case of dithranol/polymer solution, 10 μL of a silver trifluoroacetate solution (2 g L^{-1} in THF) was added to favor ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptides or porphyrine derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems.

Synthesis of the TEMPO-Capped Polystyrene Macroinitiator. The polystyrene macroinitiator (PSt-T) was synthesized by thermal self-initiation of styrene in the presence of TEMPO. A solution of TEMPO in styrene (0.06 mol L^{-1}) was degassed by two freeze–thaw cycles under vacuum. The tube was sealed off and then immersed for 6 h in an oil bath thermostated at 130 °C. After polymerization, the content of the tube was poured under stirring into an excess of methanol. The polymer was isolated by filtration, washed with methanol, and dried. Styrene conversion (6.0 %) was determined by gravimetry, and molar mass was measured by SEC ($M_n = 1820$ g mol^{-1}, $M_w/M_n = 1.09$). The polymer was analyzed by MALDI-TOF mass spectrometry using the DHB matrix without added salt. It has the following structure: D–$(St)_x$–T (Scheme 1), where D represents a Diels–Alder dimer of styrene which is mainly responsible for thermal self-initiation when polymerization is carried out in the presence of nitroxide.[11–13]

Table 1. Free-Radical Polymerization of BMA in Bulk at 130 °C for 6.75 h (Experimental Conditions and Polymer Characterization)

expt	alkoxyamine initiator	alkoxyamine concn (mol L^{-1})	$[TEMPO]_0$ (mol L^{-1})	exptl final monomer conversion (%)	calcd final monomer conversion (%)	M_n (SEC[b])	M_w/M_n (SEC[b])	N_{BMA}[a] (SEC[b])
PE-B1	PE-T	1.4×10^{-3}	1.6×10^{-4}		2.4	16050	1.78	112
PE-B2	PE-T	5.3×10^{-3}	5.0×10^{-4}	2.7	2.9	4710	1.35	33
PE-B3	PE-T	1.0×10^{-2}	1.2×10^{-3}		2.3	3040	1.62	21
PSt-B0	PSt-T	3.9×10^{-2}	0	13		4900	2.08	
PSt-B1	PSt-T	4.0×10^{-2}	5.3×10^{-3}		2.1	2850	1.08	7 (5[c])
PSt-B2	PSt-T	5.1×10^{-3}	8.6×10^{-4}	~1	1.7	5240	1.31	24 (26[c])
PSt-B3	PSt-T	5.1×10^{-3}	5.5×10^{-3}		0.3	2500	1.12	5

[a] Average number of BMA units in the polymer. [b] Calculated on the basis of polystyrene calibration. [c] From ^1H NMR.

Polymerization of BMA. In each experiment, the TEMPO-based alkoxyamine initiator (either PE-T or PSt-T) was dissolved in BMA in the presence of a given amount of added TEMPO. The polymerization procedure was the same as described above. A sufficiently long reaction time (6.75 h) was applied in order to reach the final monomer conversion[5,9] (see Table 1). When initiation was performed with PSt-T, the block copolymer was precipitated into an excess of methanol and dried under vacuum. When the initiator was the low molar mass alkoxyamine PE-T, polymer precipitation could not be easily performed, and the residual monomer was eliminated by vacuum evaporation. In both cases BMA conversion was always very low and, due to the successive precipitation/filtration steps, could not be measured with enough accuracy. Nevertheless, when available, conversions determined by gravimetry are provided in Table 1.

Results and Discussion

Polymerization of BMA Initiated by PE-T. The monomer *n*-butyl methacrylate was first polymerized in bulk using the low molar mass alkoxyamine PE-T as an initiator in the presence of added TEMPO (experiments PE-B1, PE-B2, and PE-B3 in Table 1). After 6.75 h reaction time, a very low monomer conversion was reached (see Table 1), as previously reported.[5,9] The SEC analysis of the crude reaction mixture showed a complete consumption of the PE-T initiator and allowed the determination of the polymer molar mass using a polystyrene calibration (Table 1). After evaporation of the nonconverted monomer, the product was characterized by ^1H NMR spectroscopy (Figure 1). All the characteristic peaks of poly(BMA) were found together with those of a methylene ω-unsaturation (5.4 and 6.1 ppm) and those of an aromatic ring (7.0−7.2 ppm) coming from the attached initiator. No trace of remaining PE-T alkoxyamine could be observed. Moreover, no peak assignable to a terminal TEMPO-based alkoxyamine could be seen; especially, there was no peak at 0.6 ppm that would come from one of the methyl groups on the piperidine ring. Another observation is that the polymer was contaminated by an unsaturated low molar mass species (or a mixture of compounds with similar structures) which could also be observed in the SEC chromatograms (equivalent molar mass = 230 g mol^{-1}). This same molecule was also found when BMA was heated at 130 °C for 6.75 h in the presence of 0.05 mol L^{-1} of TEMPO. In that case, no polymer was recovered, but only this compound, which, although not fully characterized, was assigned to a thermally formed unsaturated dimer or trimer of BMA.[14] Therefore, owing to the existence of this impurity, accurate quantitative analysis of the polymer (degree of polymerization, end functionality) could not be performed, and due to the small amounts of recovered polymer, no thorough purification was undertaken. Thus, MALDI-TOF mass spectrometry was used as a complementary technique for structural investigation, and in contrast to NMR analysis, no elimination of the low molar mass impurities was needed. It was carried out for sample PE-B2, using a dithranol matrix and silver trifluoroacetate as a cationization agent. The complete spectrum is reported in Figure 2 together with an expansion of the region between m/z = 1460 molar mass units (u) and m/z = 1570 u.

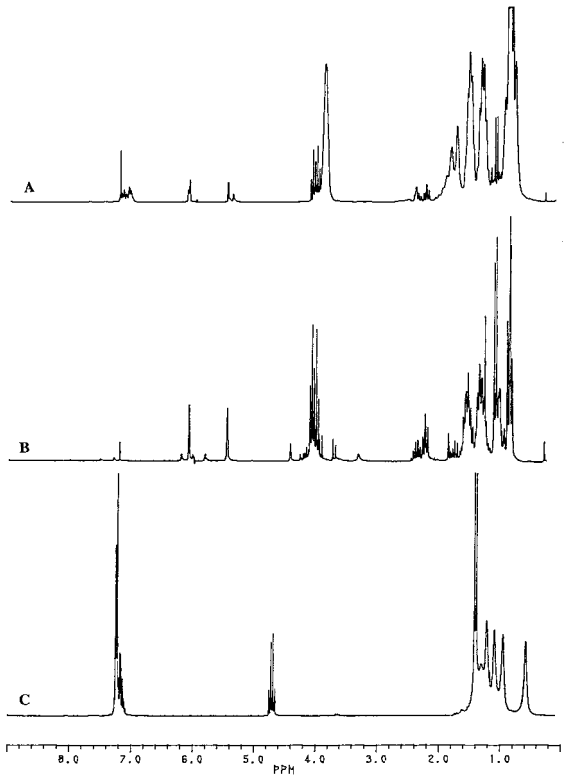


Figure 1. The 200 MHz proton NMR spectra obtained in $CDCl_3$ at room temperature: (A) product of the experiment PE-B2 after vacuum evaporation of the volatile species; (B) product obtained upon heating BMA at 130 °C in the presence of 0.05 mol L^{-1} of TEMPO for 6.75 h (after vacuum evaporation of the volatile species); (C) PE-T unimolecular initiator (2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine).

Two main series can be observed, both corresponding to a molar mass distribution of poly(BMA) with 142.2 u between the peaks. For a given series and a given degree of polymerization, the multiplicity of the peak corresponds to the isotopic distribution which is a function of the various atoms existing in the structure, including the metal cation. As reported in Table 2, the main series (A) could be assigned to poly(BMA) with a phenylethyl group at one end and a methylene unsaturation at the other end and bearing Ag^+ as a metal cation ($[PE-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Ag]^+$). The less in-

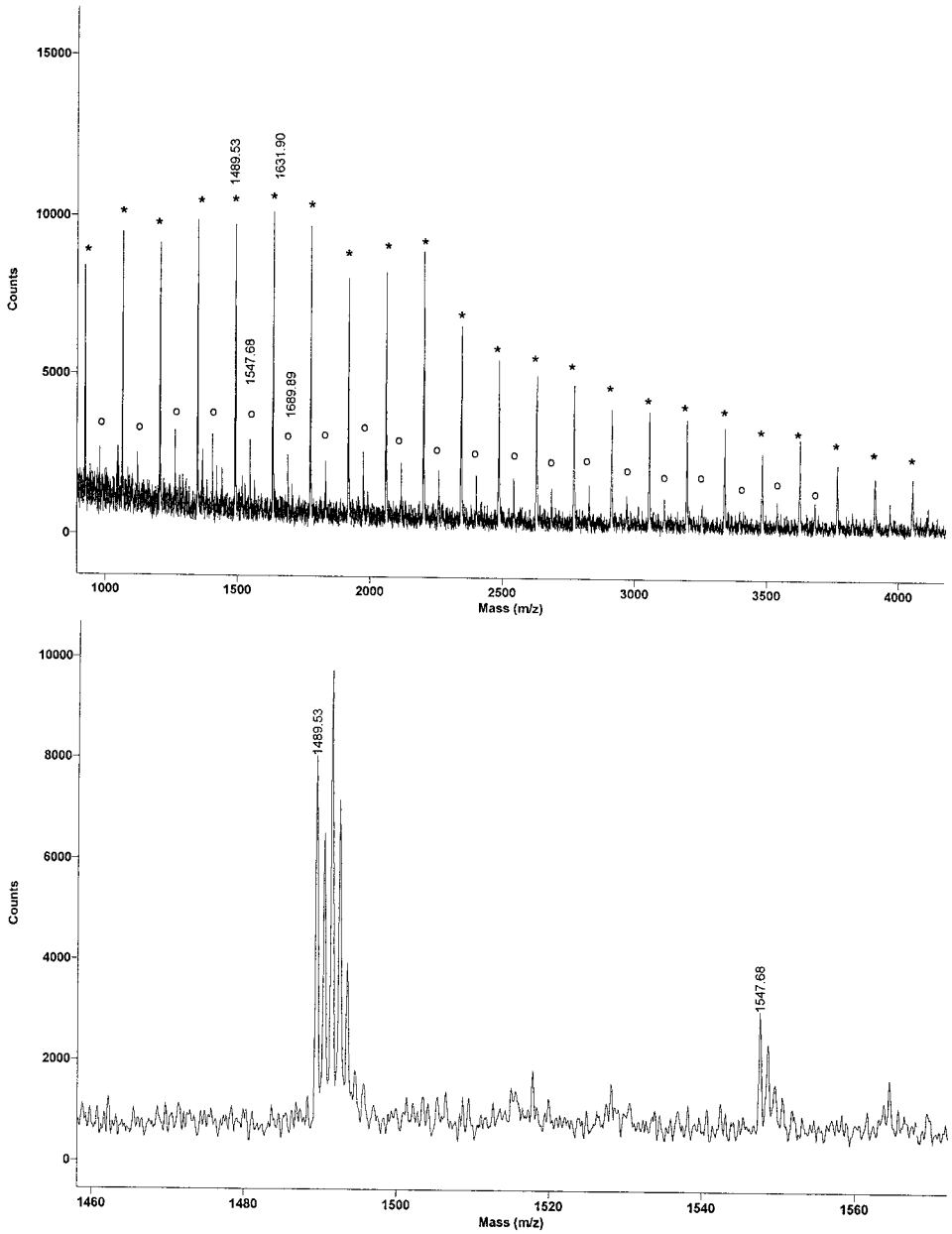


Figure 2. MALDI-TOF mass spectrum of PE-B2 (reflector mode) obtained with dithranol/silver trifluoroacetate matrix and expansion between $m/z = 1460$ u and $m/z = 1570$ u. (★) Series A: $[PE-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Ag]^+$. (○) Series B: $[PE-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Na]^+$.

Table 2. Poly(BMA) Initiated by PE-T: Calculated Molar Mass of the Monoisotopic Peak (First Peak of the Isotopic Distribution) for the Various Possible Structures and Comparison with the Experimental Values

structure	y	calcd molar mass of the monoisotopic peak (u)	exptl molar mass of the monoisotopic peak (u)
$[PE-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Ag]^+$	9	1489.86	1489.53
$[PE-(BMA)_{y-1}-CH_2-CH(COOC_4H_9)-CH_3, Ag]^+$	9	1491.88	no corresponding peak
$[PE-(BMA)_{y-1}-T, Ag]^+$	9	1504.91	no corresponding peak
$[PE-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Na]^+$	10	1548.05	1547.68
$[PE-(BMA)_{y-1}-CH_2-CH(COOC_4H_9)-CH_3, Na]^+$	10	1550.06	no corresponding peak
$[PE-(BMA)_{y-1}-T, Na]^+$	10	1563.09	no corresponding peak

tense series (B) corresponds to a polymer with identical structure but bearing the Na^+ attached cation. In both cases, the experimental isotopic distributions were compared with the theoretical ones (Figure 3). Perfect fitting was observed, which is an indication that each molar mass distribution represents a single structure. Particularly, no saturated polymer could be identified such as ($[PE-(BMA)_{y-1}-CH_2-CH(COOC_4H_9)-CH_3, Ag]^+$) or ($[PE-(BMA)_{y-1}-CH_2-CH(COOC_4H_9)-CH_3, Na]^+$) which would also be formed simultaneously to the unsaturated polymer by a disproportionation reaction between two propagating radicals. Indeed, if such a structure existed, owing to the shift of only 2 molar mass units with respect to the unsaturated compound, no well-separated series would be evidenced but only a discrepancy between the experimental isotopic distribution and the theoretical one (with a broadening of the experimental distribution). Another observation is that

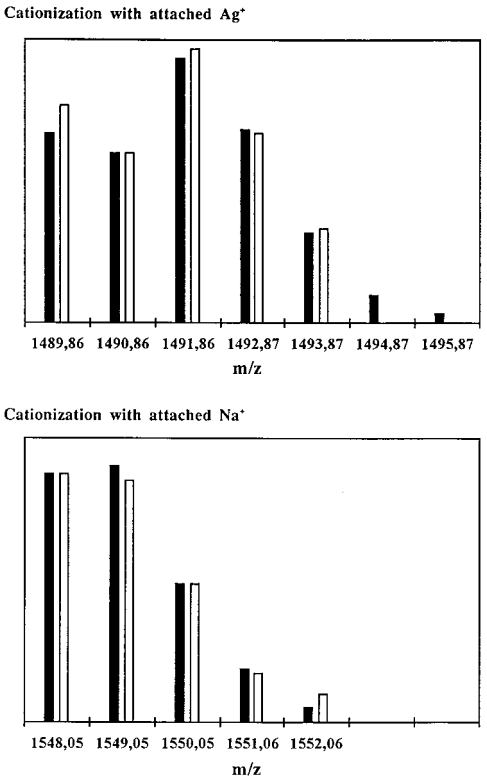


Figure 3. Comparison of the experimental isotopic distribution to the theoretical one for the following structures: $[PE-(BMA)_8-CH_2-C(COOC_4H_9)=CH_2, Ag]^+$ (cationization with Ag^+); $[PE-(BMA)_9-CH_2-C(COOC_4H_9)=CH_2, Na]^+$ (cationization with Na^+). (■) Theoretical distribution; (□) experimental distribution.

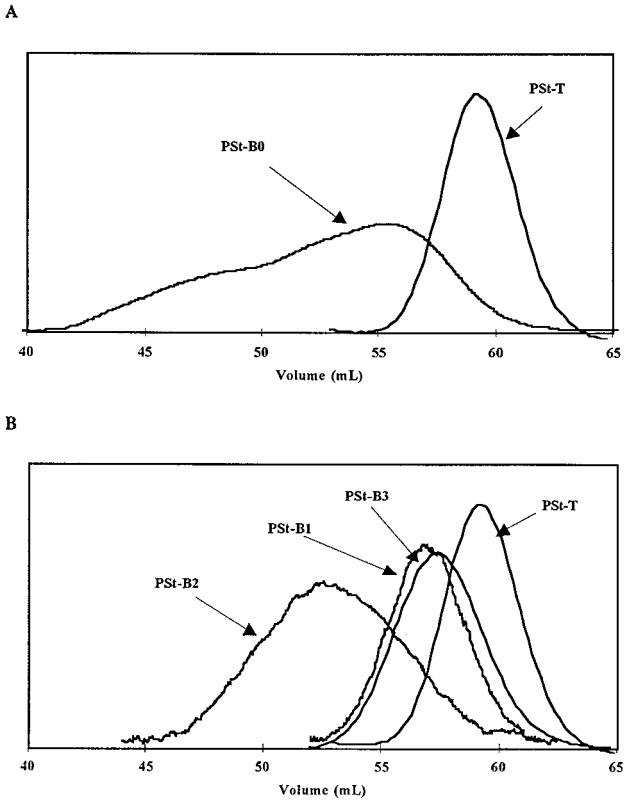


Figure 4. Size exclusion chromatograms for the experiments PSt-B0 (A) and PSt-B1, PSt-B2, PSt-B3 (B) and superposition with the polystyrene macroinitiator PSt-T.

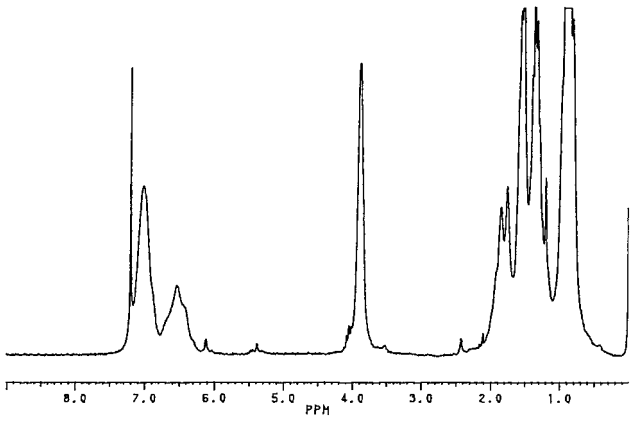


Figure 5. The 200 MHz proton NMR spectrum of PSt-B2 obtained in $CDCl_3$ at room temperature.

no polymer with a TEMPO-based alkoxyamine functionality at the ω-end was detected. It is however possible that, if it existed, this species would be unstable under the MALDI-TOF mass spectrometry conditions. This was shown before for TEMPO-capped polystyrene, which could not be analyzed when using the dithranol matrix with silver trifluoroacetate salt owing to decomposition of the end group and fragmentation of the chain.[13,15] On the basis of the NMR investigation, however, there is a strong evidence for the absence of alkoxyamine-terminated macromolecules. In that case, the MALDI-TOF-MS analysis enables to conclude that all the polymer chains have the same structure with a phenylethyl group coming from the initiator at the α-end and a methylene unsaturation at the ω-end. Therefore, the measured conversions correspond to final ones; no further polymerization was possible owing to the complete disappearance of the alkoxyamine-terminated living chains.

Polymerization of BMA Initiated by PSt-T. In the second part of this study, BMA was polymerized in bulk with initiation by a polystyrene macroinitiator, PSt-T, either with or without added TEMPO in the reaction mixture. As it was also the case when the low molar mass alkoxyamine was used for initiation, no trace of remaining polystyrene macroinitiator could be found after 6.75 h reaction time, indicating complete initiation and, thus, formation of block copolymers. This very efficient reinitiation can be explained by a good structural integrity of the TEMPO-capped polystyrene macroinitiator: the proportion of dead chains was negligible because polymerization was stopped at low styrene conversion. After precipitation into methanol, the block copolymers were analyzed by SEC, ^1H NMR spectroscopy, and MALDI-TOF mass spectrometry. When no free TEMPO was added in the reaction mixture (experiment PSt-B0, Table 1), the resulting polymer had bimodal molar mass distribution as illustrated in Figure 4A. In contrast, when TEMPO was introduced at the beginning of the reaction, the copolymers chromatogram displayed a monomodal peak with narrow molar mass distribution (Table 1 and Figure 4B). As expected, the ^1H NMR spectrum of the copolymer PSt-B2 showed the characteristic peaks of polystyrene and poly(BMA) (Figure 5). Two small peaks at 5.4 and 6.1 ppm were assigned to the two protons of the terminal methylene group.

The block copolymer PSt-B1 was analyzed by MALDI-TOF mass spectrometry using the dithranol/silver trifluoroacetate matrix. No direct comparison with the

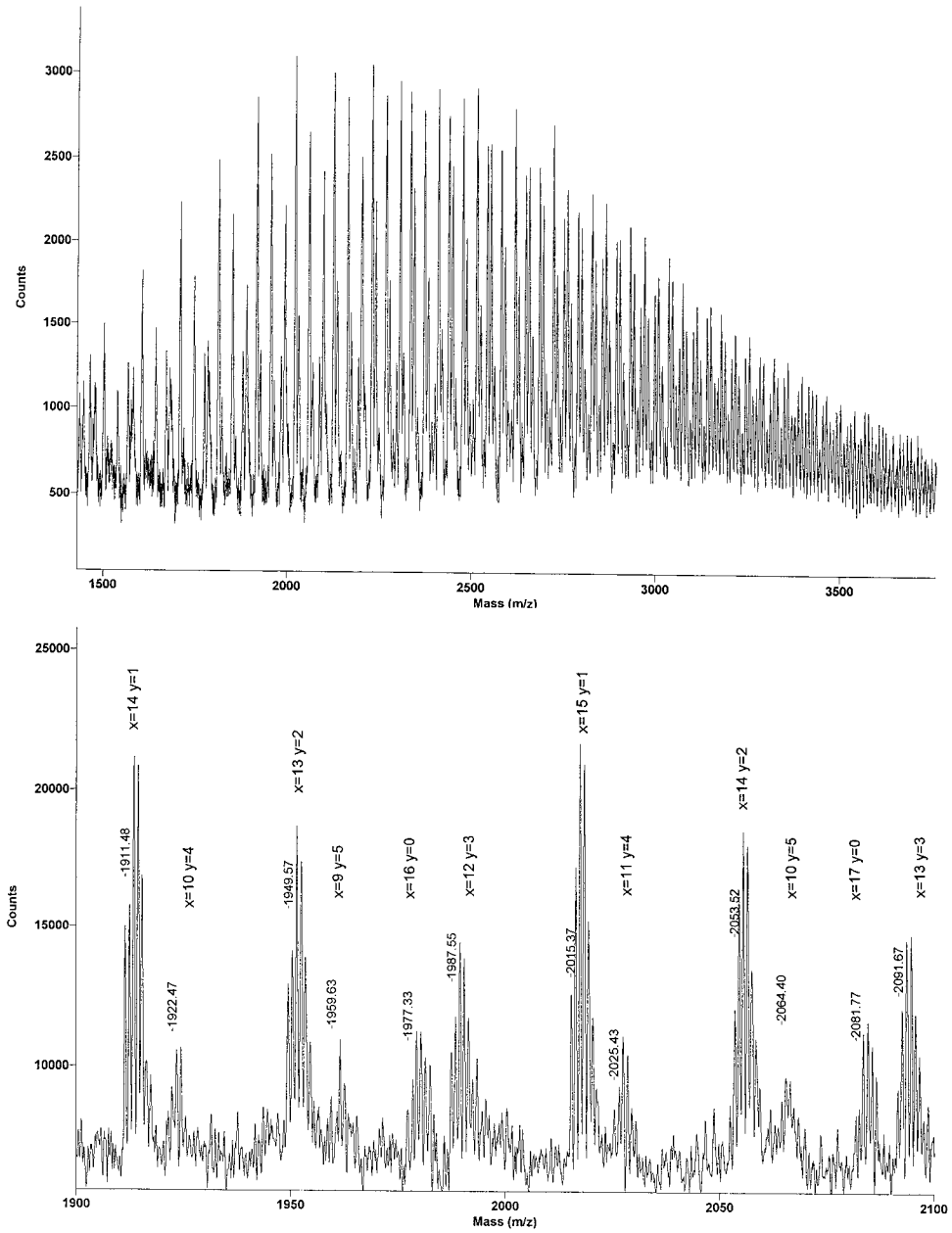


Figure 6. MALDI-TOF mass spectrum of the block copolymer PSt-B1 (reflector mode) obtained with dithranol/silver trifluoroacetate matrix and expansion between $m/z = 1900$ u and $m/z = 2100$ u. Structure is the following: $[D-(St)_x-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Ag]^+$ (see Scheme 1).

polystyrene macroinitiator could be performed under the same analytical conditions since TEMPO-capped polystyrene decomposes during the MALDI experiment when using this matrix.[13,15] The complete spectrum is displayed in Figure 6. The interpretation of block copolymers spectra is made difficult by the superimposition of the respective distributions of each block. However, assignment could be done in an expanded window of the spectrum, between $m/z = 1900$ and $m/z = 2100$ u (Figure 6). All the peaks observed in this expanded window can be assigned to the following structure

$$[D-(St)_x-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2, Ag]^+$$
(see Scheme 1)

with various values of x and y. This means that a block copolymer was formed under the chosen experimental conditions and that, similarly to the poly(BMA) initiated by PE-T, it has the expected structure with a terminal unsaturation. The low amount of unreacted polystyrene macroinitiator which could also be observed in the spectrum ($y = 0$) has an endo terminal unsaturation; this is the signature of dead chains (Scheme 1) which have lost the alkoxyamine functionality during the first step of the synthesis.

Effect of TEMPO Initial Concentration on Final Conversion and on Poly(BMA) Block Length. The various analyses have shown that the poly(BMA) which was formed in the presence of TEMPO had a well-defined structure with a methylene ω-unsaturation, $PE-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2$ or $PSt-(BMA)_{y-1}-CH_2-C(COOC_4H_9)=CH_2$, depending upon the initiator. The absence of an α-end group other than the initiator means that neither chain transfer nor thermal self-initiation occurred. The absence of saturated chains which would form upon termination by disproportionation between two propagating radicals indicates that this reaction is not the main chain

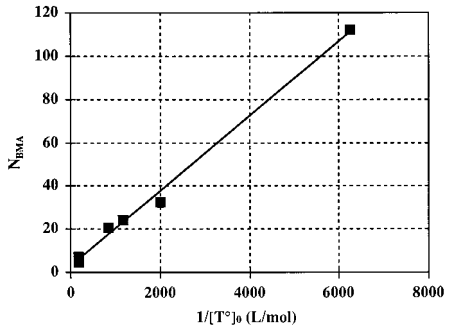


Figure 7. Number of BMA units in the polymers (N_{BMA}) versus $1/[T^\bullet]_0$. Experiments: PE-B1, PE-B2, PE-B3, PSt-B1, PSt-B2, and PSt-B3.

breaking event. Thus, the main termination event is the reaction between a propagating radical and TEMPO. This leads to an ω-unsaturated chain and to the hydroxylamine through a bimolecular process involving hydrogen transfer from the growing polymer to the nitroxide. Decomposition of the intermediate alkoxyamine following a unimolecular elimination mechanism would also lead to the same products. Scheme 2 gives an illustration of the possible reactions that can take place in the polymerization of BMA initiated by a TEMPO-based alkoxyamine in the presence of TEMPO.[5]

The values reported in Table 1 show that the length of the poly(BMA) block is most probably a function of the initial concentration of TEMPO ($[T^\bullet]_0$) which is added in the reaction mixture and not a function of the initial concentration of initiator (experiments PSt-B1, PSt-B2, and PSt-B3): the smaller the value of $[T^\bullet]_0$, the longer the poly(BMA) block. This is illustrated in Figure 7 where the number of BMA units in the polymer (N_{BMA}) is plotted versus the reverse of the initial concentration of TEMPO. A linear relationship is observed.

In a previous publication,[9] the authors had reported that, without addition of TEMPO at the beginning of the reaction, the polymethacrylate block length was dependent on the initial concentration of macroinitiator. This is not in contradiction with our own results since, even if not deliberately added, TEMPO is released in the reaction mixture owing to the initially favored bimolecular termination reactions between two propagating radicals. In that case, the concentration of nitroxide that is reached at the pseudoequilibrium depends on the macroinitiator initial concentration. For experiment PSt-B0, no TEMPO was added in the reaction mixture, and the resulting block copolymer had a broad molar mass distribution with a shoulder on the high molar mass side of the peak (Figure 4A). It was supposed that the high molar mass species were formed initially, when the concentration of TEMPO was not high enough to react with the growing polymer radicals. In that case, the conventional termination reaction was not negligible.

The average degree of polymerization of the poly(BMA) block (N_{BMA}) can be calculated according to the following equation:

$$N_{BMA} = \frac{[M]_0 - [M]_f}{[PSt\text{-}T]_0}$$

where $[M]_0$ is the initial concentration of monomer ($[M]_0 = 6.3$ mol L^{-1} in bulk), $[M]_f$ is the final concentration of monomer, and $[PSt\text{-}T]_0$ is the initial concentration of alkoxyamine initiator. Since the final monomer conversion was always found very low, its concentration does not change dramatically throughout the polymerization. Thus, the concentration of converted monomer can be calculated by

$$[M]_0 - [M]_f = k_p[M]_0 \int [P^\bullet]\, dt$$

where the rate constant of propagation of BMA $k_p = 3926$ L mol^{-1} s^{-1} at 130 °C in bulk[16] and $[P^\bullet]$ is the concentration of propagating poly(BMA) radicals. Considering that the bimolecular mechanism for the TEMPO-induced termination reaction is the major one (reaction 6 in Scheme 2, rate constant k_{dis}) and that radical−radical termination is negligible, the rate of formation of the ω-unsaturated dead chains $P^=$ is

$$\frac{d[P^=]}{dt} = k_{dis}[P^\bullet][T^\bullet]_0$$

where k_{dis} is the rate constant for the disproportionation reaction between $P^\bullet$ and TEMPO and $[T^\bullet]_0$ is the initial concentration of TEMPO. The concentration of TEMPO should not change during the reaction if termination reactions between two growing radicals are negligible. Indeed, the amount of TEMPO that is turned into hydroxylamine should match the initial amount of alkoxyamine initiator. Therefore, the concentration of free nitroxide should remain constant throughout the polymerization and be equal to its initial value.

The final concentration of dead chains is given by

$$[P^=]_f = k_{dis}[T^\bullet]_0 \int [P^\bullet]\, dt = [PSt\text{-}T]_0$$

Therefore, the average degree of polymerization is given by the very simple relationship

$$N_{BMA} = \frac{k_p[M]_0}{k_{dis}[T^\bullet]_0} \qquad (1)$$

In Figure 7, the slope of the plot of N_{BMA} versus $[T^\bullet]_0^{-1}$ was found to be 0.0173 mol L^{-1}, which enables to calculate $k_{dis} = 1.4 \times 10^6$ L mol^{-1} s^{-1}. This value is significantly lower than the rate constant of recombination between a propagating radical and TEMPO (which is usually on the order of magnitude of 10^8 L mol^{-1} s^{-1}). Such a conclusion was previously postulated by Moad et al.[5] although they did not propose any experimental value.

On the basis of reactions 5 and 6 in Scheme 2, and neglecting the less probable reaction 7, the rate of disappearance of a poly(BMA)-based alkoxyamine (PBMA-T) can be calculated according to the following equation:

$$\frac{d[PBMA\text{-}T]}{dt} = -k_{dis}[PBMA^\bullet][T^\bullet]$$

$$= -k_{dis}K[PBMA\text{-}T] \quad (\text{if } k_{dis} \ll k_{rec})$$

$$[PBMA\text{-}T]_t = [PBMA\text{-}T]_0 e^{-k_{dis}Kt} \qquad (2)$$

Then, the monomer conversion can be calculated by

$$-\frac{d[M]}{dt} = k_p[P^\bullet][M] = k_pK\frac{[PBMA\text{-}T]}{[T^\bullet]}[M]$$

which gives, after integration (assuming like previously

that [T•] remains constant),

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = \ln\left(\frac{1}{1 - \text{conversion}}\right) = \frac{k_p[\text{PBMA-T}]_0}{k_{dis}[T^\bullet]_0}(1 - e^{-k_{dis}Kt})$$

At infinite time, a limited value of monomer conversion is reached as given by

$$\ln\left(\frac{[M]_0}{[M]_f}\right) = \ln\left(\frac{1}{1 - \text{final conversion}}\right) = \frac{k_p[\text{PBMA-T}]_0}{k_{dis}[T^\bullet]_0} \quad (3)$$

Calculated values are reported in Table 1 for all the performed polymerizations. A good agreement was observed with the available experimental data. Final conversions can be increased by increasing the [alkoxyamine initiator]$_0$/[T•]$_0$ molar ratio. However, [T•]$_0$ is not always easy to control since, even when not deliberately added or when added at a too low concentration, TEMPO is released in the reaction mixture owing to the initially favored bimolecular termination reactions between two propagating radicals. For instance, for reaction PSt-B0 in which no free TEMPO was added, the final conversion was 13% for an initiator concentration of 3.9×10^{-2} mol L^{-1}. In that case as observed by Lokaj et al.,[9] the final conversion depends on the alkoxyamine initiator concentration.

If one is not aiming for ω-unsaturation, but for a stable alkoxyamine ω-end group, i.e., for controlled nitroxide-mediated radical polymerization of methacrylic ester monomers, the key parameter seems to be the nature of the chosen nitroxide. For that purpose, the lifetime of the corresponding PBMA-T alkoxyamine should be long enough with respect to propagation time. It depends on ($k_{dis}K$), i.e., on the rate constant of disproportionation and on the equilibrium constant of the reversible decomposition. For instance, the half-lifetime of TEMPO-based PBMA-T is only 69 s if $K = 10^{-8}$ mol L^{-1} s^{-1}. (K is supposed to be some orders of magnitude higher for methacrylic esters than for styrene.[5,20]) Therefore, the structure of the nitroxide should be designed in order to decrease the rate constant of disproportionation k_{dis} with respect to the rate constant of recombination, k_{rec}.

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