Synthesis and Characterization of PMMA-*b*-PBMA Block Copolymers by Atom Transfer Radical Polymerization

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ABSTRACT: The synthesis of diblock copolymers using atom transfer radical polymerization, ATRP, of *n*-butyl methacrylate, BMA, and methyl methacrylate, MMA, is reported. These copolymers were prepared from 2-bromoisobutyryl-terminated macroinitiators of poly(MMA) and poly(BMA), using copper chloride, CuCl,/*N,N,N′,N″,N″*-pentamethyldiethylenetretramine, PMDETA, as the catalyst system, at 100°C in bulk and in benzonitrile solution. The block copolymers were characterized by means of size-exclusion chromatography, SEC, and ^{1}H-NMR spectroscopy. The SEC analysis of the synthesized diblock copolymers confirmed important differences in the molecular weight control depending on the reaction medium (solvent effect) and the chemical structure of the macroinitiator used. In addition, differential scanning calorimetry, (DSC) measurements were performed, showing for all the copolymers a phase separation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2683–2691, 2002

Key words: diblock copolymers; polymerization (ATRP); kinetics; differential scanning calorimetry; phase separation

INTRODUCTION

Block copolymers have many useful properties as well as practical and interesting applications.[1] However, their synthesis has been somehow limited due to a variety of factors, such as incompatibility of group or the requirements of extreme reaction conditions.

Atom transfer radical polymerization, ATRP, is a relatively new and versatile method in the synthesis of polymers with controlled molecular weights and low polydispersities.[2] Controlled polymerization in ATRP is achieved by establishing a dynamic equilibrium between the propagating and dormant species, with copper complexes acting as a reversible halogen atom transfer reagent. As a result, the concentration of the propagating species is greatly diminished, and the contribution of termination to the overall reaction is practically suppressed. To satisfy the requirement for low polydispersity, initiation must be fast relative to propagation. Furthermore, at the end of the polymerization, the chain end still contains a halogen group, which can be used to initiate a subsequent polymerization. Therefore, these kinds of polymerization methods provide an efficient tool for macromolecular synthesis and the preparation of a wide range of copolymers, such as block, gradient, and hyperbranched polymers.

ATRP can be applied to block copolymer synthesis in two ways.[3,4] The first one consists in a simple addition of a second monomer to the reaction medium after nearly complete consumption of the first monomer. The second method involves the isolation and purification of the first polymer

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and its consecutive utilization as a macroinitiator. Although the first method is easy to operate, the resulting second block is usually not pure.[5]

It is well known that the block copolymers of (meth)acrylic monomers are interesting because of the morphological, phase, and mechanical properties of such polymers. The variety of these monomers allows the fine tuning of the glass transition temperature, T_g, and the (im)miscibility of the constitutive blocks of the copolymers.[6] In contrast to the number of articles about others acrylic block copolymers, such as *n*-butyl acrylate, BA, and methyl methacrylate, MMA, block copolymers[3,5,7–10] prepared by ATRP, only an article reported by Kotani et al.[11] referred to the preparation of a PMMA-*b*-PBMA-*b*-PMMA triblock copolymer by successive addition of BMA and MMA monomers without isolating the intermediate products. This work was done via transitions of a metal-mediated system, using a ternary initiating systems that consists of carbon tetrachloride, tris(triphenylphosphine)ruthenium dichloride, $[RuCl_2(PPh_3)_3]$, and aluminum compounds such as $MeAl(ODBP)_2$ (ODBP, 2,6-di-*tert*-butylphenoxy), and $Al(OiPr)_3$.

In this article the synthesis by ATRP of poly(methyl methacrylate)-*block*-poly(*n*-butyl methacrylate), PMMA-*b*-PBMA is reported. For this purpose, two macroinitiators are obtained from ATRP of MMA and BMA using ethyl-2-bromoisobutyrate as the initiator and copper bromide/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine as the catalyst system at 100°C. From the performed macroinitiators block copolymers are obtained in bulk and in benzonitrile solution using a mixed halide system as the catalyst. The first family of block copolymers are prepared from the chain extension of poly(*n*-butyl methacrylate) with MMA. The second one is performed by the resumption of poly(methyl methacrylate) with BMA.

EXPERIMENTAL

Materials

Methyl methacrylate, MMA (98%, Merck) and *n*-butyl methacrylate, BMA (98%, Merck) were passed through an alumina column and distilled prior to use.

Ethyl 2-bromoisobutyrate, EBrIB (99%, Aldrich), copper bromide, CuBr (99.999%, Aldrich), copper chloride, CuCl (99.99% Aldrich), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, PMDETA (99%, Aldrich), and benzonitrile, Bzn (anhydrous 99%, Aldrich) were used as received.

Polymerizations

Polymerizations were carried out in Pyrex tube ampoules sealed off at high vacuum in a thermostatic oil bath at 100.0°C, regulated with a precision of ±0.1°C. After a desired time, the reaction mixture was passed through over alumina to remove the catalyst, and then rotated-evaporated to eliminate the eluent. The solution was poured into a large excess of methanol. Finally, the polymers were dried under vacuum until reaching constant weight. Polymer yields were determined by gravimetry.

Polymers Characterization

The molecular weight distributions were measured by size-exclusion chromatography, SEC, using a chromatographic system (Waters Division Millipore) equipped with a Waters Model 410 refractive index detector. Tetrahydrofuran, THF (Scharlau) was used as eluent at a flow rate of 1 cm^3/min operated at 35°C. Styragel-packed columns, HR1, HR3, HR4E, and HR5E were used. Poly(methyl methacrylate) standards, PMMA (Polymer Laboratories LTD) in the range between $1.4\ 10^6$ and $5.0\ 10^2$ g mol^{-1} were used to calibrate the columns. PBMA samples were analyzed using the calibration curve obtained with poly(MMA) standards and Mark-Houwink constants taken from the literature.[12]

^{1}H-NMR spectroscopy was used to determine copolymer compositions and molecular weight. Spectra were recorded at 50°C on about 8% solutions in deuterochloroform by using a Varian Oxford 300 spectrometer operating at 300 MHz. Typical parameters for the proton spectra were a 9-μs pulse width (45°), pulse delay 0 s, acquisition time 3 s, 400 Hz spectral width, and 256 scans.

Glass Transition Temperatures

Differential scanning calorimetry measurements were performed in a Perkin-Elmer DSC/TA7DX, PC series with an Intracooler for low temperatures. The temperature scale was calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples (~20 mg) weighed were heating up from 0 to 150°C at 10°C/min rate under dry nitrogen (20 cm^3/min).

The actual value for the glass transition temperature, T_g, was estimated as the temperature at the midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The current value is the average for several measurements realized for each sample.

RESULTS AND DISCUSSION

Preparation of Macroinitiators

Although there are numerous works about ATRP of MMA, the studies concerning living radical polymerization of BMA are scarce.[11,13–15] Therefore, homopolymerizations of BMA were performed by ATRP by using EBrIB as the initiator, 1 molar equivalent of CuBr as the catalyst, and 1 molar equiv. of PMDETA as the ligand (both relative to ethyl 2-bromoisobutyrate), ([BMA] : [EBrIB] : [CuBr] : [PMDETA] = 200 : 1 : 1: 1). These reactions were performed at 100.0°C in bulk and also in benzonitrile (25% v/v) solution. This solvent has a notable influence on the ATRP of MMA, because it improves the initiation efficiency without appreciable modification on the polymer polydispersity.[16]

As seen in Figure 1(a), relatively straight lines in the semilogarithmic plot of conversion vs. time are obtained for BMA homopolymerizations, indicating a constant number of propagating species throughout the polymerization. From the slope the apparent propagation constant, k_p^{app}, is obtained, which, in the case of bulk polymerization, is $3.5\ 10^{-4}\ \mathrm{s}^{-1}$. A higher value, $k_p^{\mathrm{app}} = 5.7\ 10^{-4}\ \mathrm{s}^{-1}$, is found in benzonitrile solution. Nevertheless, in both kinetics, a deviation from linear first-order occurs at monomer conversion around 50%. A similar phenomenon has also been observed in other systems,[14,16–18] which can be explained as a consequence of some side reactions. The differences on polymerization rates observed between bulk and benzonitrile solution are unexpected, because the decrease of monomer, initiator, and catalyst concentrations would lead to a reduction on the polymerization rate.[19] Thus, when benzonitrile is used in the reaction medium a remarkable solvent effect is observed. This fact has also been often observed in other polymerization systems[16,19] and is ascribed to an increase of the initiation efficiency.

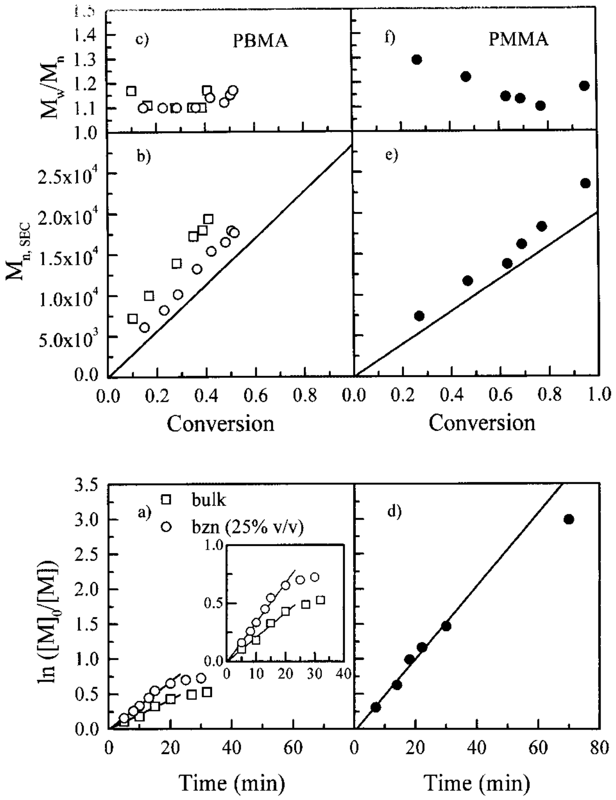

Figure 1 (a) Semilogarithmic kinetic plots for the homopolymerization of *n*-butyl methacrylate in bulk and 25% v/v benzonitrile solution at 100°C. [BMA] : [EBrIB] : [CuBr] : [PMDETA], 200 : 1 : 1 : 1. (b) Dependence of PBMA number-average molecular weight, $M_{n\mathrm{SEC}}$, with monomer conversion. (c) Dependence of PBMA polydispersity, M_w/M_n, with monomer conversion. (d) Semilogarithmic kinetic plot for the homopolymerization of methyl methacrylate in bulk at 100°C. [MMA] : [EBrIB]: [CuBr] : [PMDETA], 200 : 1 : 1 : 1. (e) Dependence of PMMA number-average molecular weight, $M_{n\mathrm{SEC}}$, with monomer conversion. (f) Dependence of PMMA polydispersity, M_w/M_n, with monomer conversion.

The dependence of molecular weight and molecular weight distribution with conversion for PBMAs obtained is depicted in Figure 1(b) and 1(c), respectively. Although, the experimental number-average molecular weights, M_n (SEC analysis), are higher than those theoretically predicted, larger differences are found in the samples prepared in bulk than those obtained when the homopolymerizations were performed in benzonitrile solution. An initiation efficiency, *f*, of 0.80 ($f = M_{n,\ \mathrm{th}}/M_{n,\ \mathrm{SEC}}$) is calculated for the benzonitrile solution, and a value of 0.60 is determined for bulk. However, a linear increase on molecular weight with monomer conversion is observed, and polydispersities remain quite low ($M_w/M_n \leq 1.2$) throughout the reaction.

MMA was polymerized in bulk with the same experimental conditions as BMA. Figure 1(d) shows a first-order kinetic plot over almost all conversion range, with a k_p^{app} value of 8.4 10^{-4} s^{-1} · M_ns increase linearly with the conversion [Fig. 1(e)], with values slightly higher than calculated ones, and narrow polydispersities (M_w/M_n = 1.3–1.1), which decrease as the conversion increases [Fig. 1(f)]. Similar results have been found in the literature for the ATRP of MMA using this type of multidentate amine ligands[3,20–23] where it has been successfully demonstrated their use as new ligands in the copper-mediated atom transfer radical polymerization.

Comparing the rate polymerization obtained in bulk for MMA and BMA using the same catalyst/initiator system it can be observed that an increase in the size of the ester group produces a decrease in the rate of polymerization by a factor of approximately 2. This result is the opposite to that observed in classical free radical polymerization where a slight increase on propagation rate constant, k_p, is found from BMA to MMA. According to Beuermann et al.,[24] the absolute propagation rate constant for *n*-butyl methacrylate obtained by pulsed laser experiments is 2361 M^{-1} s^{-1} (extrapolated) at 100°C, whereas for methyl methacrylate[25] it is 1976 $M^{-1}s^{-1}$. Therefore, the concentration of active species is higher in the case of MMA, and the equilibrium is clearly shifted toward the dormant species in the case of BMA compared to MMA.

PBMA-Br selected as macroinitiator was obtained in benzonitrile solution where higher initiation efficiency was found. PMMA-Br macroinitiator was synthesized in bulk. In addition, the macroinitiators were selected at conversion where ln $[M]_o/[M]$ is linear to maintain a high-end functionality and therefore, to ensure a good blocking efficiency.

Preparation of Block Copolymers from PBMA Macroinitiator

The copolymerization reactions were performed in bulk and in 25% v/v benzonitrile solution at 100°C, using an exchange halide macroinitiator/catalyst system ([MMA]:[PBMA-Br]: [CuCl] : [PMDETA] = 1100 : 1 : 1 : 1). Recent studies have shown the copper(I) chloride complexed with simple linear amine ligands, and in association with bromo-terminated macroinitiators, are successfully used for preparation of several block copolymers, such as polystyrene-*block*-poly(*t*-butyl acrylate)[26] poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate),[5] and poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate)[9]. The success is due to the fact that the Br group initially provides fast initiation, but the replacement of the bromide atom at the chain end by chloride shortly after the polymerization is started. This allows diminishment of the termination reactions by decreasing the radical concentration, while the initiation is maintained fast by comparison with propagation.[27–30] Hence, the rate of initiation is increased relative to the propagation rate, thereby improving initiation efficiency.[3]

The employed macroinitiator had M_n = 15,400 with M_w/M_n = 1.1 for the reactions in bulk and solution. Figure 2(a) displays a linear dependence of ln $[M]_o/[M]$ with the time for both polymerizations, which indicates that the concentration of growing radical is constant. The value of k_p^{app} obtained for each polymerization is the same, 2.2 10^{-4} s^{-1}, although a lower k_p^{app} value should be expected for benzonitrile solution because of a dilution effect.

The ratio between the k_p^{app} values obtained in the MMA homopolymerizations using EBrIB and PBMA-Br is the same as the ratio between the initiator concentrations. This seems to indicate that the chain length of the macroinitiator does not have appreciable influence on the initiation efficiency. However, it is important to note that these values have to be taken with caution because an exchange halide is used in the block copolymerization from the macroinitiator.

Figure 2(b) and (c) contains the plots of the number-average molecular weight and polydispersity values vs. conversion, respectively. The molecular weight of the copolymers, experimentally determined by SEC, increased linearly with monomer conversion, being in good agreement with the theoretical values. At the same time the polydispersities remain narrow.

The molecular weight distribution curve of the macroinitiator and some of these diblock copolymers are shown in Figure 3(a) and (b). As can be observed in Figure 3(a), the samples prepared in bulk did not show the remaining PBMA macroinitiator, even at low MMA conversion. Moreover, a clear shift is found on the distribution curves with the monomer conversion. These curves were monomodal through the copolymerization reaction, and there was not a significant tail on the low molecular weight side of the copolymer MWDs. The increase of the molecular weight, without a significant increase in M_w/M_n, indicates that an effective initiation of methyl methacrylate ATRP takes place and the polymerization appears to proceed in a controlled manner. The differences of the MWD curves for PBMA-*b*-PMMAs prepared in bulk with those samples synthesized in solution [Fig. 3(b)] are not relevant. However, copolymers prepared at low conversions in benzonitrile solution show bimodality because of the macroinitiator. The amount of PBMA macroinitiator is very small, and disappears with the conversion. No remainders of macroinitiator are presented after 25% of the monomer is consumed. The polydispersities decrease as the polymerization proceeds, indicating a good control of the system in solution. Although, from the conversion–time plots MMA polymerization initiated by PBMA-Br in bulk is apparently equal to that in benzonitrile solution, the remainder PBMA-Br macroinitiator in the MWD curves at low MMA conversion seems to indicate a slightly slower polymerization rate in solution.

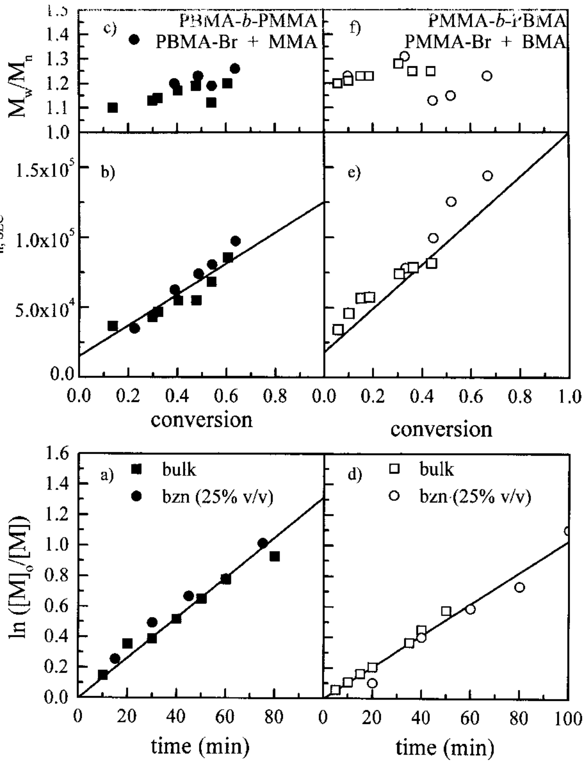

Figure 2 (a) Semilogarithmic kinetic plots for ATRP of MMA using PBMA-Br as macroinitiator in bulk and 25% v/v benzonitrile solution at 100°C. [MMA] : [PBMA-Br] : [CuCl] : [PMDETA], 1100 : 1 : 1 : 1. (b) Dependence of PBMA-*b*-MMA number-average molecular weight, $M_{n,\mathrm{SEC}}$, with monomer conversion. (c) Dependence of PBMA-*b*-MMA polydispersities, M_w/M_n, with monomer conversion. (d) Semilogarithmic kinetic plots for ATRP of BMA using PMMA-Br as the macroinitiator in bulk and 25% v/v benzonitrile solution at 100°C. [BMA] : [PMMA-Br] : [CuCl] : [PMDETA], 1100 : 1 : 1 : 1. (e) Dependence of PMMA-*b*-BMA number-average molecular weight, $M_{n,\mathrm{SEC}}$, with monomer conversion. (f) Dependence of PMMA-*b*-BMA polydispersities, M_w/M_n, with monomer conversion.

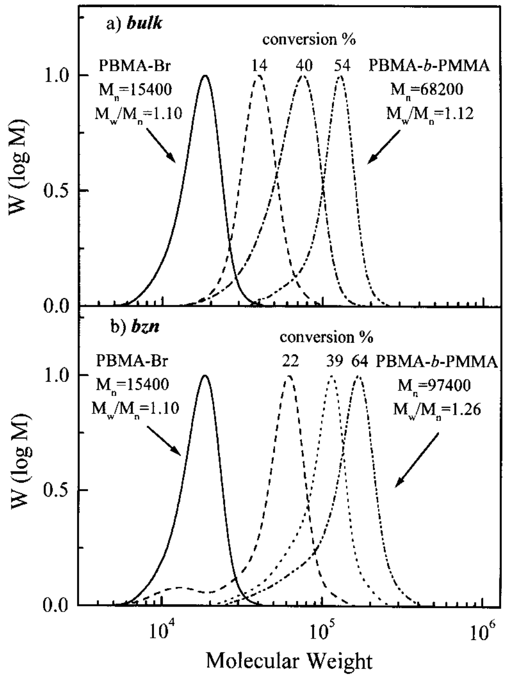

Figure 3 (a, b) MWD curves for ATRP of MMA using PBMA-Br as the macroinitiator at 100°C in bulk and 25% v/v benzonitrile solution, respectively. [MMA] : [PBMA-Br] : [CuCl] : [PMDETA], 1100 : 1 : 1 : 1.

^{1}H-NMR spectroscopy was used to complete the characterization of block copolymers. Figure 4 shows spectra of PBMA-Br macroinitiator and various PBMA-*b*-PMMA copolymers performed at different conversion degrees. In addition, the spectrum of PMMA is also displayed. The presence of both blocks derived from BMA and MMA and the increase in the amount of MMA in the polymer with reaction time are observed. RMN spectra allow determination of the molar composition from the relative intensity of the resonance signals at 4.04 ppm (—OCH_2 protons of the butyloxy) for *n*-butyl methacrylate and at 3.60 ppm

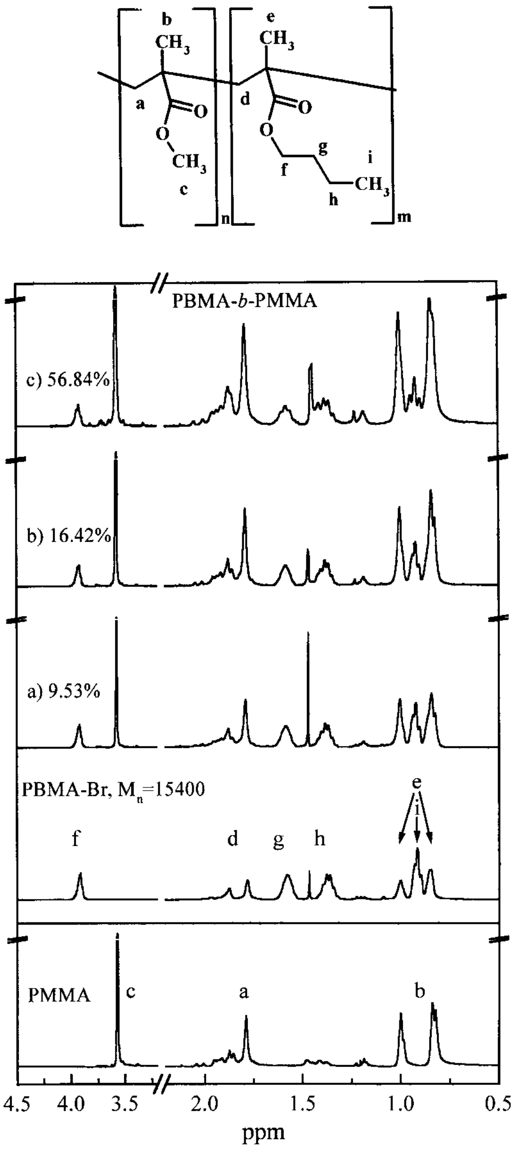

Figure 4 ^{1}H-NMR spectra of the PBMA-Br macroinitiator, PMMA, and PBMA-*b*-PMMA copolymers.

(—OCH_3 of the methyloxy) for methyl methacrylate. Based in the knowledge of the macroinitiator molecular weight and the molar fraction composition of the block, the molecular weight of the copolymers can be calculated using the equation:[8]

$$M_{n,\mathrm{NMR}} = M_{n,\mathrm{PBMA\text{-}Br}} + (\mathrm{F}_{\mathrm{MMA}}/1-\mathrm{F}_{\mathrm{MMA}})(M_{n,\,\mathrm{PBMA\text{-}Br}})(M_o{}^{\mathrm{MMA}}/M_o{}^{\mathrm{BMA}})$$

$M_{n,\mathrm{PBMA\text{-}Br}}$ being the number-average molecular weight of macroinitiator, F_{MMA} the molar fraction of methyl methacrylate in the copolymer, and M_o^{MMA} and M_o^{BMA} the molar mass of both monomers.

Table I shows the kinetic data and the molecular weights measured by SEC, ^{1}H-NMR, and the theoretical ones, $M_{n,\mathrm{th}}$, ($M_{n,\mathrm{th}}$ = [MMA]/[Macroinitiator] × conversion + $M_{n,\mathrm{PBMA\text{-}Br}}$) of these copolymers. They are in good agreement, indicating efficient diblock copolymers formation.

Preparation of Block Copolymers from PMMA Macroinitiator

The copolymerization reactions were carried out on identical experimental conditions than those mentioned before for PBMA-*b*-PMMA copolymer synthesis. Figure 2(d) shows the trend of a semilog plot with the reaction time for the extension reaction of PMMA-Br with BMA carried out in bulk and in benzonitrile solution, using an exchange halide macroinitiator/catalyst system ([BMA] : [PMMA-Br] : [CuCl] : [PMDETA] = 1100 : 1 : 1 : 1). The linearity of the kinetic plot for bulk and benzonitrile solution suggests a constant number of actives species during the polymerization. The two kinetics present practically the same values of the polymerization apparent rate constant (k_p^{app} = 1.7 10^{-4} s^{-1}). Assuming a first order with respect to initiator concentration, k_p^{app} obtained when the system is initiated by the macroinitiator is slightly higher than when EBrIB is used as initiator. This means that the macroinitiator have not virtually lost the active center before and after BMA addition.

The molecular weight increases linearly with conversion, and polydispersity remains narrow [Fig. 2(e) and (f)]. Again, the main criteria for the controlled radical polymerization of BMA are also fulfilled.

The MWD curves of the macroinitiator and the products of the chain extension with BMA reaction as a function of monomer conversion are shown in Figure 5(a) and (b). The evolution of these curves shows the slow disappearance of the macroinitiator, which is responsible for the bimodality at least up to the BMA conversion of ca. 40% for bulk and benzonitrile solution copolymerization. When the EBrIB initiator is used, the MMA is polymerized with higher k_p^{app} than the BMA. A similar behavior is observed by comparison of Figure 2(a) with (d). As previously stated, BMA has a polymerization rate lower than MMA as a consequence of increasing the concentration of the dormant species. Then, the observed bimodality can be explained by this fact.

Table I BMA–MMA Block Copolymer Synthesis Using PBMA as Macroinitiator (M_n = 15,400; M_w/M_n = 1.10) and Catalyzed by CuCl/PMDETA at 100°C.

Solvent	Time (min)	Conversion (%)	Composition (^{1}H-NMR) BMA : MMA	$M_{n\ \mathrm{NMR}}$	$M_{n\ \mathrm{theo}}$	$M_{n\mathrm{SEC}}$	M_w/M_n
Bulk	10	13.7	39:61	15.4K + 17.1K	30,500	36,900	1.10
	20	29.8	25:75	15.4K + 32.7K	48,200	43,100	1.13
	30	32.1	23:77	15.4K + 36.5K	50,700	46,700	1.14
	40	40.3	21:79	15.4K + 41.0K	59,700	54,800	1.17
	50	47.7	17:83	15.4K + 53.2K	67,900	55,100	1.19
	60	54.0	16:84	15.4K + 57.2K	74,800	68,200	1.12
	80	60.5	15:85	15.4K + 61.8K	82,000	85,700	1.20
Bzn (25% v/v)	15	22.4	27:73	15.4K + 29.5K	40,000	35,000	1.38
	30	38.9	21:79	15.4K + 41.0K	58,200	62,500	1.20
	45	48.7	18:82	15.4K + 49.6K	69,000	74,000	1.23
	60	54.2	16:84	15.4K + 57.2K	75,000	80,800	1.19
	75	63.7	14:86	15.4K + 66.9K	85,500	97,400	1.26

Similarly as described before, copolymer composition and the number-average molecular weights were determined by ^{1}H-NMR spectroscopy. The results from these copolymerizations as well as the theoretical ones are collected in Table II. The SEC and NMR number-average molecular weights are also in concordance with the theoretical ones.

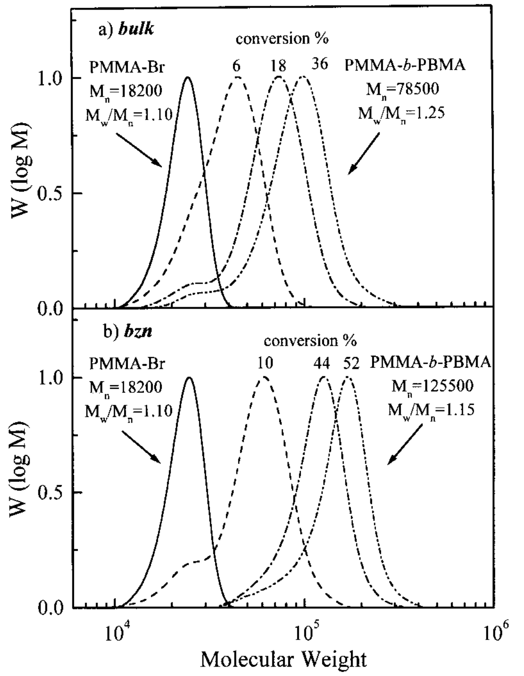

Figure 5 (a, b) MWD curves for ATRP of BMA using PMMA-Br as the macroinitiator at 100°C in bulk and 25% v/v benzonitrile solution, respectively. [BMA] : [PMMA-Br] : [CuCl] : [PMDETA], 1100 : 1 : 1 : 1.

Analysis of the Glass Transition Temperature

The phases study of diblock copolymers was carried out by measuring their glass transition temperatures. The experiments were performed for two different series of diblock copolymers. The first group contains diblock copolymers, which are constituted by a BMA constant block length and an MMA block, where the length is changing. The second one contains copolymers, which are constituted by an MMA constant block length and a BMA block, where the length is varying.

The glass transition temperatures were measured for copolymers, where the SEC curves indicate the absence of macroinitiator.

The glass transition temperature of the BMA macroinitiator (constant block on the first set) was 33.1°C. Likewise, the glass transition temperature of the MMA macroinitiator (constant block on the second set) was 109.4°C. Their values are lower than those found in the literature for homopolymers synthesized by conventional free radical polymerization.[31] This is expected, because the glass transition temperature decreases as does the molecular weight.

The glass transition temperatures of copolymers synthesized from the PBMA macroinitiator are collected in Table III. The results obtained indicate that, in our experimental conditions, the length of the MMA block does not sensitively affect T_g. The first scan of heating is performed

Table II MMA–BMA Block Copolymer Synthesis Using PMMA as Macroinitiator (M_n = 18,200; M_w/M_n = 1.10) and Catalyzed by CuCl/PMDETA at 100°C

Solvent	Time (min)	Conversion (%)	Composition (^{1}H-NMR) MMA : BMA	$M_{n\ \mathrm{NMR}}$	$M_{n\ \mathrm{theo}}$	$M_{n\mathrm{SEC}}$	M_w/M_n
Bulk	5	5.6	69:31	18.2K + 11.6K	27,000	34,200	1.20
	10	10.1	53:47	18.2K + 22.9K	44,300	45,700	1.21
	15	15.0	45:55	18.2K + 31.6K	54,100	56,700	1.23
	20	18.5	43:57	18.2K + 34.3K	57,200	57,300	1.23
	35	30.6	37:63	18.2K + 44.0K	68,200	74,000	1.28
	40	36.3	32:68	18.2K + 54.9K	74,900	78,500	1.25
	50	45.8	26:74	18.2K + 73.6K	89,700	81,700	1.25
Bzn (25% v/v)	20	9.7	50:50	18.2K + 25.8K	36,000	46,100	1.23
	40	33.1	38:62	18.2K + 42.2K	69,900	78,200	1.31
	60	44.5	27:73	18.2K + 69.9K	87,700	99,600	1.13
	80	51.9	26:74	18.2K + 73.6K	99,300	125,500	1.15
	100	66.8	22:78	18.2K + 91.6K	122,500	144,000	1.23

after decreasing the temperature from room temperature to 0°C, then, the sample is heated up to 150°C. Two separate T_gs are observed for block copolymers synthesized from this macroinitiator. Consecutively to the heating process, the sample was cooled down at the same rate. After a new successive heating run, the phase separation disappears and only one T_g is observed. However, the repetition of this measurement when the sample pan is kept at room temperature for 1 day shows the phase separation. As mentioned above, after cooling at 10°C/min and then heated again, the phase separation does not appear. Therefore, for these copolymers a long time is necessary to reach the segregation within the phases. The existence of these two T_gs announces that these block copolymers present phase-separated morphologies. The lower T_g phase, T_{g1}, is predominantly comprised of a BMA segment, which is saturated with an MMA segment to the limit of miscibility. Likewise, the higher T_g phase, T_{g2}, is of an MMA block saturated with a BMA block.

The block copolymers synthesized from the PMMA macroinitiator present two separate T_gs, which are in Table III. It is important to note that the BMA block length does not appreciable modify the glass transition temperatures. Furthermore, the two T_gs also appear in the second scan. Therefore, when the length of the MMA block is constant and the length of the BMA increases, the cooling rate is slow enough to allow the phase segregation. In this case, the range of phase separation is practically identical than that found for the copolymers synthesized with the BMA macroinitiator. In both systems, PBMA-*b*-PMMA and PMMA-*b*-PBMA, this behavior could indicate that for these compositions and molecular weight the copolymer phase separation pro-

Table III Characterization of the Diblock Copolymers

	Solvent	$M_{n,\ \mathrm{RMN}}$	M_w/M_n	Composition (^{1}H-RMN) BMA : MMA	T_{g1} (°C)	T_{g2} (°C)
PBMA-*b*-PMMA	Bulk	15.4K + 17.1K	1.10	39:61	35.2	116.7
		15.4K + 32.7K	1.13	25:75	35.3	110.7
		15.4K + 41.0K	1.17	21:79	37.6	121.0
		15.4K + 61.8K	1.20	15:85	40.5	106.3
PMMA-*b*-PBMA	Bzn (25% v/v)	18.2K + 69.9K	1.13	73:27	38.4	111.1
		18.2K + 73.6K	1.15	74:26	36.3	113.0
		18.2K + 91.6K	1.23	78:22	37.5	114.3

duced is almost complete, because the T_gs are very similar to those of the corresponding pure segments.

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