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The importance of solvent polar character on the synthesis of PMMA-*b*-PBA block copolymers by atom transfer radical polymerization

Marta Fernández García, José Luis de la Fuente, Marina Fernández-Sanz,
Enrique López Madruga*

Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006, Madrid, Spain

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Abstract

The synthesis of diblock copolymers using atom transfer radical polymerization (ATRP), of methyl methacrylate (MMA), and butyl acrylate (BA), is reported. These copolymers were prepared from bromo-terminated macroinitiators of poly(MMA) and poly(BA), using copper chloride, CuCl,/N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), as 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 the importance of solvent on the molecular weight control. In addition, differential scanning calorimetry (DSC), measurements were performed, showing for all the copolymers a phase separation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PMMA-*b*-PBA block copolymers; Bulk and solution ATRP; Glass transition temperature

1. Introduction

Synthesis of (meth)acrylic block copolymers has industrial advantages since they can cover a large range of glass transition temperatures only by varying the alkyl substituent of the ester group. In addition, poly(alkyl methacrylates) and poly(alkyl acrylates) are immiscible, except in the case of small alkyl groups and low molecular weight [1].

Atom transfer radical polymerization (ATRP), is a relatively new and versatile method in the synthesis of polymers with controlled molecular weights and low polydispersities [2–9]. ATRP can be applied to block copolymer synthesis in two ways [10,11]. The first one consists of 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 and its utilization as a macroinitiator. Although the first method is easy to operate, the resulting second block is usually not pure [12].

There are two factors that govern the success of block copolymer synthesis using ATRP: chain end functionality and cross-propagation efficiency [13]. Producing fully functionalized chains requires the minimization of termination and transfer reactions, and can be increased by altering the reaction conditions. Efficient cross-propagation depends on relative reactivity ratios, propagation rate constants and equilibrium constants of both macroinitiator and growing chain.

Recently, there have been several reports on the synthesis by ATRP of acrylic di and triblock copolymers [10,12,14–18]. However, these papers were mainly focused on the preparation of triblock copolymers constituted by two outer blocks of methyl methacrylate (MMA), and an inner block of butyl acrylate (BA). Jérôme's group [15–17] carried out the synthesis and characterization of poly(MMA)-*b*-poly(BA)-*b*-poly(MMA) by two-step ATRP catalyzed by $NiBr_2(PPh_3)_2$. On the other hand, Matyjaszewski's group [10] has described the synthesis of diblock copolymers of methyl methacrylate with either butyl acrylate or methyl acrylate, paying attention to the functionality and the initiation efficiency of the macroinitiator. They have demonstrated that, in general, macroinitiators of PMMA provides a good efficiency, however, using polyacrylates as macroinitiators requires that the end group is Br and as catalyst CuCl. In one article, this group [12] presented the one-pot synthesis of the di and triblock, where the monomers are added in a sequential manner. The experiments were always performed using BA as first monomer, halide exchange techniques and multidentate amines as complexed

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* Corresponding author. Tel.: +349-1562-2900; fax: +349-1564-4853.
E-mail address: ictlm17@ictp.csic.es (E.L. Madruga).

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ligand. However, the disadvantages of this procedure is that the second block is a gradient (statistical) copolymerization of BA and MMA where a small amount of BA was incorporated into the second segment. On the contrary, Uegaki et al. [18] referred the preparation of PMMA-*b*-PBA diblock copolymer, but in this case by successive addition of BA when the MMA feed is almost consumed (90% conversion). This work was carried out using a ternary initiating system that comprised $CCl_3Br/NiBr_2(Pn{-}Bu_3)_2$ and aluminum compounds such as $Al(OiPr)_3$.

In this article, the synthesis by ATRP of poly(methyl methacrylate)-*block*-poly(butyl acrylate), PMMA-*b*-PBA is reported. For this purpose, two macroinitiators are obtained; one from ATRP of MMA using ethyl-2-bromoisobutyrate as initiator and the other from BA using methyl-2-bromopropionate, with copper bromide/N,N,N′,N″,N″-pentamethyldiethylenetriamine as catalyst system at 100°C. From these macroinitiators block copolymers are obtained either in bulk or in benzonitrile solution using mixed halide system as catalyst. The first family of block copolymers are prepared from the chain extension of poly(butyl acrylate) with MMA, while the second are synthesized from the chain extension of poly(methyl methacrylate) with BA. For all copolymerizations the monomer conversion as a function of time, and the molecular weight evolution as a function of monomer conversion are analyzed. The copolymer glass transition temperatures are measured to assess the phase separation behavior.

2. Experimental

2.1. Materials

Methyl metacrylate (MMA), (98%, Merck) and butyl acrylate (BA), (98%, Merck) were passed through an alumina column and distilled prior to use.

Ethyl 2-bromoisobutyrate, EBrIB, (99%, Aldrich), methyl 2-bromopropionate, MBrP (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.

2.2. Polymerizations

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

2.3. Polymers characterization

The molecular weight distributions (MWD), 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 $1\ cm^3\ min^{-1}$ operated at 35°C. Styragel packed columns, HR1, HR3, HR4E and HR5E (Waters Division Millipore) were used. Poly(methyl methacrylate) standards, PMMA, (Polymer Laboratories Ltd.) in the range between 1.4×10^6 and $5.0 \times 10^2\ g\ mol^{-1}$ were used to calibrate the columns. PBA samples were analyzed using the calibration curve obtained with poly(MMA) standards and Mark-Houwink constants taken from the literature [19].

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

2.4. Glass transition temperatures

Differential scanning calorimetry (DSC) measurements were performed in a Perkin Elmer DSC/TA7DX, PC series with an Intra-cooler 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 scanned at $10°C\ min^{-1}$ under dry nitrogen ($20\ cm^3\ min^{-1}$). The first heating scan was performed after decreasing the temperature from room temperature to −80°C, then the sample was heated up to 150°C. Consecutively to the heating process, the sample was cooled down at the same rate and after that a new successive heating run was performed.

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 quoted value is the average of several measurements on each sample.

3. Results and discussion

3.1. Preparation of macroinitiators

MMA was polymerized in bulk at 100°C by using EBrIB as initiator, 1 M equivalent of CuBr as catalyst and 1 M equivalent of PMDETA as ligand (both relative to ethyl 2-bromoisobutyrate), ([MMA] : [EBrIB] : [CuBr] : [PMDETA] = 200 : 1 : 1 : 1).

Fig. 1(a) shows a first-order kinetic plot over almost all

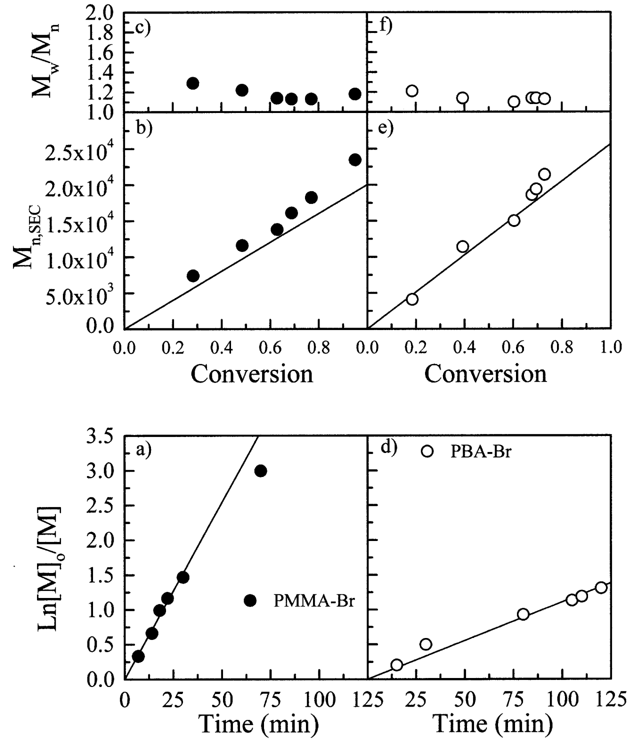

Fig. 1. (a) Semilogarithmic kinetic plot for the homopolymerization of methyl methacrylate in bulk at 100°C. [MMA]:[EBrIB]:[CuBr]:[PMDETA], 200:1:1:3. (b) Dependence of PMMA number-average molecular weight, $M_{n,SEC}$, with monomer conversion. (c) Dependence of PMMA polydispersity, M_w/M_n, with monomer conversion. (d) Semilogarithmic kinetic plots for the homopolymerization of *n*-butyl acrylate in bulk and at 100°C. [BA]:[MBrP]:[CuBr]:[PMDETA], 200:1:1:3. (e) Dependence of PBA number-average molecular weight, $M_{n,SEC}$, with monomer conversion. (f) Dependence of PBA polydispersity, M_w/M_n, with monomer conversion.

conversion range with a k_p^{app} value of $8.4 \times 10^{-4}\ s^{-1}$. Molecular weights increase linearly with the conversion (Fig. 1(b)), with values slightly higher than calculated ones. The PMMAs possess narrow polydispersities ($M_w/M_n = 1.1$–1.3), which decrease as the conversion increases (Fig. 1(c)). Similar results have been found in the literature for the ATRP of methacrylic monomers using this type of ligand [10,20–23].

The homopolymerizations of BA were performed by ATRP in bulk at 100°C by using MBrP as initiator, 1 M equivalent of CuBr as catalyst and 1 M equivalent of PMDETA as ligand (both relative to methyl 2-bromopropionate), ([BA] : [MBrP] : [CuBr] : [PMDETA] = 200 : 1 : 1 : 1).

As seen in Fig. 1(d), a straight line in the semilogarithmic plot is obtained ($k_p^{app} = 1.8 \times 10^{-4}\ s^{-1}$), indicating a constant number of propagating species over the entire conversion range. The dependence of molecular weight and molecular weight distribution with conversion for PBAs obtained is depicted in Fig. 1(e) and (f), respectively. Experimental number-average molecular weights, M_n (SEC analysis), are practically the same to those theoretically predicted, a linear increase on molecular weight with monomer conversion is observed, and polydispersities remain quite low ($M_w/M_n \leq 1.2$), decreasing as the conversion increases. These results are concordant with those reported in the literature [24,25].

3.2. Preparation of block copolymers from PMMA macroinitiator

The copolymerization reactions were performed in bulk and in 25% v/v benzonitrile solution at 100°C, using a halide exchange macroinitiator/catalyst system ([BA] : [PMMA − Br] : [CuCl] : [PMDETA] = 1100 : 1 : 1 : 1). Recent studies have showed that copper(I) chloride complexed with simple linear amine ligands in association with bromo-terminated macroinitiators, are successfully used for preparation of several block copolymers [12,26]. This fact is because the Br group initially provides fast initiation, but the replacement of the bromin atom at the chain end by chlorin shortly after the polymerization is started, suppresses undesirable secondary reactions by decreasing the radical concentration, while initiation remains fast compared to propagation [27–30]. Hence, the rate of initiation is increased relative to the propagation rate, thereby improving initiation efficiency [10].

The employed macroinitiator had $M_n = 13800$ with $M_w/M_n = 1.14$ for the reactions in bulk and in solution. Fig. 2(a) displays a relatively linear dependence of ln $[M]_0/[M]$ with time for both polymerizations, which indicates that the concentration of growing polymer radicals is constant. From the slope the apparent propagation constant, k_p^{app}, is obtained which in the case of bulk polymerization is $1.7 \times 10^{-5}\ s^{-1}$. A smaller value, $k_p^{app} = 3.8 \times 10^{-6}\ s^{-1}$, is found in benzonitrile solution. Nevertheless, a deviation from linear first-order occurs at monomer conversion around 80% in bulk reactions, which can be attributed to transfer to butyl acrylate monomer [25]. In addition, similar deviations have been also observed in other systems [31–34], which have been explained as a consequence of some side reactions.

Fig. 2(b) and (c) contain the plots of the number-average molecular weight and polydispersity values against conversion, respectively. The molecular weight of block copolymers, experimentally determined by SEC, increases linearly with monomer conversion, and is in good agreement with the theoretical values; the nature of the reaction medium, bulk or solution, does not affect their 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 Fig. 3(a) and (b) for bulk and benzonitrile solution, respectively. As can be observed in these figures, there is no remaining PMMA macroinitiator, even at low BA conversion. Moreover, a clear shift is found on the distribution curves with the monomer conversion. These curves are monomodal through the copolymerization, and there is no

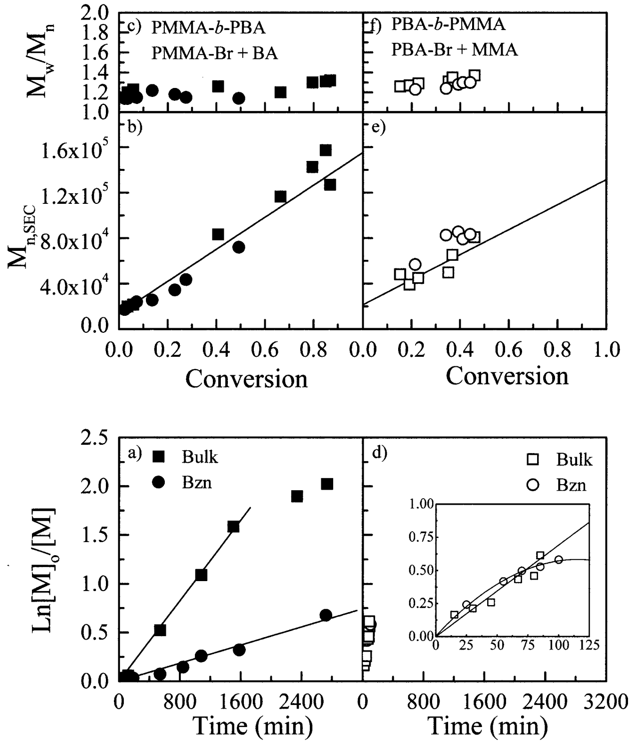

Fig. 2. (a) Semilogarithmic kinetic plots for ATRP of BA using PMMA-Br as macroinitiator in bulk and 25% v/v benzonitrile solution at 100°C. [BA]:[PMMA-Br]:[CuCl]:[PMDETA], 1100:1:1:1. (b) Dependence of PMMA-*b*-PBA number average molecular weight, $M_{n,SEC}$, with monomer conversion. (c) Dependence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

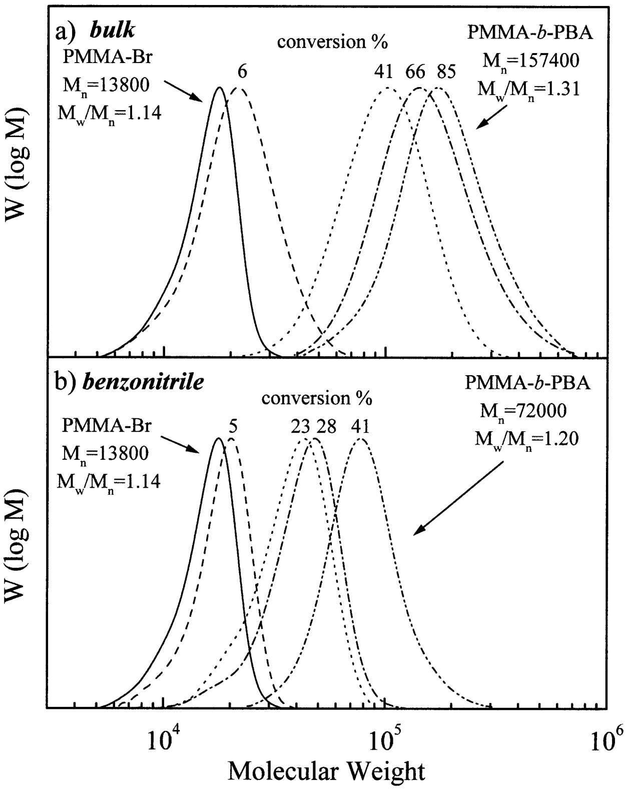

Fig. 3. (a) and (b) MWD curves for ATRP of BA using PMMA-Br as macroinitiator at 100°C in bulk and 25% v/v benzonitrile solution, respectively. [BA]:[PMMA-Br]:[CuCl]:[PMDETA], 1100:1:1:1.

significant tail on the low molecular weight side of the copolymer MWDs. The increase on the molecular weight, without a significant increase on M_w/M_n, indicates that effective initiation of butyl acrylate ATRP is achieved and the polymerization appears to proceed in a controlled manner. The differences of the MWD curves for PMMA-*b*-PBAs prepared in bulk with those samples synthesized in solution (Fig. 3(b)) are not large, although a slightly improved control of polymerization in benzonitrile seems to take place, as judged by the polydispesities. This could be due to a lower radical concentration, diminishing the probability of transfer to monomer, which has been confirmed in the radical polymerization of BA [26]. Besides, the use of solvent diminishes the solution viscosity and/or modifies the solution properties of the macroinitiator that could improve the initiation.

The block character of the copolymers obtained was confirmed by ^{1}H-NMR spectroscopy. Fig. 4 shows spectra of PMMA-Br macroinitiator and various PMMA-*b*-PBA copolymers at different conversions. In addition, the spectrum of PBA is also displayed. This demonstrates the presence of both blocks derived from BA and MMA and the increase in the amount of BA in the polymer with reaction time. NMR spectra allow the molar compositions to be determined from the relative intensity of the resonances at 4.04 ppm (–OCH_2 protons of the butyloxy) for butyl acrylate and at 3.60 ppm (–OCH_3 of the methyloxy) for methyl methacrylate. Based on 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 following equation:

$$M_{n,NMR} = M_{n,PMMA\text{-}Br} + (F_{BA}/1 - F_{BA})(M_{n,PMMA\text{-}Br}) \times (M_0^{BA}/M_0^{MMA})$$

being $M_{n,PMMA\text{-}Br}$ the number-average molecular weight of macroinitiator, F_{BA} the molar fraction of butyl acrylate in the copolymer, and M_0^{MMA} and M_0^{BA} the molar mass of both monomers.

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

Table 1
MMA-BA block copolymer synthesis using PMMA as macroinitiator ($M_n = 13,800$; $M_w/M_n = 1.14$) and catalyzed by CuCl/PMDETA at 100°C

Solvent	Time (min)	Conversion (%)	Composition (^{1}H-NMR) MMA:BA	$M_{n,NMR}$	$M_{n,theo}$	$M_{n,SEC}$	M_w/M_n
Bulk	60	3.5	76:24	$13.8K + 5.6K$	18,700	19,900	1.20
	120	5.8	66:34	$13.8K + 9.1K$	22,000	21,600	1.23
	540	40.7	21:79	$13.8K + 66.4K$	71,100	83,300	1.26
	1080	66.4	14:86	$13.8K + 108.5K$	107,300	116,600	1.20
	1500	79.5	12:88	$13.8K + 129.5K$	125,700	142,600	1.30
	2340	85.0	11:89	$13.8K + 142.9K$	133,500	157,400	1.31
	2735	86.8	11:89	$13.8K + 142.9K$	136,000	127,000	1.32
Bzn (25% v/v)	90	2.3	83:17	$13.8K + 3.6K$	17,000	17,200	1.14
	185	3.5	76:24	$13.8K + 5.6K$	18,700	19,200	1.14
	540	7.2	59:41	$13.8K + 12.3K$	23,900	24,000	1.15
	840	13.6	44:56	$13.8K + 22.5K$	32,900	25,600	1.22
	1080	22.9	32:68	$13.8K + 37.5K$	46,000	34,500	1.18
	1580	27.5	28.72	$13.8K + 45.4K$	52,500	43,600	1.15
	2720	49.2	18:82	$13.8K + 80.5K$	83,100	72,000	1.20

3.3. Preparation of block copolymers from PBA macroinitiator

It is known that activation of a dormant PBA chain end to a radical species is slower than the activation of a dormant PMMA chain end [15,32]. The result is slow initiation of the macroinitiator, which leads to poor molecular weight control (i.e. broad dispersity and/or bimodality). Chambard et al. [35] have analyzed the solvent effect on the activation rate parameters for poly(butyl acrylate) macroinitiators in atom transfer radical polymerization. In this study, it was observed that increasing solvent polarity increases the activation of a PBA initiator. Recently, our group has demonstrated that using benzonitrile improves the initiation of MMA polymerization when an inefficient initiator as methyl 2-halopropionate is used [31]. Therefore, benzonitrile, a solvent with a relatively high polarity ($\mu = 4.18$ D), may be a successful tool to improve the molecular structure of block copolymers prepared by ATRP, when a PBA macroinitiator is used.

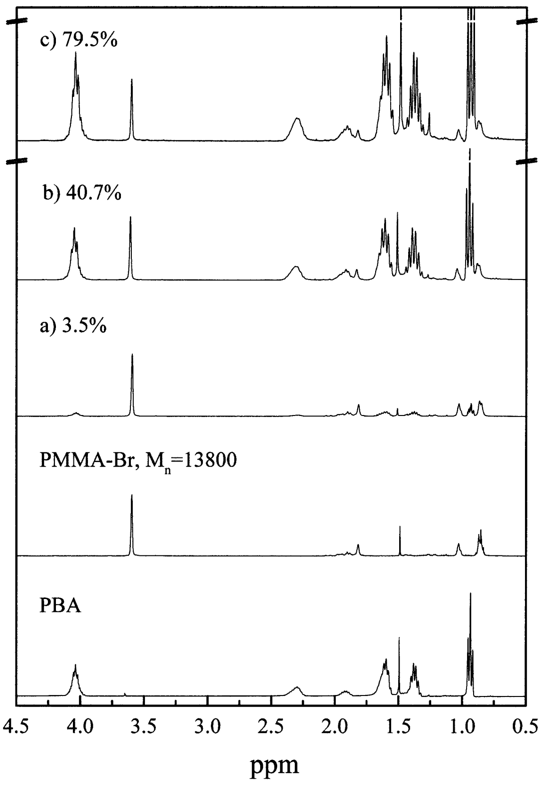

Fig. 4. ^{1}H-NMR spectra of PMMA-Br macroinitiator, PBA and PMMA-*b*-PBA copolymers.

The copolymerizations were carried out under identical experimental conditions to those described for the PMMA-*b*-PBA copolymer synthesis. The employed macroinitiator had $M_n = 21,400$ with $M_w/M_n = 1.14$ for the reactions in bulk and in solution. Fig. 2(d) shows the semilog plot with reaction time for the extension reaction of PBA-Br with MMA carried out in bulk and in benzonitrile solution, using a halide exchange macroinitiator/catalyst system ([MMA]:[PBA-Br]:[CuCl]:[PMDETA] = 1100:1:1:1). There is a dramatic increase on the polymerization rate, in contrast with the resumption of PMMA-Br polymerization with BA. The polymerization rate is not first-order with respect to monomer when the polymerization is performed in benzonitrile solution. Curvature of the kinetic plot is observed at monomer conversions higher than 40%, suggesting that the radical concentration decreases at moderate conversions. However, when the ATRP of MMA is performed in bulk, a linear dependence of ln $[M]_0/[M]$ vs time is found. The two kinetics present practically the same values of the apparent polymerization rate constant (considering the linear part of the kinetic curve obtained in benzonitrile solution, $k_p^{app} = 1.1 \times 10^{-4}\ s^{-1}$). This kinetic behavior has also been observed for the polymerization of MMA by ATRP using methyl 2-bromopropionate as initiator, copper halide and 2,2′-bipyridine [31].

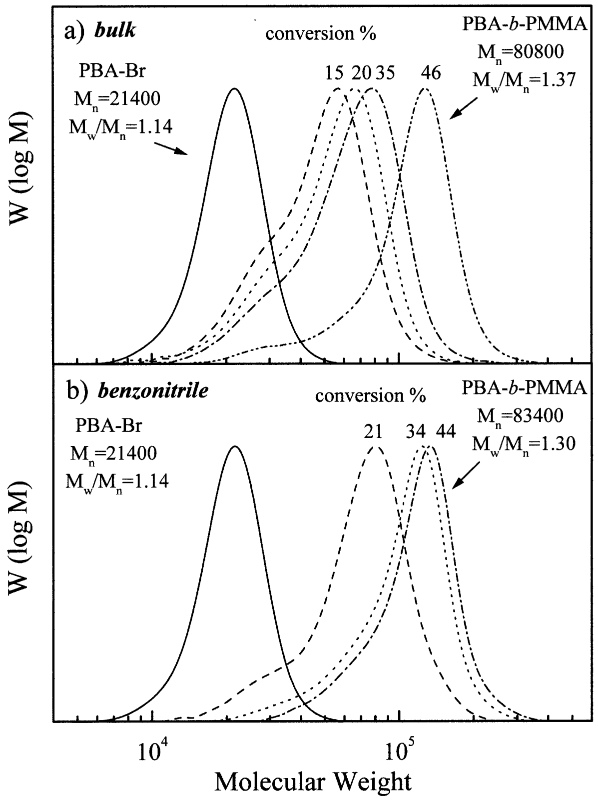

Fig. 5. (a) and (b) MWD curves for ATRP of MMA using PBA-Br as macroinitiator at 100°C in bulk and 25% v/v benzonitrile solution, respectively. [MMA]:[PBA-Br]:[CuCl]:[PMDETA], 1100:1:1:1.

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 MMA are also achieved.

The MWD curves of the macroinitiator and the products of the chain extension with MMA as a function of monomer conversion are shown in Fig. 5(a) and (b). In contrast to BA polymerization with PMMA-Br, the evolution of these curves shows the slow disappearance of the macroinitiator, which is responsible for the bimodality, at least up to MMA conversion higher than 40% for bulk copolymerization. However, this bimodality is considerably reduced when the polymerization is performed in benzonitrile solution. The comparison of the MWDs at 20% conversion for the two reaction conditions is very relevant. It is clear that benzonitrile strongly affects the activation of the PBA macroinitiator. For conversions higher than 20%, there are no sign of bimodality and, only a small amount of low molecular weight tailing is observed. However, although very beneficial, the use of benzonitrile in our experimental conditions, is not sufficient to completely suppress the bimodadilty of the MWD curves recorded at the first step of the process. The SEC and NMR number-average molecular weights are also in concordance with the theoretical values, see Table 2.

3.4. Analysis of the glass transition temperature

The glass transition temperatures were measured to analyze the phase behavior of the diblock copolymers. The experiments were performed for two different series of diblock copolymers. The first group contains diblock copolymers, which are constituted by a MMA block with constant block length and a variable BA block. The second one contains copolymers comprising a BA block of constant block length and a variable MMA block. The glass transition temperatures were measured for copolymers whose SEC curves indicated the absence of macroinitiator.

The glass transition temperature of BA macroinitiator (constant block on the first set) was −50°C. Likewise, the glass transition temperature of 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 [36]. This is expected, since their molecular weights are lower than those found in conventional polymerizations.

The glass transition temperatures of copolymers synthesized from the PMMA and PBA macroinitiators are collected in Table 3. The results obtained indicate that,

Table 2
BA-MMA block copolymer synthesis using PBA as macroinitiator ($M_n = 21,400$; $M_w/M_n = 1.14$) and catalyzed by CuCl/PMDETA at 100°C

Solvent	Time (min)	Conversion (%)	Composition (^{1}H-NMR) MMA:BA	$M_{n,NMR}$	$M_{n,theo}$	$M_{n,SEC}$	M_w/M_n
Bulk	15	15.3	50:50	$21.4K + 16.7K$	38,200	48,200	1.26
	30	19.2	56:44	$21.4K + 21.3K$	42,500	39,300	1.27
	45	22.8	61:39	$21.4K + 26.1K$	46,500	44,900	1.29
	67	35.2	70:30	$21.4K + 39.0K$	60,100	49,900	1.31
	80	36.8	71:29	$21.4K + 40.9K$	61,900	65,300	1.35
	85	45.9	75:25	$21.4K + 50.1K$	71,900	80,800	1.37
Bzn (25% v/v)	25	21.5	58:42	$21.4K + 23.1K$	45,100	56,900	1.23
	55	34.2	69:31	$21.4K + 37.2K$	59,000	82,700	1.24
	70	39.2	72:28	$21.4K + 42.9K$	64,500	85,500	1.28
	85	41.1	73:27	$21.4K + 45.1K$	66,600	79,200	1.30
	100	44.1	74:26	$21.4K + 47.5K$	66,900	83,400	1.30

Table 3
Characterization of the diblock copolymers

	$M_{n,RMN}$	M_w/M_n	Composition (^{1}H-NMR) MMA:BA	T_{g1} (°C)	T_{g2} (°C)
PMMA-*b*-PBA	13.8*K* + 142.9*K*	1.31	11:89	−43.9	115.4
	13.8*K* + 142.9*K*	1.32	11:89	−46.0	103.5
	13.8*K* + 80.5*K*	1.20	18:82	−47.7	113.0
	13.8*K* + 66.4*K*	1.26	21:79	−46.1	108.9
	13.8*K* + 45.4*K*	1.15	28:72	−45.4	108.9
PBA-*b*-PMMA	21.4*K* + 37.2*K*	1.24	69:31	−53.1	110.8
	21.4*K* + 42.9*K*	1.28	72:28	−48.5	122.9
	21.4*K* + 47.6*K*	1.30	74:26	−50.8	109.8
	21.4*K* + 50.1*K*	1.37	75:25	−47.5	124.8

under our experimental conditions, the length of the BA or MMA block does not sensitively influence T_g. Two separate T_gs are observed for block copolymers synthesized from both macroinitiators. For both PMMA-*b*-PBA and PBA-*b*-PMMA this behavior could indicate that, for these compositions and molecular weights, the copolymer phase separation produced is almost complete, since the T_gs are very similar to those of the corresponding pure segments.

4. Conclusions

The results presented here have clearly demonstrated the utmost importance of the solvent used in ATRP where the sequential addition of different (meth)acrylates is concerned. PMMA-Br combined with CuCl induces faster initiation, which enables efficient control of the molecular weight over the whole polymerization. Moreover, the use of benzonitrile maintains a low radical concentration, which minimizes premature chain termination, leading to low polidispersities. The PBA-Br macroinitiator produces slow initiation, causing bimodality in block copolymers up to 40% of conversion. The use of benzonitrile increases the initiation efficiency and the bimodality is vanished from 20% of conversion. However, a decrease in the rate is observed at moderate conversions. Despite the kinetic characteristics, PMMA-*b*-PBA and PBA-*b*-PMMA block copolymers present, for all block lengths and copolymer compositions, two glass transition temperatures, which indicate efficient phase separation.

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