

Synthesis, Characterization, and Glass Transition Temperature of Poly(styrene-*b*-butyl methacrylate) Block Copolymers by Stable Free Radical Polymerization

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ABSTRACT: The synthesis of controlled polystyrenes with different molecular weights has been performed in the presence of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyl-oxy)ethane (PETEMPO). The polystyrenes have served as macroinitiators for the formation of poly(styrene-*b*-butyl methacrylate) block copolymers. Using differential scanning calorimetry (DSC) it has been shown that all block copolymers synthesized do not present phase segregation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 14–21, 2001

Key words: stable free radical copolymerization; styrene; butyl methacrylate; block copolymer; glass transition temperature

INTRODUCTION

The growing interest in the accurate control of the macromolecular structure is a consequence of the desire to synthesize advanced materials with new and/or improved physical, chemical, and mechanical properties. Classically, it has been achieved by using the classical living ionic^{1,2} polymerization techniques. These methods offer the possibility not only of making materials with controlled molecular weight and narrow polydispersities, but also block copolymers and end-functionalized polymers.³ However, generally, the ionic living

polymerization is limited by the incompatibility of the growing chain end (either anionic or cationic) with different functional groups and by the demanding rigorous experimental requirements. For this reason, neither technique results are as attractive as the controlled radical polymerization methods⁴ where a wide range of functional groups are compatible and the reaction can be performed with small traces of impurities and without monomers of high purity. Nitroxide-mediated controlled free radical polymerization enables the synthesis of macromolecules with well-defined architectures.⁵ Although the versatility of this new type of technique is actually restricted by a limited number of applicable monomers and elevated temperatures, higher than 100°C, it offers a great potential for the preparation of well-defined block copolymers. In addition, because the initial N-oxy-capped polymers are stable in air and at room temperature, they can be isolated and stored for their posterior used as macroinitiators.

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The initial work of stable free-radical polymerization⁵ was performed with a bimolecular initiating system, consisting of a traditional radical initiator, benzoyl peroxide, in combination with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as the stable free radical. Later, it was demonstrated that the use of unimolecular initiator offers a better control over the molecular weight and polydispersity than the corresponding bimolecular system.⁶ This idea has special interest on the synthesis of block copolymers, because the control of morphology in block copolymers has become important in the design of new physical properties through a structure–property relationship.^{7,8}

The synthesis of styrene-*b*-methyl methacrylate, p(S-*b*-MMA),⁹ styrene-*b*-2-dimethylamino ethyl methacrylate, p(S-*b*-DAMA),¹⁰ styrene-*b*-styrene-*co*-butyl methacrylate, p(S-*b*-S-BMA),¹¹ and styrene-*b*-butyl methacrylate, p(S-*b*-BMA)¹² have been reported. In all the cases polystyrene–TEMPO end capped has been used as the macroinitiator. However, the results are very different. For p(S-*b*-MMA), it was necessary for the presence of camphorsulfonic acid. For p(S-*b*-DAMA), the block length was controlled for the concentration of the macroinitiator, but for p(S-*b*-BMA), the GPC curves were bimodal in the absence of TEMPO. Having in mind the differences found between those articles, it is necessary to go deeply into the knowledge of the synthesis of block copolymers by stable free radical polymerization. To our knowledge, the properties of these kinds of block copolymers have not been described. In this sense, the aim of this article is the synthesis and characterization of poly (styrene-*b*-butyl methacrylate) block copolymers by using stable free radical polymerization. First of all, the synthesis of styrene in the presence of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane, PETEMPO, as a unimolecular initiator has been studied. Subsequently, some of the obtained polystyrenes have been used as macroinitiators in the preparation of p(S-*b*-BMA) block copolymers. The morphological analyses of the resulting copolymers through the calorimetric characterization and the influence on the glass transition temperature with the block length have been made.

EXPERIMENTAL

Materials

Styrene and butyl methacrylate were commercially available (Fluka and Merck, respectively) and purified by conventional methods.

Synthesis of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane, PETEMPO

This compound was prepared following the method proposed by Hawker.⁶

Polymerization of Styrene

Mixtures of styrene and PETEMPO were added to a Pyrex glass ampoule, degassed (via freeze-thaw cycles), and sealed off under high vacuum. The monomer/initiator ratios were 100 : 1, 250 : 1, and 400 : 1. The solutions were heated at 125°C in a temperature-controlled oil bath at different times. The resulting polystyrenes were dissolved in chloroform and precipitated with a large excess of methanol. The polymers were purified by reprecipitation with a chloroform/methanol system. The precipitated solids, filtered and dried in vacuum, were subjected to GPC analysis after appropriately being diluted with tetrahydrofuran. The monomer conversion was determined gravimetrically.

Synthesis of poly (styrene-*b*-butyl methacrylate) block copolymers, poly(S-*b*-BMA)

The polystyrene macroinitiators (PS-MI) were dissolved in butyl methacrylate in a glass ampoule, degassed using freeze-thaw cycles, and sealed off under high vacuum. The monomer/macroinitiator ratios were 200 : 1, 400 : 1, and 800 : 1 for each macroinitiator chosen. All the polymerizations were carried out in an oil bath regulated at 125°C for 6 h. After dilution with chloroform the solution was poured into a 20-fold amount of methanol. The precipitated polymers were reprecipitated with methanol from chloroform solutions, and dried in vacuum to give a poly(S-*b*-BMA) block copolymers. The comonomer conversion was determined gravimetrically.

Polymer Characterization

Molecular weights and molecular weight distributions of synthesized macroinitiators and copolymers were estimated by gel permeation chromatography (GPC) using a Waters system equipped with a 515 HPLC pump, 410 differential refractometer, and the following Waters/Styragel columns in series of HR1, HR4E, and HR5E. All samples were run in tetrahydrofuran, THF (Scharlau), at 35°C. Calibration of the equipment was made with 19 polystyrene standards (Polymer Laboratories) in a range from 1.62×10^2 to 3.53×10^6 .

Macroinitiator and copolymer $^1\text{H-NMR}$ spectra were recorded at room temperature and 50°C , respectively, with a 300 MHz (Varian VXR-300S) spectrometer using CDCl_3 as a deuterated solvent (10% w/v) with tetramethylsilane as an internal reference.

Differential scanning calorimetry (DSC) measurements were performed in a Perkin-Elmer DSC/TA7DX, PC series with a water circulating system for temperatures over ambient, and a Perkin-Elmer DSC-2 Data Station 3700 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 (~ 10 mg) were weighed to ± 0.002 mg with an electronic autobalance (Perkins-Elmer AD4) and quenched from room temperature at the maximum cooling rate ($-320^\circ\text{C}/\text{min}$) to -15°C , and then scanned at $10^\circ\text{C}/\text{min}$ from -15 to 130°C under dry nitrogen ($20\text{ cm}^3/\text{min}$). Three subsequent scans were performed at $10^\circ\text{C}/\text{min}$ for each sample. There was no waiting time between runs, and the cooling rate was $10^\circ\text{C}/\text{min}$. The heat capacity increase, ΔC_p , associated with the glass transition of each block copolymer was evaluated by measuring the difference in height between the extrapolated baselines recorded before and after the transition at the temperature that corresponds to the half-height of the base line shift.

RESULTS AND DISCUSSION

Polymerization of styrene with PETEMPO

Styrene is polymerized in bulk at 125°C using PETEMPO as the initiator. The monomer : initiator concentration relationship varies between 100 : 1 and 400 : 1. In all the cases, as can be observed in Figure 1, it is found that $\ln[M_o]/[M]$ linearly increases over time up to conversion around 60%. Afterwards, a deviation from the linearity is noted. Similar phenomenon has been also observed for other authors,^{13–15} which is attributed to the presence of side reactions, self-initiation, and a changing termination rate coefficient. The molecular weight increases linearly with conversion, being in good agreement with those theoretically calculated from the monomer: initiator concentration ratios. The molecular weight distribution values slightly vary with the conversion, but the broadening of distribution increases as the

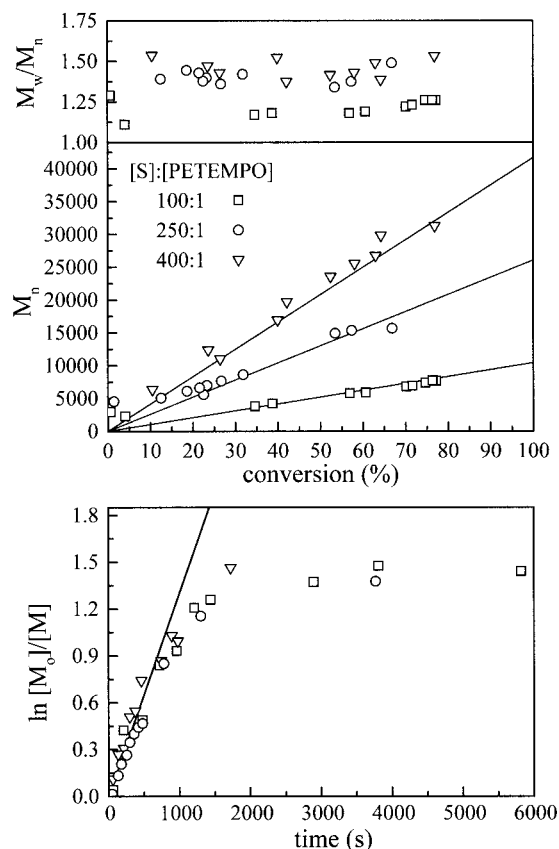


Figure 1 Semilogarithmic kinetic plot, the molecular weight, M_n , and molecular weight distributions, M_w/M_n as a function of conversion for the styrene polymerization in the presence of various concentrations of PETEMPO; [S] : [PETEMPO], \square 100 : 1, \circ 250 : 1, and ∇ 400 : 1.

initiator concentration decreases, although the values are always lower than 1.5.

The invariable concentration of active species and the linear increase of the molecular weight with conversion are often taken as criterion for defining a “living” or controlled process.

In analogy with other living polymerization processes, the polymerization of styrene in the presence of PETEMPO give rise to chains in which a ethyl phenyl radical is introduced at one chain end while the 2,2,6,6 tetramethyl-1-piperidinyloxy radical is present at the growing chain end.

Figure 2 displays the spectrum of the polystyrene bulk polymerized in the presence of PETEMPO, $M_n = 2300$. The end-group analysis in the polymer is possible because it presents enough end-group concentration to be detected by NMR. Thus, the peaks at 0.2, 0.4, 0.9, and 1.1

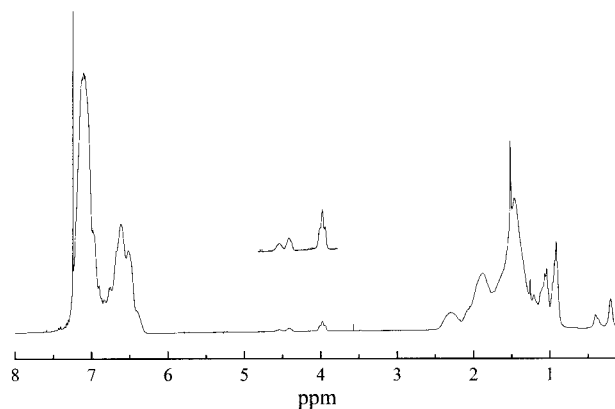


Figure 2 $^1\text{H-NMR}$ spectrum of the polystyrene bulk polymerized in the presence of PETEMPO, $\overline{M}_n = 2300$.

ppm are assignable to methyl protons of the 2,2,6,6-tetramethyl-1-piperidiniloxy (TEMPO) end group.¹⁶ The methine proton of the monomer unit bounded to the TEMPO end seems to be split to 4.0 and 4.5 ppm. The main peaks at 1.2–2.5 and 6.2–7.4 ppm are assignable to the methine, methylene, and phenyl protons of the polystyrene chain, together with the methyl protons of the ethyl phenyl moiety.

Considering the low polydispersity of polymers and taking into account that the end groups of the obtained polymers are essentially the same than those of the initiator, a similar reactivity of the polymer and the PETEMPO would be expected. Therefore, the thermolysis of such a polymer in the presence of a dissimilar unsaturated monomer would lead to the reactivation of the active chain ends and the formation of block copolymers. In particular, and within all of polystyrene samples synthesized, four polystyrene macroinitiators, PS-MI (their characteristics are collected in Table I) have been chosen to synthesize block copolymers. The selected polymers from the 100 : 1 [monomer] : [initiator] ratio have conversion values of 34.6 and 56.9%, practically the same

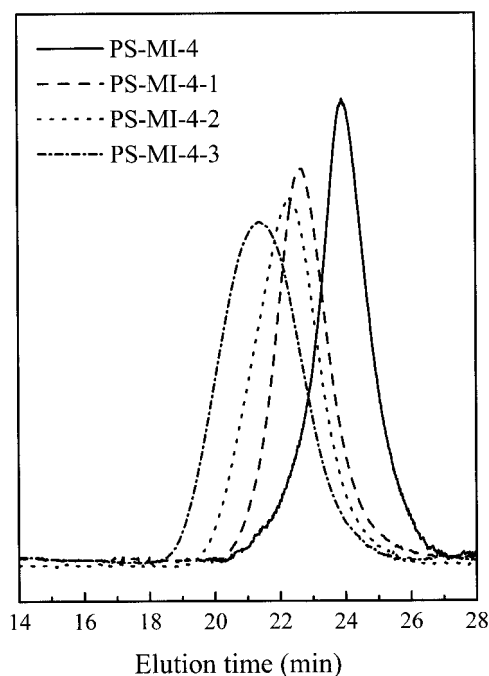


Figure 3 GPC curves of the P(S-*b*-BMA) copolymers.

that the polymers from the 400 : 1 [monomer] : [initiator] ratio (26.4 and 58.0%).

Polymerization of Butyl methacrylate Initiated by PS-MI

Four series of poly(styrene-*b*-butyl methacrylate) are obtained by polymerizing butyl methacrylate in bulk at 125°C using the four selected polystyrene macroinitiators with 200 : 1, 400 : 1, and 800 : 1 [butyl methacrylate] : [macroinitiator] ratios. For all the reactions the time applied was 6 h.

Figure 3 shows the GPC eluograms of the poly(S-*b*-BMA) copolymers produced, and Table II collects the molecular weight of the final products. In the figure the absence of the polystyrene macroinitiator in the final product as well as an increase of the shift to higher molecular weight

Table I Characteristics of Polystyrene Macroinitiators

Polystyrene Macroinitiator	[M]/[PETEMPO] ^a	Conversion (%)	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	T_g (°C)
PS-MI-1	100 : 1	34.6	3800	1.17	88.9
PS-MI-2	100 : 1	56.9	5800	1.17	95.0
PS-MI-3	400 : 1	26.4	12,400	1.47	100.8
PS-MI-4	400 : 1	58.0	25,500	1.43	104.2

^a Ratio used for the synthesis of the macroinitiator.

Table II Characteristics of Copolymers

Copolymer	[M]/[PS-MI] ^a	Conversion (%)	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	F _{STY} (NMR)	F _{STY} (GPC)	T _g (°C)
PS-MI-1-1	200 : 1	3.9	5600	1.36	0.77	0.75	69.8
PS-MI-1-2	400 : 1	6.4	7300	1.64	0.56	0.60	55.8
PS-MI-1-3	800 : 1	8.2	11,100	2.05	0.33	0.41	39.7
PS-MI-2-1	200 : 1	7.7	9200	1.32	0.76	0.70	68.2
PS-MI-2-2	400 : 1	10.5	11,500	1.74	0.56	0.58	56.3
PS-MI-2-3	800 : 1	10.2	16,700	2.15	0.40	0.42	50.3
PS-MI-3-1	200 : 1	8.0	15,100	1.43	0.86	0.86	82.6
PS-MI-3-2	400 : 1	9.5	17,500	1.67	0.72	0.77	68.7
PS-MI-3-3	800 : 1	10.7	24,300	2.06	0.55	0.58	58.7
PS-MI-4-1	200 : 1	3.9	28,300	1.35	0.97	0.93	98.1
PS-MI-4-2	400 : 1	10.7	31,600	1.34	0.90	0.85	90.2
PS-MI-4-3	800 : 1	7.8	33,700	1.49	0.80	0.81	88.5

^a Ratio used for the synthesis of the copolymer.

upon increasing the [monomer] : [macroinitiator] ratio can be noticed.

When the macroinitiator behaves as a unimolecular initiator the theoretical molecular weight, $\overline{M}_n(\text{theo})$, will be defined as the molecular weight polystyrene macroinitiator, $\overline{M}_n(\text{PS})$, plus the corresponding weight of poly(butyl methacrylate) block. Thus,

$$\overline{M}_n(\text{theo}) = \overline{M}_n(\text{PS}) + \frac{[\text{BMA}]}{[\text{Macroinitiator}]} \times \text{conversion} \times 142$$

being 142 the molecular weight of BMA monomer. In this case and as is depicted in Figure 4, the

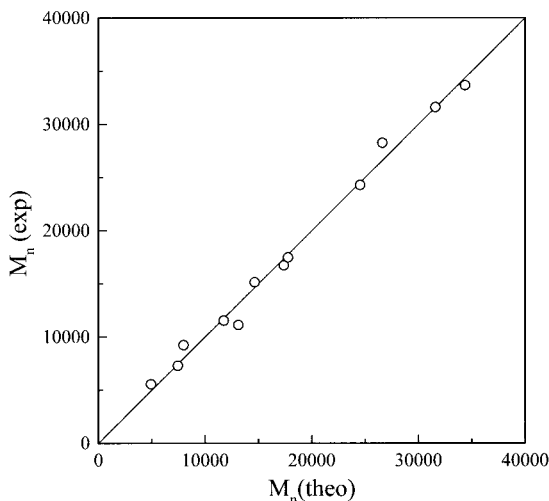


Figure 4 Calculated molecular weight vs. experimental molecular weight for P(S-b-BMA) copolymers.

experimental molecular weights of block copolymers determined by GPC with polystyrene standards are very close to the theoretically calculated values. However, because the molecular weight of block copolymers determined by GPC has no absolute meaning, the agreement observed in the figure between the experimental and calculated values could not serve as evidence for a controlled process. On the same premise, the apparent broadening of the molecular weight distributions may be taking with some caution.

¹H-NMR spectrum of polystyrene, obtained in this work, poly(butyl methacrylate), prepared in a classical free radical polymerization, and some block copolymers are displayed in Figure 5. In addition to the characteristic peaks of PS and PBMA, the block copolymers show two peaks at 5.4 and 6.1 ppm whose intensity increases as the BMA molar fraction in the block copolymer increases. Peaks at 5.4 and 6.1 ppm correspond to the absorption bands of a methylene ω -unsaturation.^{12,17} The methylene ω -unsaturation is commonly observed when a methacrylic monomer is polymerized in the presence of nitroxides, and emerges as a consequence of a side reaction, i.e., bimolecular termination by disproportion of the propagation species with nitroxide radicals.¹⁷ It has also been proposed^{14,18} that the terminal methylene unsaturation can be due to unimolecular elimination of hydroxylamine. Independently of which mechanism is operative, the formation of methylene ω -unsaturation will limit the conversion and block purity, and it will lead to an increase in polydispersity.

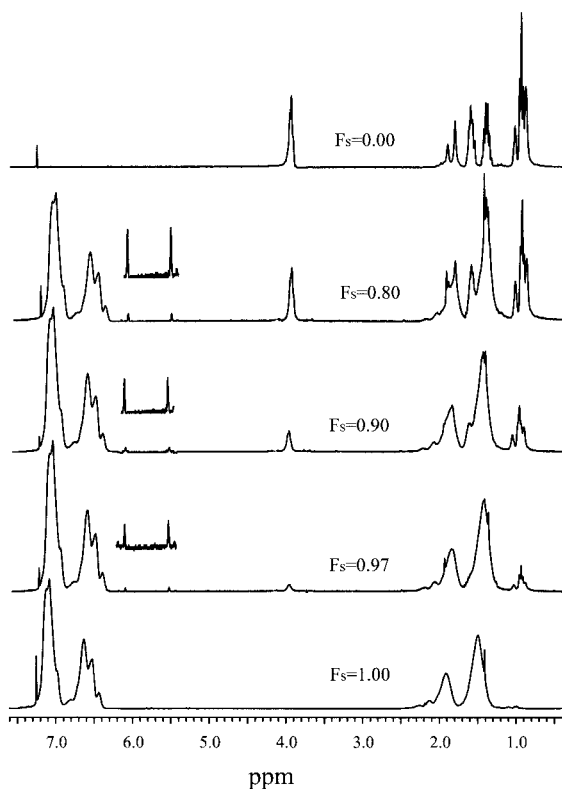


Figure 5 $^1\text{H-NMR}$ spectra of the polystyrene and poly(butyl methacrylate) along with P(*S-b*-BMA) copolymers of different compositions.

The block copolymer compositions are determined from both GPC and $^1\text{H-NMR}$ measurements. From GPC, the difference between the number-average molecular weight of the copolymer and that of the macroinitiator gives the length of poly(butyl methacrylate) block, and then the copolymer composition is easily determined.

From $^1\text{H-NMR}$, the copolymer composition can be obtained by comparison of the integrated area of the resonance peak of the aromatic protons (PS) and the proton in the OCH_2 position of the ester group (PBMA). The results obtained from both techniques are close (see Table II).

Glass transition temperature, T_g

The DSC results on the T_g of PS samples used as macroinitiators are presented in Figure 6, and their values are collected in Table I. As expected, the glass transition temperature increases with the molecular weight, which seems to reach a plateau at high values. This phenomenon can be rationalized by the reduction in free volume as the number of chain ends decreases with increas-

ing molar mass. There are different empirical models^{19–22} to describe the glass transition temperature dependence with the chain length, so there is no simple consensus on the subject. O'Driscoll and Sanayei²² have studied different sets of vinyl polymers, i.e., polystyrenes, which have been theoretically well fitted. Figure 6 also includes the polystyrene fitted curve obtained by these authors. The experimental values are higher than the theoretically fitted by O'Driscoll and Sanayei.²² This feature has been also observed in the poly-4-hydroxystyrenes glass transition temperatures²³ where narrow poly-4-hydroxystyrenes obtained by stable free radical polymerization exhibit higher T_g s than the broad poly-4-hydroxystyrenes obtained by classical radical polymerization over the entire range of molecular weights investigated. This fact was attributed to a probable decrease in the free volume.²³

The common characteristic of the majority of multicomponent amorphous block polymer systems in the solid state is their ability to exhibit microphase-separated structures.²⁴ The phase behavior of the obtained block copolymers is studied by using differential scanning calorimetry, DSC, which gives information on the morphology depending on the existence and the position of the glass transition.²⁵ Interestingly, and as can be seen in Figure 8 and Table II, a single glass transition temperature is observed for all block copolymers. The block copolymers T_g s are lower than those obtained for polystyrene macroinitiators, and independently of the set considered, the block copolymers T_g decreases as the molecular weight

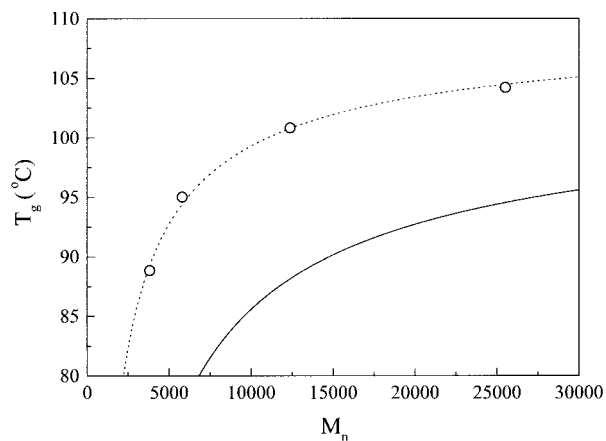


Figure 6 T_g as a function of molecular weight for PS macroinitiators; ○ experimental values, — fitted curve described by O'Driscoll and Sanayei;²² ···· fitted curve to the experimental values.

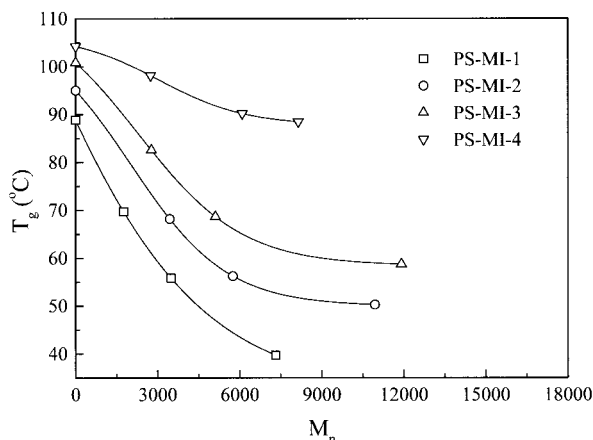


Figure 7 Block copolymer T_g s as a function of both number-average molecular weight of the polystyrene macroinitiator and number-average molecular weight of the poly(butyl methacrylate) block.

of poly(butyl methacrylate) block increases. However, it can be clearly observed in Figure 7 that this diminishment depends on the polystyrene macroinitiator molecular weight, i.e., in the set weight obtained with the PS-MI-1 macroinitiator the decrease is around 30°C, while in the set obtained using the PS-MI-4 macroinitiator, the decrease is only 10°C. However, this fact is only apparent. Establishing ΔT_g as the differences between the T_g of the pure polystyrene macroinitiators and those of the block copolymers, Figure 8 represents the variation of ΔT_g with the weight molar fraction of BMA in the block copolymer chain. In this figure the T_g reducing of the pure polystyrene by the butyl methacrylate is observed, and is only dependent on the weight molar fraction of the butyl methacrylate and independent on the molecular weight of the macroinitiator. Besides, the ΔT_g values seem to follow a similar curve to the characteristic for random copolymers, which could indicate that these block copolymers form a single phase. Notwithstanding, some interactions between the polystyrene block and poly(butyl methacrylate) block seem to exist.

In Figure 9 the DSC curves for the PS-MI-1 and PS-MI-4 block copolymer series are represented. It is clear in all the cases that the increase on molecular weight of the PBMA block produces a broadening on the DSC curves and also motives a reduction on the ΔC_p , which could be due to incompletely developed phase separation in these samples. Recently, it has been described that the morphological behavior of styrene–butyl methac-

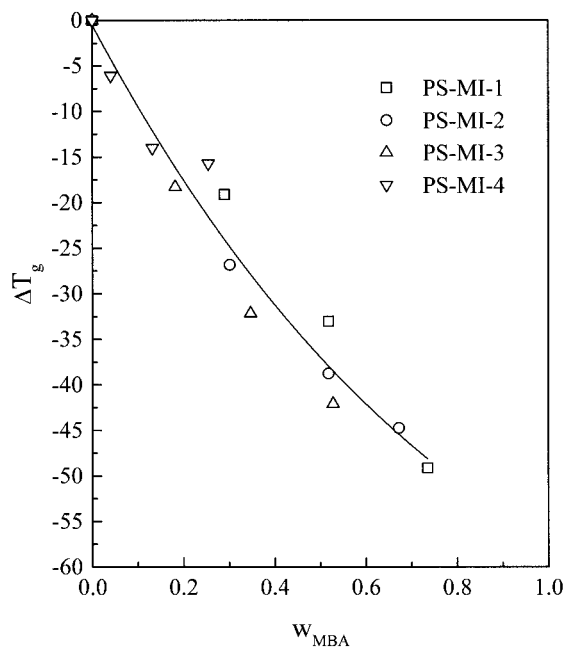


Figure 8 Variation of ΔT_g with the weight molar fraction of BMA, w_{BMA} , in the block copolymer chain.

rylate block copolymer is synthesized by anionic polymerization.²⁶ In this work it is assumed that the unsymmetrical block copolymers are in a disordered state, and the phase behavior is presented by nearly symmetrical block copolymers. However, it is important to remember that these authors indicate that an order–disorder transition for symmetrical diblock copolymers occurs when M_n is 130,000. In the present work, the molecular weights could be not enough large to present a phase separation, or the sensibility of the equipment is not sufficient to detect it. There-

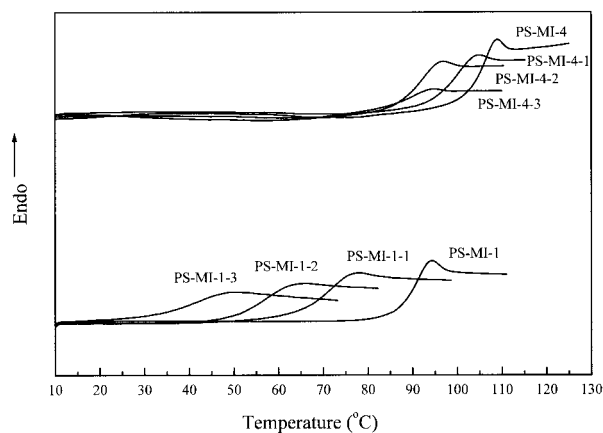


Figure 9 DSC curves for block copolymer series performed using PS-MI-1 and PS-MI-4 macroinitiators.

fore, it will be necessary for further investigations to elucidate the morphology of these block copolymers.

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