Synthesis of Graft Copolymers. III. Polystyrene-*g*-Poly(butyl acrylate)

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ABSTRACT: Polystyrene (PS) chains functionalized with pendant 1,2-bis(trimethylsilyloxy)tetraphenylethane (TPSE) groups are used as macroinitiators to initiate the polymerization of *n*-butyl acrylate (BuA) to synthesize PS-*g*-poly(BuA) (PS-*g*-PBuA) copolymers at 130°C. The TPSE groups are known to function as initers in the polymerization of several vinyl monomers. The homolytic decomposition of TPSE results in a diphenylmethyl (DPM) radical attached to the main chain and a free DPM radical. The former is responsible for the polymerization initiation and the latter momentarily stops the growth of the growing grafts by the formation of a dormant species. Unfortunately, side reactions like the combination between growing grafts take place and the polymerization can only be controlled in a limited range of conversion. The most appropriate conditions for the synthesis of PS-*g*-PBuA are reported to present their potential use as thermoplastic elastomers with relatively controlled structures. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 19–26, 2002

Key words: graft copolymers; tetraphenylethanes; controlled polymerization; macroinitiator

INTRODUCTION

It is known that poly(*n*-butyl acrylate) (PBuA) is an industrially important polymer because of its low glass-transition temperature (−54°C) and durability. As a consequence of these properties it can be used as a soft segment in thermoplastic elastomers. However, it is also well known that in the synthesis of polyacrylate polymers and copolymers via anionic methods, a number of side reactions take place[1,2] and it is necessary for the polymerization to be carried out under strict conditions such as at very low temperatures or in the presence of metal salts. Several methods have been applied to overcome these problems[3,4]; however, many acrylate polymers and copolymers are still synthesized by free-radical polymerization. However, free-radical polymerizations are difficult to control.

In the past decades several methods were developed to control free-radical polymerizations, and they are essentially based on controlled or "living" free-radical mechanisms in which a dynamic equilibrium between growing and dormant species is established. Different methods are reported in the literature for the synthesis of polyacrylates such as the use of macromonomers,[5] dithiocarbamates,[6,7] alkoxyamines,[8,9] and atom transfer radical polymerization.[10,11] The latter was used to prepare ABA block copolymers with acrylonitrile, 2-ethylhexyl acrylate, and BuA.[12] Rare earth metal complexes are used to synthesize methyl methacrylate (MMA)/BuA/MMA triblock copolymers,[4] but there are very few re-

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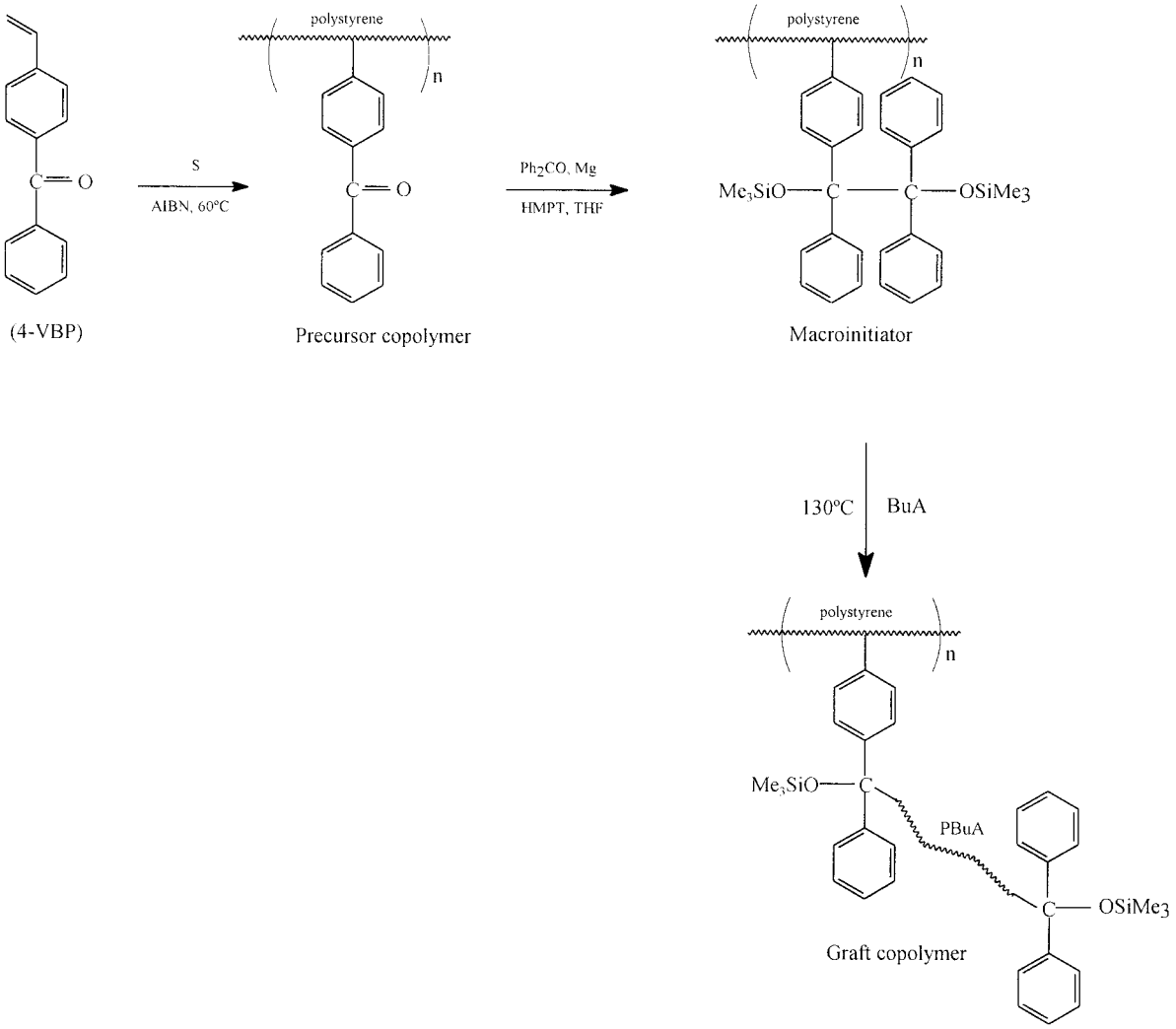

Scheme 1 The general synthetic route to prepare PS-*g*-PBuA graft copolymers using TPSE-based macroinitiators.

ports[13] about the synthesis of graft copolymers with BuA by controlled or living processes.

In this study we describe the graft controlled radical polymerization of BuA using polystyrene (PS)-based macroinitiators functionalized with 1,2-bis(trimethylsilyloxy)tetraphenylethane (TPSE) groups. We report the effect of several parameters on the synthesis of PS-*g*-PBuA in order to obtain graft copolymers that have a high molecular weight and high content of PBuA and have potential use as thermoplastic elastomers.

EXPERIMENTAL

Styrene was distilled over sodium under a vacuum, and BuA and BuMA were distilled over sodium hydroxide under a vacuum. All the monomers were distilled just before polymerization. Toluene and chlorobenzene were purified by distillation and used immediately. The NMR spectra were obtained with a Varian 200-MHz spectrometer. The size exclusion chromatography (SEC) analysis was made in THF on a Waters 150 LC with PS standards.

The synthesis of the functional monomer 4-vinylbenzophenone (4-VBP), its copolymerization with styrene, and the synthesis of the macroinitiators were carried out as described in an earlier article.[14] Scheme 1 shows the general synthetic route to prepare graft copolymers using TPSE-based macroinitiators. The characteristics of the macroinitiators used in this study are given in Table I.

Table I Characteristics of Macroinitiators Used in Synthesis of PS-*g*-PBuA Copolymers

Macroinitiator	A (% mol Bz)	M_n of a ($\times 10^{-3}$ g/mol)	TPSE ^{1}H-NMR (mol %)	δ	M_n ($\times 10^{-3}$ g/mol)[a]	Z (%)
XII	4-VBP-*co*-St (6.0)	9.4	1.72	1.63	11.0	27.7
XIII-1	4-VBP-*co*-St (2.6)	10.4	1.07	1.20	12.7	41.2
XIII-2	4-VBP-*co*-St (2.6)	10.4	0.63	0.72	12.6	24.9

The macroinitiators were synthesized according to Figure 1. A, precursor copolymer; Bz, benzophenone; δ, the average number of active sites (TPSE) by the polymeric chain; Z, the conversion of bonded benzophenone calculated by ^{1}H-NMR; and St, styrene.
[a] The molecular weight of the macroinitiators determined by SEC.

Synthesis of PS-*g*-BuA

The graft polymerization of BuA initiated with styrene-based macroinitiators was carried out as follows: the macroinitiator (1.488 g, [TPSE] = 6.4×10^{-3} *M*) was dissolved in the monomer (5.94 g), and it was necessary to add toluene as a solvent (24-mL total volume) to prevent the increase of viscosity in the early stages of the polymerization. Equal amounts of the solutions were placed in six glass tubes. The tubes were degassed, sealed, and finally immersed in an oil bath at 130°C for predetermined periods of time. The conversion of pure thermal BuA polymerization was measured under the same experimental conditions. The polymers were isolated by two precipitations from a large excess of methanol to eliminate the residual homopolymer that was formed. After filtration the polymers were dried under a vacuum at 50°C to constant weight. In all cases the molecular weight relative to linear PS was determined by SEC.

RESULTS AND DISCUSSION

It was demonstrated in the synthesis of PS-*g*-poly(MMA) (PS-*g*-PMMA) using TPSE-functionalized macroinitiators[15] that one of the principal parameters responsible for the formation of gel in the synthesis of graft copolymers was the average number of active sites (δ) from the macroinitiator molecule. If the δ is ≤2 the synthesis of graft copolymers is possible without the formation of crosslinked structures. It was also established that a temperature of 130°C allows better conditions for this synthesis. At this temperature no induction period exists as a consequence of the instant decomposition of the TPSE groups (at 130°C $t_{1/2}$ = 5 s) and their capacity to initiate the polymerization of a vinyl monomer.

In the synthesis of PS-*g*-PBuA copolymers, 30% crosslinked products were obtained when a PS-based macroinitiator (δ 4.81) was used to initiate the polymerization, contrary to what Kollefrath et al.[13] reported when using poly(dimethylsiloxane) macroinitiators. These authors only detected formation of gel when the macroinitiators had an average number of initiating sites of 33 at 80°C. In our case, it was only possible to obtain total soluble graft copolymers when the average number of active sites in the macroinitiator was ≤2. A macroinitiator with a δ of 1.63 yielded total soluble graft copolymers even at 80% conversion.

To ascertain the optimal conditions for the synthesis of PS-*g*-PBuA to make it act like a thermoplastic elastomer, the effect of several parameters such as the effect of the dilution media, concentration of TPSE, and initial concentration of the initiator were studied. For this purpose, three macroinitiators were synthesized that had similar molecular weights but a different number of TPSE groups in the macromolecular chain. Macroinitiators (XII), (XIII-1), and (XIII-2) were obtained with free benzophenone/chlorotrimethylsilane/magnesium molar ratios of 0.1:0.1:0.05, 0.05:0.05:0.025, and 0.03:0.03:0.016, respectively. After the transformation reaction, the macroinitiators were analyzed by SEC and ^{1}H-NMR; their characteristics are listed in Table I.

Effect of Dilution in Synthesis of PS-*g*-PBuA Copolymers

The three macroinitiators described in Table I were used in a series of experiments to initiate

Table II Experimental Conditions and Characteristics of PS-*g*-PBuA Copolymers at Different Polymerization Times

Macroinitiator	No.	Polymerization Time (h)	Conversion (%)		Composition (%)		M_n ($\times 10^{-3}$ g/mol)[b]	PBuA (%)[c]	
			Total	Partial[a]	Copolymer	PBuA		Calculated[d]	^{1}H-NMR
PS (XII) (i)	1	1.5	9.1	1.8	81.38	18.61	21.1	7	22
	2	2.5	24.2	6.9	64.10	35.89	21.0	22	35
	3	3.5	34.4	9.8	57.98	42.01	20.2	29	36
	4	4.5	41.5	18.2	64.66	35.33	19.0	43	45
	5	5.5	38.6	19.9	70.50	29.50	19.5	45	41
PS (XIII-1) (i)	1	1.5	15.4	10.3	91.91	8.08	29.5	29	36
	2	2.5	49.4	26.2	68.76	31.24	28.2	51	52
	3	3.5	57.6	31.9	68.80	31.20	28.3	56	56
	4	4.5	62.7	31.2	64.09	35.90	28.9	56	59
	5	5.5	62.7	28.2	60.70	39.30	27.8	53	51
PS (XIII-2) (i)	1	1.5	59.4	48.2	86.74	13.26	33.4	66	59
	2	2.5	72.9	58.5	85.29	14.71	32.8	70	80
	3	3.5	71.8	62.9	90.80	9.20	33.8	72	77
	4	4.5	73.1	64.5	91.22	8.78	32.2	72	78
	5	5.5	—	64.2	—	—	34.4	72	82

The conditions were 130°C, [TPSE] = $6.4 \times 10^{-3}M$, and a concentration of initiator with respect to the monomer of 20 wt %.
[a] The partial conversion is the waste of monomer in the graft formation.
[b] The molecular weight determined by SEC.
[c] The percentage of PBuA in the purified copolymer.
[d] The composition determined gravimetrically.
No. = experiment number.

the polymerization of BuA at 130°C. In all cases the concentration of initiator with respect to monomer was 20 wt % and the polymerizations were carried out using toluene as a solvent. The amounts of macroinitiator used correspond to a concentration of TPSE of 6.4×10^{-3} M. After polymerization for predetermined periods of time the polymers were isolated by two precipitations from a large excess of methanol. As expected, there was no formation of gel as a consequence of the low value of δ. The conversion was calculated gravimetrically and the molecular weight was determined by SEC. The experimental conditions and characteristics of the graft copolymers obtained are reported in Table II. The evolution of the conversion with time for the three macroinitiators is presented in Figure 1.

From Figure 1 it can be observed that, in spite of the concentration of the active sites being the same in all three cases, the values of conversion are greater when the concentration of the monomer is higher. That is the case when macroinitiator PS (XIII-2) is used. The molar concentration of the monomer in this particular case is $3.3M$, which is than in the other two cases, so the rate of polymerization is larger for the same polymerization time. It can also be observed that, independent of the macroinitiator used, the conversion increases in the first stage of the polymerization as a consequence of the growth of the chains because of the dissociation of TPSE groups attached to the main chain and the insertion of more monomer molecules. After 3.5 h of polymerization, the conversion and the composition of PBuA in the copolymers that are synthesized (Table II) remains the same. This indicates that after that period of time the graft chains progressively deactivate and produce death graft chains.

However, the percentage of homopolymer increases with time as can be observed from the values reported in Table II. It can be attributed to two factors: the capacity of the diphenylmethyl (DPM) radicals to initiate the polymerization and pure thermal polymerization of BuA, which is relevant at 130°C (15%/h). These last two reactions are responsible for the decrease of the efficiency of the initiator that decreases the control over the polymerization.

As mentioned previously, no crosslinked structures were obtained in the synthesis of PS-*g*-PBuA, which was independent of the macroinitiator used, as a consequence of the low δ presented

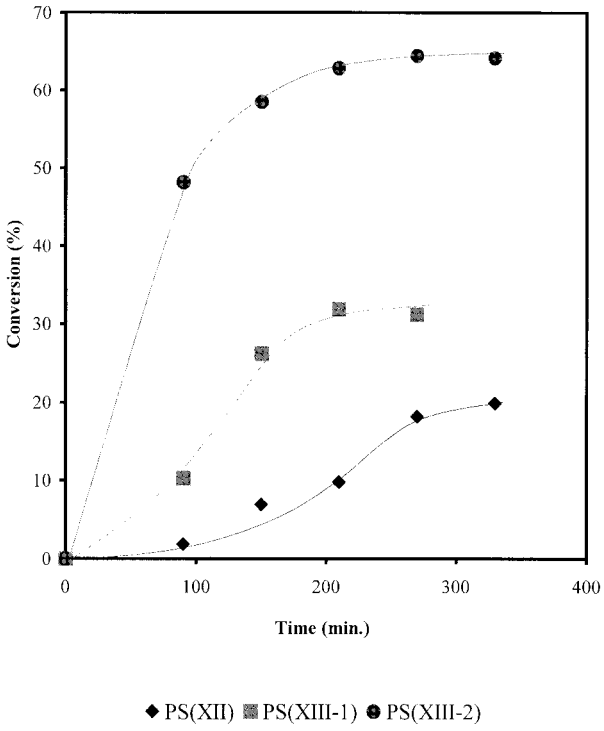

Figure 1 The evolution of the conversion with time for the polymerization of BuA initiated with PS (XII), PS (XIII-1), and PS (XIII-2) macroinitiators under the experimental conditions cited in Table II.

by them. However, macroinitiator PS (XIII-1) was considered as the best one for studying the other parameters that influence the synthesis of graft copolymers because the values of conversion were moderated (on the order of 30%), the molecular weights of the polymers obtained were double that of the initiator, and the composition of PBuA in the copolymers was approximately 50:50.

Effect of Average Number of Active Sites by Macroinitiator Molecule in Synthesis of PS-*g*-PBuA Copolymers

In order to study the effect of the δ in the synthesis of graft copolymers, equal amounts of macroinitiators (XII, XIII-1, XIII-2), monomer, and solvent were used in a series of experiments. The establishing of these conditions for the three macroinitiators implies variations in the molar concentration of TPSE of 6.4×10^{-3} *M* for PS (XIII-1), 3.7×10^{-3} *M* for PS(XIII-2), and 9.6×10^{-3} *M* for PS (XII). After polymerization for predetermined periods of time, the polymers were isolated by twofold precipitation from methanol as in the early example. Figure 2 shows the conversion curves for the polymerization of BuA initiated with the three macroinitiators as a function of time.

From the results presented in Figure 2 it can be observed that the values of conversion increase according to the number of active sites by the macroinitiator molecule and with the concentration of TPSE. In a similar way, the pendant of the curves increases with the initial concentration of TPSE, which means that the polymerization rate increases as well. Taking into account that the values of conversion for using the PS (XII) and PS (XIII-1) macroinitiators are more relevant than using PS (XIII-2), the former were analyzed by SEC and the results are presented in Figure 3. The curves of this figure reveal that, when the concentration of TPSE increases, the molecular weights decrease for a certain value of conversion.

The copolymers were analyzed by ^{1}H-NMR to determine their composition, which was found to be on the order of 20, 50, and 60 wt % of PBuA for PS (XIII-2), PS (XIII-1), and PS (XII), respectively. Once again the graft copolymers synthesized from PS (XIII-1) with a δ of 1.21 and a TPSE concentration of 6.4×10^{-3} *M* present acceptable values of conversion (30%) and the highest molecular weights.

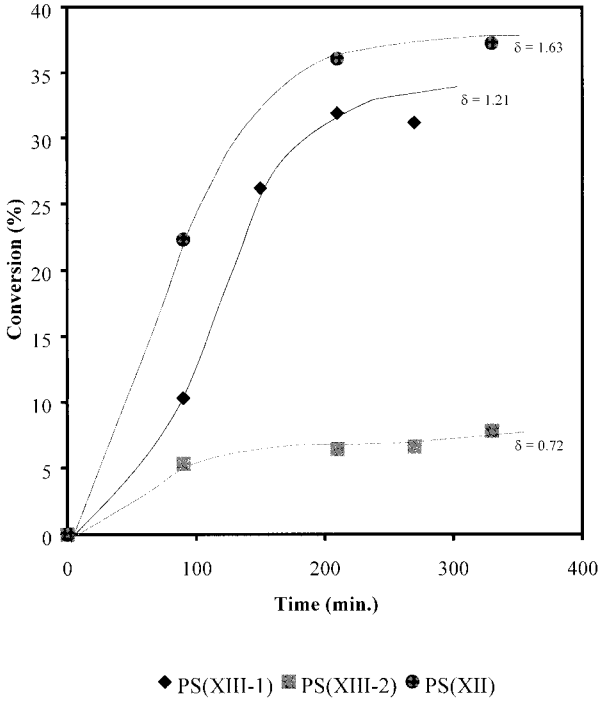

Figure 2 The conversion versus the polymerization time for the synthesis of PS-*g*-PBuA with different macroinitiators and variable TPSE concentrations ($\times 10^{-3}$ *M*) of (♦) 6.4, (■) 3.7, and (●) 9.6 at 130°C.

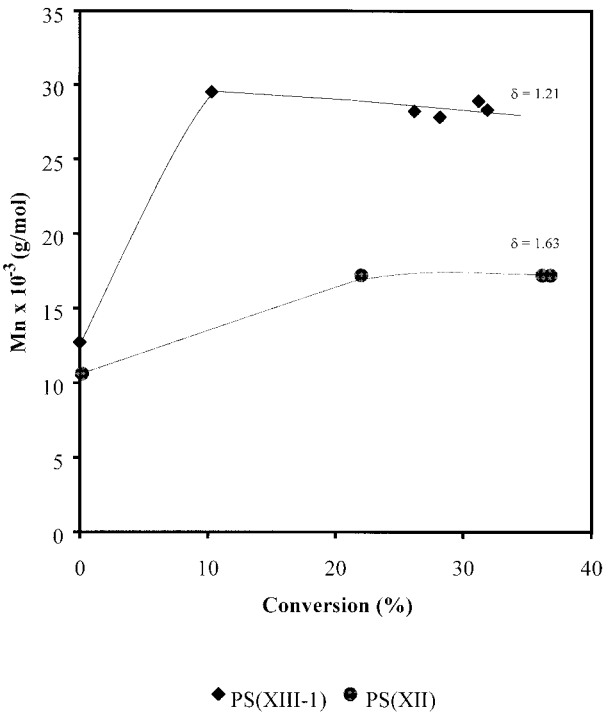

Figure 3 The molecular weight versus conversion for the synthesis of PS-*g*-PBuA with different macroinitiators and variable TPSE concentrations ($\times 10^{-3}$ *M*) of (♦) 6.4 and (●) 9.6 at 130°C.

Effect of Initiator Concentration in Synthesis of PS-*g*-PBuA Copolymers

Taking into account the previous results, we decided to use the PS (XIII-1) macroinitiator to initiate the polymerization of BuA with a TPSE concentration of 6.4 $\times$ 10^{-3} *M*; however, in this case the concentration of macroinitiator with respect to monomer increases to 10 wt %. This change was made in order to have a larger concentration of monomer (4.36*M* compared to 1.93*M* with a 20 wt % concentration of initiator with respect to monomer) and to reach higher values of conversion. Consequently, the copolymers synthesized would have higher molecular weights and the content of PBuA in the copolymers would increase as well, allowing their behavior as thermoplastic elastomers to be increased as reported for other similar systems.[16,17] Under the experimental conditions cited earlier, the copolymers obtained were isolated by twofold precipitation from a large excess of methanol. The conversion was gravimetrically determined and the results are shown in Figure 4.

As can be seen from Figure 4 and as expected, the values of conversion obtained in this case are substantially higher, reaching 72.5% of conversion without the formation of gel. Once again, the conversion increases in the first 60 min of polymerization as a consequence of the DPM radicals formed upon homolytic cleavage of the TPSE groups attached to the main chain, allowing the growth of the grafts. However, as explained, the DPM radicals can either recombine with the growing chains to generate a dormant species or initiate a new polymeric chain. This latter reaction is responsible for the slow decline of the controlled character of the polymerization that was noticed from 60 min of polymerization. Because DPM radicals can be irreversibly consumed in the formation of new chains, they progressively tend to give up their role as scavengers of the growing radicals and the probability for a bimolecular termination reaction is therefore bound to increase, provoking the deactivation of the grafts. A real linear variation of conversion with time can be observed during the first stage of polymerization, but as the conversion increases the system progressively loses its controlled character because of substantial irreversible termination.

The variation of the molecular weight with conversion was also followed (Fig. 5). Observe in the

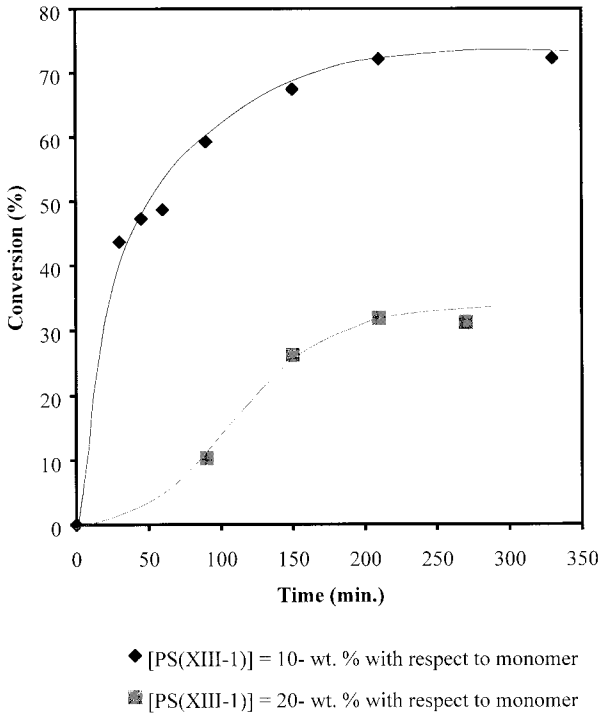

Figure 4 The conversion versus time for the synthesis of PS-*g*-PBuA with different initiator concentrations at 130°C.

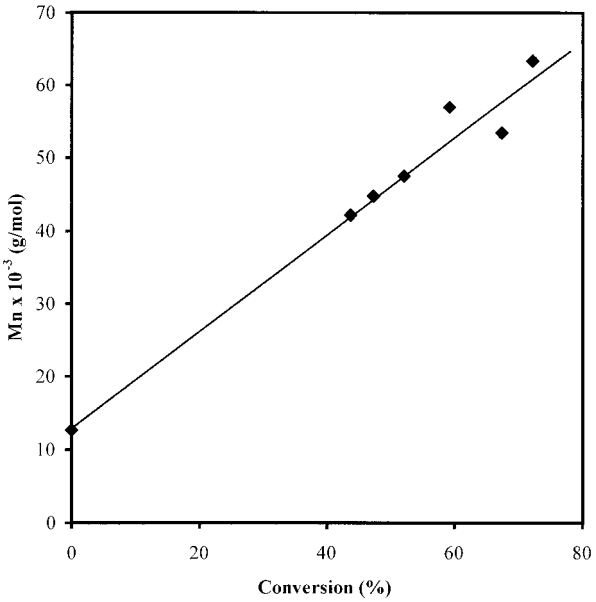

Figure 5 The molecular weight versus conversion for the synthesis of PS-*g*-PBuA [PS(III-1)] at 10 wt % with respect to the monomer at 130°C.

figure that the molecular weight increases with conversion, which attests that a certain degree of control was achieved with the use of TPSE radicals. The amount of PBuA in the copolymers was calculated by ^{1}H-NMR and found to be 79.7, 80.9, 81.4, 82.4, 84.3, 85.8, 86.7, 86.3, and 86.7 wt % for 30, 45, 60, 75, 90, 150, 210, 300, and 360 min, respectively.

Effect of Nature of Propagating Radical

The studies of different parameters like the ones analyzed previously allowed us to establish the optimal experimental conditions for the synthesis of PS-*g*-PBuA copolymers with the desired macromolecular parameters (i.e., high molecular weights and high contents of PBuA in the copolymers). However, instead of these results it was observed in all the cases that the polymerization mechanism is controlled for a limited range of conversion and molecular weight.

It was discussed earlier for this particular system and others that the main reason for the gel formation was the multifunctionality of the macroinitiator used. Another factor of no less importance is the mode of termination of the polymerizable monomer: when MMA is the monomer to be grafted, the fact that the termination reaction takes place preferentially by disproportionation makes it possible to avoid recombination between growing chains to the same extent. Moreover, it is known that carbon-centered radicals lead to a termination reaction by recombination and/or disproportionation. The disproportionation/recombination ratio depends on the structures of the implied radicals. In this way, as the substitution on the radical center increases, a persistent radical can be formed[18] and the diminishing of the spin electronic density in the α-carbon delays recombination reactions in favor of the disproportionation ones.

Having these facts in mind for our particular case, BuA was replaced with methyl BuA (MeBuA). This was done not only to lower the recombination reactions, but also to observe if in the presence of a more stable radical like the MeBu one (a tertiary radical) the termination reaction between growing and primary radicals is favored in such a way that the polymerization mechanism would be controlled for a longer period of time.

In this way MeBuA was polymerized in the presence of PS (XIII-1) under the identical experimental conditions used for the synthesis of PS-*g*-PBuA copolymers. Table III summarizes the experimental conditions and the characteristics of the copolymers obtained in this manner.

The results reported in Table III reveal similar behavior than those for BuA. However, contrary to the former, the polymerization can be controlled for longer periods of time. With MeBuA the conversion and the molecular weight increase during the first 60 min of polymerization. After this time it is observed once again that there is a loss in control as a consequence of irreversible termination reactions instead of the more stable radical. These reactions are responsible for the decrease in functionality of the growing chains and the destruction of the DPM active radicals. Therefore, it can be pointed out that the polymerization presents a controlled character in the first stages and then this character is progressively lost due to secondary reactions that eventually stop the polymerization before the total consumption of the monomer.

CONCLUSION

For the synthesis of PS-*g*-PBuA copolymers initiated with PS-based macroinitiators functionalized with TPSE the formation of gel depends exclusively on the δ of the macroinitiator molecule. A δ of ≤ 2 allows the synthesis of totally soluble graft copolymers. With respect to the polymeriza-

Table III Experimental Conditions and Characteristics of PS (XIII-1)-*g*-PMeBuA Copolymers at Different Polymerization Times

			Composition (%)		PMeBuA (% P/P)[b]		
Experiment	Polymerization Time (min)	Conversion (%)[a]	Graft Copolymer	PMeBuA	^{1}H-NMR	Gravimetrically	M_n ($\times 10^{-3}$ g/mol)
1	15	28.0	96.7	3.3	75	72	35.6
2	30	47.3	97.5	2.5	82	81	44.0
3	60	66.2	98.1	1.9	87	86	53.3
4	75	68.2	98.4	1.6	86	86	55.5
5	90	72.5	95.9	4.1	88	87	52.6
6	150	81.2	97.8	2.2	90	88	56.0
7	210	85.3	97.7	2.3	88	88	51.1
8	270	88.1	98.0	2.0	90	89	56.1
9	330	88.0	97.8	2.2	90	89	56.0

The conditions were 130°C, [TPSE] = $6.4 \times 10^{-3}M$, and a concentration of initiator with respect to the monomer of 10 wt %.
[a] The consumption of monomer in the graft formation.
[b] PMeBuA composition in the purified copolymer.

tion mechanism, it can be pointed out that it presents a certain degree of control for low values of conversion (≤30%). In this interval of conversion, the conversion and molecular weight are both linearly increased with the polymerization time. Outside of this interval the polymerization is affected by secondary reactions that decrease the controlled character because of the loss of functionality in the growing chains. In the methacrylic monomers such as MeBuA it is possible to access total soluble graft copolymers above 100°C with a better degree of control.

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