Synthesis of Graft Copolymers. II. Synthesis of Polystyrene-*g*-Poly(methyl methacrylate)

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ABSTRACT: The thermolysis of labile 1,2-bis(trimethylsilyloxy)tetraphenylethane groups pendant along polystyrene chains in the presence of various vinyl monomers leads to the direct synthesis of graft copolymers. Depending on the monomer chosen, the polymerization temperature, and the number of active sites by the macroinitiator molecule, crosslinked or total soluble graft copolymers can be prepared. Several conditions were studied in order to attain soluble polystyrene-*g*-poly(methyl methacrylate) copolymers under a controlled polymerization mechanism. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 12–18, 2002

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

INTRODUCTION

Polymer alloys and blends continue to show significant promise because the properties of the blends can be tailored by varying the type and quantity of polymers that go into the mixture. However, most polymers are immiscible and the mixtures separate into distinct domains. It is well known that block and graft copolymers can act as "compatibilizers" in such blends and enhance the structural integrity of these composites by localizing at the interface between the immiscible polymers, lowering the interfacial tension, and dispersing the incompatible polymers into smaller domains. A significant challenge in the past decades has been the synthesis of block and graft copolymers with well-defined architectures for use as compatibilizing agents.

Various methods have been applied to the synthesis of such architectures. Radical polymerization has found many applications with a large variety of monomers that can be polymerized and copolymerized and due to its undermanned experimental conditions. However, the control over the macromolecular structure in radical polymerizations is poor and worse than in ionic polymerizations. Because the possibility of controlling the molecular weight, molecular weight distribution, sequences, blocks, end groups, and branching is encouraging for the preparation of new materials, it is desirable to improve the control of the macromolecular structure in radical processes. Since the discovery of living anionic polymerization by Szwarc et al.,[1] many attempts have been made to improve the poor chemoselectivity of free-radical polymerization by establishing a dynamic equilibrium between growing radicals and dormant species. Such an equilibrium decreases the contribution of the termination reaction with the reduction of the radicals concentration; however, it is not eliminated. These kinds of polymerizations are called "controlled" radical polymerization[2] in

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contrast to the concept of "living" radical polymerization described by Szwarc et al.[1]

Several methods are applied in controlled radical processes, and they have advantages and limitations. The most investigated one is nitroxyl-mediated polymerization[3–5]; however, it seems to have little efficiency when applied to methacrylic monomers.[6] The atom transfer radical polymerization method developed by Matyjaszewski et al.[7] is used to control the radical polymerization of various monomers,[8,9] but its limitation consists of the use of substantial amounts of catalyst that must be removed after polymerization. In addition, the alkyl dithiocarbamates[10] and organometallic derivatives[11,12] are other dormant species that are reported.

There is also a family of compounds referred to as "initers" that can generate radicals upon decomposition that can initiate polymer chains and at the same time reversibly scavenge growing radicals, imparting some control to radical polymerization in a limited range of conversion and molecular weight. The most well known of these are tetraphenyl-based derivatives that include 1,2-bis(trimethylsilyloxy)tetraphenylethane (TPSE) groups. With thermally induced fragmentation these groups yield an unusually high concentration of diphenylmethyl (DPM) radicals that, in spite of relative stability due to a resonance effect, are able to initiate the radical polymerization of vinyl monomers.[13] Contrary to classical radical polymerization, in polymerization initiated by DPM radicals the molecular weight increases with the monomer conversion similar to a controlled radical process.

TPSE groups can be introduced into a polymer chain, and the macroinitiator obtained can be used to prepare block copolymers. The use of these kinds of macroinitiators made it possible to prepare poly(methyl methacrylate)-*b*-poly(butyl acrylate) (PMMA-*b*-PBuA) and PMMA-*b*-polystyrene (PMMA-*b*-PS).[14,15]

Taking advantage of the controlled character of the polymerizations initiated by DPM radicals studied earlier, it seems useful to utilize them to synthesize graft copolymers through the macroinitiator technique.

The synthesis of such macroinitiators (i.e., PS- and/or PMMA-based macroinitiators functionalized with pendant TPSE) was reported[15,16] and different kinds of graft copolymers could be obtained from them, for example, PS-*g*-PMMA, PMMA-*g*-PS, PS-*g*-polyacrylonitrile (PS-*g*-PAN), and PS-*g*-PBuA, which are justified for use as blend compatibilizers.

However, in all the graft polymerizations cited the controlled character of the polymerization was affected by the formation of homopolymers and crosslinked structures. These problems can be attributed to the fact that once the dissociation of the center C—C bond of the TPSE groups takes place, the DPM radical attached to the main chain and the free DPM radicals have the same structure and are both capable of initiating the monomer polymerization. Moreover, the number of TPSE groups in the polymeric chain, the reaction temperature, and the nature of the polymerized monomer affect gel formation.

The PS-*g*-PMMA and PMMA-*g*-PS showed that the polymerization of styrene or MMA initiated by the macroinitiators containing pendant TPSE groups depends on the temperature. At 100°C the formation of the gel was unavoidable as a consequence of irreversible termination reactions between growing chains. Moreover, the formation of small amounts of homopolymers was detected during graft polymerizations. On the contrary, at a temperature of 130°C the graft copolymer PS-*g*-PMMA was obtained without gel formation.

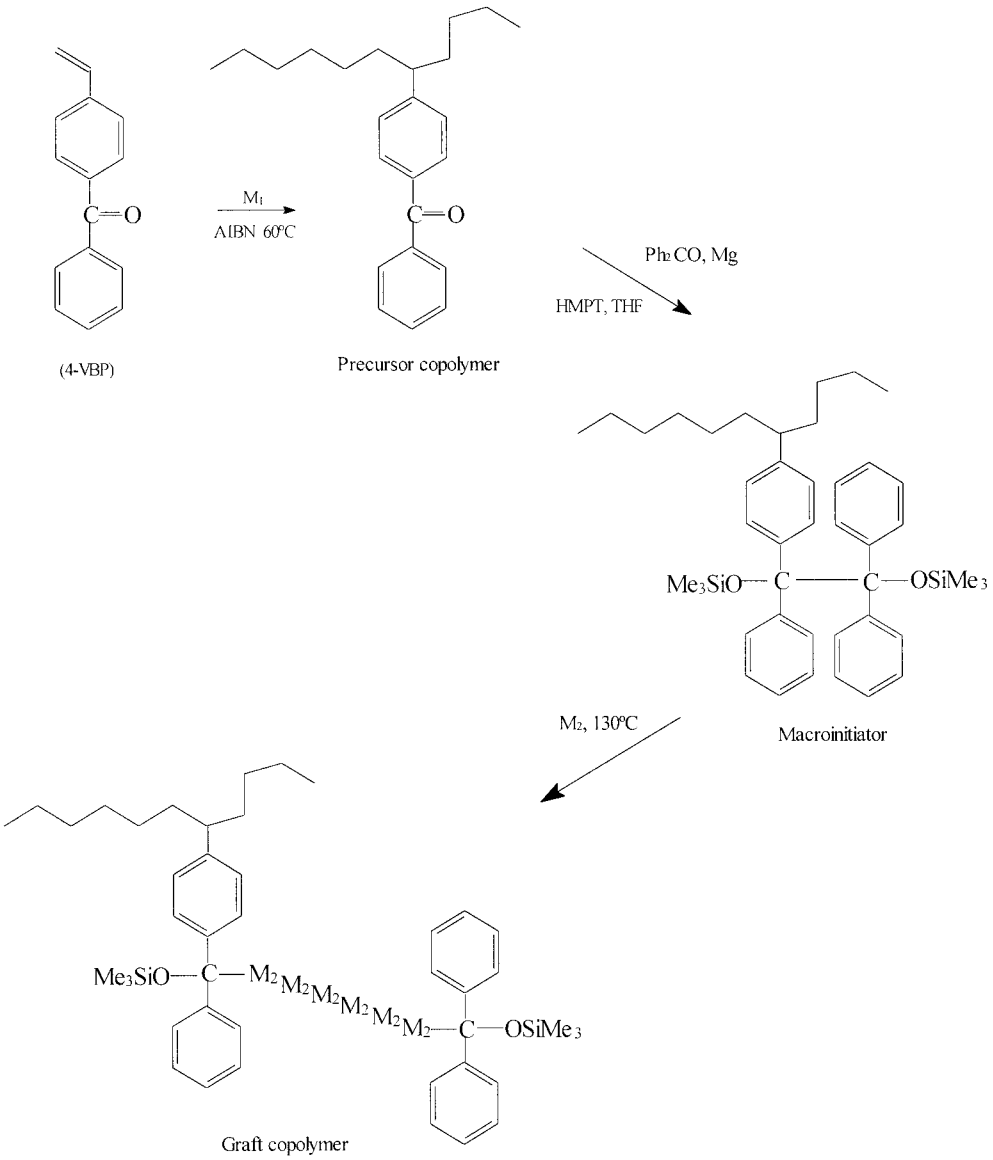
This study deals with the synthesis conditions that allow the preparation of soluble PS-*g*-PMMA prepared from TPSE-based macroinitiators and the ability of the TPSE groups to carry out the polymerizations under a controlled mechanism.

EXPERIMENTAL

Styrene was distilled over sodium under a vacuum, and MMA was distilled over sodium hydroxide under a vacuum. Toluene was purified by distillation and used immediately.

The NMR spectra were obtained with a Varian 200-MHz spectrometer. 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) and its copolymerization with styrene and the synthesis of macroinitiators were carried out as described in an earlier article.[16] Scheme 1 shows the general synthetic route to prepare graft copolymers by using TPSE-based macroinitiators. The characteristics of the macroinitiators used in this study are given in Table I.



Scheme 1 The synthesis of graft copolymers using TPSE-based macroinitiators.

Synthesis of PS-*g*-PMMA

The graft polymerization of MMA initiated with styrene-based macroinitiators was carried out as follows: the macroinitiator (0.72 g) was dissolved in the monomer (12 g) and equal amounts of the solutions were placed into six glass tubes. The tubes were degassed, sealed, and finally immersed in an oil bath at 130°C for predetermined periods of time. Conversion of pure thermal MMA polymerization was measured under the same experimental conditions. The polymers were isolated by precipitation from a large excess of methanol. After filtration they 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

The characteristics and parameters[15,16] that affect the synthesis of the precursor copolymers and the macroinitiators synthesized from them were discussed previously. These macroinitiators were then used to initiate the polymerization of several monomers (e.g., styrene, MMA, BuA, and AN). In all cases, gel formation was observed even from the beginning of polymerization.

Table I Characteristics of Macroinitiators Synthesized According to Scheme 1

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 (%)
II	4-VBP-*co*-St (2.2)	10.0	1.60	1.67	12.0	69.7
IX	4-VBP-*co*-St (5.8)	25.5	3.26	3.96	20.0	60.0
X (a)	4-VBP-*co*-St (3.4)	45.0	0.68	3.58	46.6	25.0

A, precursor copolymer; Bz, benzophenone; δ, average number of active sites (TPSE) by polymeric chain; Z, conversion of bonded benzophenone calculated by ^{1}H-NMR; and St, styrene.

[a] The molecular weight of the macroinitiators determined by SEC.

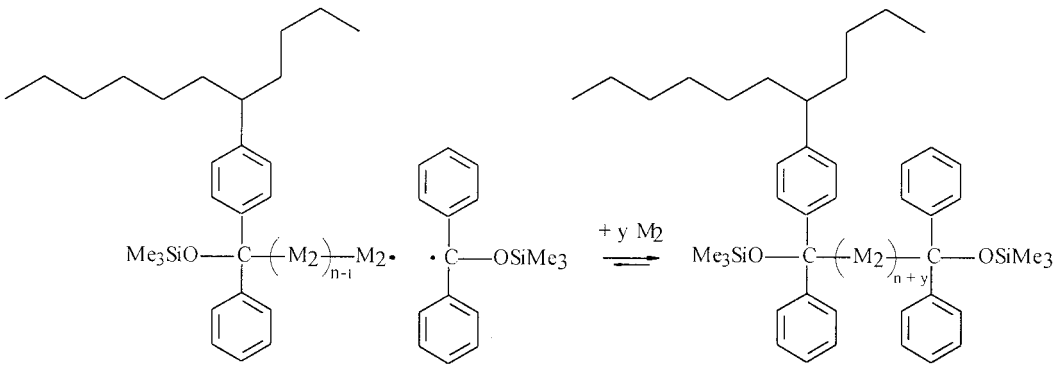
The initiation of the polymerization is due to the DPM radicals attached to the main chain. The propagation step continues by a controlled mechanism, allowing the insertion of monomer molecules in each step of dissociation between the growing radical and the DPM radical. The living polymerization mechanism proposed by Otsu[17] in Scheme 2 shows that the molecular weight increases as a consequence of successive addition and termination reactions provoked by the reversibility of the bond between the last polymerizable monomer and the DPM fragment. In an ideal case, the successive addition of monomer is from the macroradical and the primary radical DPM should only act as a moderator of the growth of the chains and be incapable of initiating new chains. In this study the "counterradical" DPM temporally stops the growing chain and at the same time it can initiate the polymerization of the monomer because it is considered an initer and produces small amounts of homopolymer in the reaction medium. Alternatively, under the experimental conditions employed, the formation of crosslinked graft copolymers from the early stages of polymerization suggests that the association described before and shown in Scheme 2 is relatively weak in that the bimolecular coupling between the growing chains can take place.

Taking into account these undesirable reactions, different strategies were studied to eliminate the formation of crosslinked structures.

Synthesis of PS-*g*-PMMA

The first studies made in the polymerization of MMA using the macroinitiator IX (see Table I), which has a number of TPSE or active sites (δ) equal to 3.96, at 90°C showed the results presented in Figure 1. In this figure the curves of conversion are a function of time for the bulk polymerization of MMA initiated with macroinitiator IX, the pure thermal polymerization of MMA (obtained under the same experimental conditions), and the amount of crosslinked product.

A comparison of curves 1 and 2 reveals that the conversion is exclusively from the TPSE groups attached to the main chain because pure thermal polymerization does not contribute significantly. It only reaches 3% after 120 min of polymerization. On the other hand, it can be observed that before 60 min there is no crosslinked polymer;



Scheme 2 The dissociation mechanism for the TPSE-based macroinitiators.

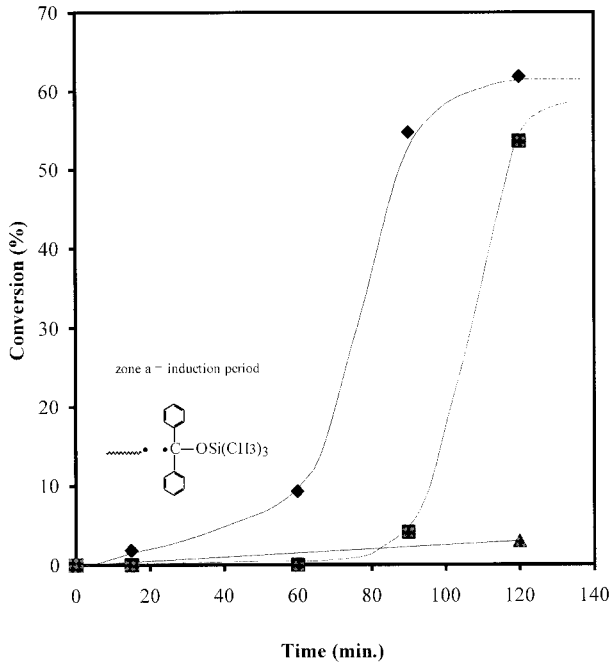


Figure 1 The conversion versus the polymerization time for the bulk polymerization of MMA initiated with (■) PS(IX), (●) content of crosslinked copolymer, and (▲) PMMA thermally produced at 90°C and with an initiator concentration with respect to the monomer of 20 wt %.

however, after that period the amount of gel increases considerably. These facts demonstrate that, although the concentration of stable radicals remains high, it is not possible that the gel formation is a consequence of primary termination reactions. When the concentration of stable radicals decrease as primary radicals are consumed in the initiation step, their effect is diminished and bimolecular termination between grafts takes place, yielding crosslinked products. It can be suggested that the radical polymerization initiated by TPSE groups does not have a relevant controlled character at high conversions. This means that a period of time exists in which these radicals control the propagation (or growing of graft chains), and it is the period in which they exist in a high concentration.

The results obtained for the PS-*g*-PMMA system were confirmed with other systems like PS-*g*-PBuA, PS-*g*-PAN, PMMA-*g*-PS, and PMMA-*g*-PBuA. In order to clarify this point, many attempts were carried out to avoid recombination between chains.

First the reaction temperature was increased up to 130°C. At this temperature it was observed that when using a α,ω TPSE-based initiator to initiate the polymerization of MMA, the molecular weight of the polymers obtained increased as a function of conversion similar to 2,2,6,6-tetramethylpiperidin-1-yloxyl's radicals for the case of styrenic monomers.

Therefore, the polymerization of MMA was carried out with a method similar to that described for the macroinitiator X (a) (δ 3.58) at 130°C. The results of such experiments reveal gel formation from the very beginning of polymerization as shown from the data reported in Table II. This can be explained by the fact that at 130°C the TPSE groups dissociate instantaneously. (At 130°C the half-life for TPSE is 5 s, and at 90°C this value is 23.4 s.) This can be interpreted that a high concentration of DPM radicals are generated in the reaction medium at 130°C, and they are consumed in the initiation and primary termination reaction at a rate considerably higher than at 90°C. From this it can be assumed that there is no induction period at 130°C.

Instead of the high concentration of primary radicals, the formation of crosslinked structures could not be avoided. As a result, another parameter that must be taken into account is the aver-

Table II Experimental Conditions and Characteristics of PS-*g*-PMMA Using Macroinitiator X (a) at Different Polymerization Times

Experiment	Polymerization Time (min)	Conversion (%)	Composition		M_n of A ($\times 10^{-3}$ g/mol)
			A (%)	Gel (%)	
1	5	46.3	60.7	39.3	103.0
2	15	60.1	54.9	45.1	135.0
3	30	67.8	49.2	50.8	99.6
4	60	90.8	35.0	65.0	127.8

The conditions were δ 3.58, 130°C, and 20 wt % initiator with respect to the monomer. A, graft copolymer.

Table III Experimental Conditions and Characteristics of PS-*g*-PMMA Using Macroinitiator II at Different Polymerization Times

Experiment	Polymerization Time (min)	Conversion (%)	Composition (%)		PMMA (wt %)[a]	M_n ($\times 10^{-3}$ g/mol)[b]
			Macroinitiator	Graft Copolymer		
1	5	10.76	16.10	83.90	72.76	41.6
2	10	19.07	9.81	90.19	83.58	54.0
3	15	30.60	9.74	90.26	86.71	56.2
4	20	38.71	4.71	95.29	89.55	57.0
5	25	46.17	5.35	94.65	89.27	83.3
6	30	59.70	4.00	96.00	92.74	103.3

The conditions were δ 1.67, a concentration of TPSE in the macroinitiator = 6.4×10^{-3} *M,* 130°C, 6 wt % initiator with respect to the monomer.

[a] The percentage of PMMA in the purified graft copolymer calculated by ^{1}H-NMR spectroscopy.

[b] The molecular weight of the purified graft copolymer.

age number of active sites (δ) by the polymeric initiator in order to diminish the probability of recombination of growing chains.

Initiator II (Table I) with a δ of 1.67 was used to initiate the polymerization of MMA at 90°C with an initiator concentration of 20 wt % with respect to the monomer. After predetermined periods of time, the polymers were isolated by precipitation in a large excess of methanol and the results revealed no formation of gel even at 90°C and the 50% conversion was reached after 1 h of polymerization. These results point out that the parameter δ has a remarkable effect on the gel point (p). It was observed that if δ decreases from PS (IX) = 3.96 to PS (II) = 1.76, the gel point could be displaced to greater conversions or even eliminated.

In order to study the effect of temperature on the polymerization reaction and taking into account that the δ of the macroinitiator is lower than 2, the polymerization of MMA was carried out at 130°C and the experimental conditions and results are reported in Table III. After polymerization the polymers were purified by precipitation in acetonitrile to remove the homopolymer that had formed. The results of this purification indicate that there is no homopolymer after polymerization as it could be observed from the corresponding ^{1}H-NMR spectra. Figure 2 shows the conversion curve for the polymerization of MMA as a function of time initiated by the PS initiator. The molecular weight versus conversion data are presented in Figure 3.

From these figures it can be appreciated that the conversion increases as a function of time and is greater than the values obtained at 90°C and the molecular weight. The most important fact is that the graft copolymers obtained are totally soluble in spite of reaching 60% conversion. These results can be explained as contributions from several factors. Alternatively, an increase in the polymerization temperature provokes a greater rate of decomposition of the TPSE groups at the same time that it causes an increase in the rate of polymerization and diminishes the induction period. An increase in the temperature increases

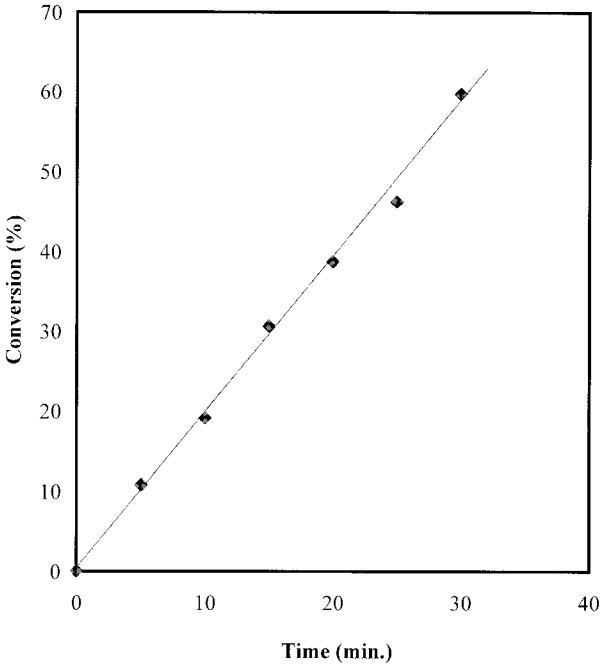


Figure 2 The conversion versus the time for the polymerization of MMA under the conditions cited in Table III.

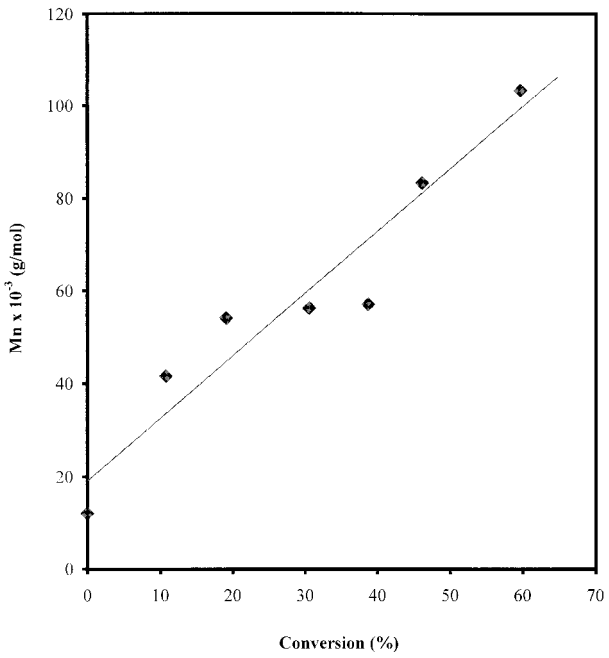


Figure 3 The conversion versus the molecular weight for the polymerization of MMA under the conditions cited in Table III.

the lability of the TPSE on the chain end, allowing better control of the chain growth.

A decrease in the δ of the macroinitiator leads to a decrease in the average number of active sites by the macroinitiator molecule and lessens the possibility of recombination of growing chains. The combined effects of these two parameters allow the synthesis of PS-*g*-PMMA copolymers that are free of gel and the polymerization mechanism can be controlled up to 60% conversion as can be seen from Figures 2 and 3.

CONCLUSION

The results obtained allow us to conclude that, under the experimental conditions employed, which was a temperature of 130°C, using a macroinitiator with $\delta \leq 2$, and a total concentration of active sites of 6.4×10^{-3}, the synthesis of PS-*g*-PMMA takes place by a controlled polymerization mechanism where the initiation reaction is as fast as the decomposition one. Under these conditions all the radicals generated upon the macroinitiator decomposition participate in the growth of chains up to 60% conversion, yielding soluble graft copolymers.

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