

Atom Transfer Radical Polymerization of Styrene Using a Novel Octafunctional Initiator: Synthesis of Well-Defined Polystyrene Stars

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ABSTRACT: A novel octafunctional calixarene derivative, namely, 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis(2-bromopropionyloxy)calix[8]arene (**1**) which was readily synthesized in one step, was used to initiate the bulk atom transfer radical polymerization (ATRP) of styrene, at 100 °C, in the presence of CuBr/2,2'-bipyridyl. Polystyrene (PS) stars of narrow polydispersity with precisely eight arms could be synthesized by restricting the polymerization to low conversion, typically below 15–20%. At higher conversions, irreversible coupling occurred between stars as evidenced by a size exclusion chromatography line equipped with a multiangle laser light scattering detector (MALLS/SEC). Octafunctional stars of molar masses up to 340 000 g mol⁻¹ could be prepared by using high ratios of the monomer to the initiator ([M]/[I] = 12 000). The precise octafunctional structure of the stars was confirmed, on one hand, by studying the kinetics of ATRP of styrene initiated by an equimolar mixture of **1** and its monofunctional equivalent, namely 4-*tert*-butylphenyl(2-bromopropionate) (**2**) and, on the other hand, by the characterization of the individual arms obtained upon hydrolysis of the ester link between the core and the branches of the stars.

Introduction

Branched polymers of controlled architecture have been designed in order to get a better understanding of the relationship between their topology and their unique solution and bulk properties, as compared to linear polymers. Among the branched structures, star polymers represent the most elementary way of arranging the subchains since each star contains only one branching point. They represent useful models for the experimental evaluation of theories about the solution properties and rheological behavior of branched polymers.¹ Star polymers have found applications in various areas (rheology modifiers, pressure sensitive adhesives, etc.)² where they serve as additives but they can also be used as such. For instance, star block copolymers with polystyrene-*b*-polybutadiene (PS-*b*-PBD) arms were shown to exhibit improved processability and mechanical properties over those of linear PS-*b*-PBD-*b*-PS copolymers.³ The polystyrene stars of Phillips⁴ and Exxon's star-branched butyls⁵ are examples of commercial star polymers.

The synthesis of well-defined star polymers is a challenging task usually achieved following a "living" polymerization route. There are essentially two methods to get access to star polymers: either by linking a given number of linear chains to a central core ("arm-first" method)^{6–8} or by growing branches from an active core ("core-first" method).^{9–12} To yield stars that would exhibit a precise number of arms, the core-first methodology requires that structurally well-defined plurifunctional initiators be used. The central core may be built upon reaction of short "living" chains with a difunctional monomer (such as divinylbenzene),^{13,14} but samples with a large fluctuation of their functionality are obtained. Initiators of high and yet precise functionality that could serve to polymerize vinylic monomers are scarce; the only examples that have been proven to afford well-

defined star polymers are those developed for use in carbocationic polymerization.¹⁰ In contrast, there are only few reports on the use of plurianionic initiators;¹⁴ this might be due to the poor solubility of the latter ones.

Compared with ionic polymerization techniques, radical processes offer the advantage of being applicable to a wide variety of vinylic monomers and having ease of preparation. The recent development of the controlled/"living" radical polymerization has opened up a new and potentially wide route to well-defined macromolecules.^{15–19} This has been achieved by maintaining a very low steady-state concentration of active growing chains which are in dynamic equilibrium with the so-called dormant species. Different approaches based on this concept have been developed which includes the method based on the Kharasch addition,^{17,18,20,21} the reversible trapping of the growing radicals by stable counter radicals such as nitroxyl derivatives^{16,19} or organo-cobalt porphyrin complexes.¹⁵ Matyjaszewski has coined the term of atom transfer radical polymerization (ATRP) for his system constituted of copper halide and bipyridyl. ATRP proceeds by successive exchanges between the halide present at the chain end of the dormant species and the transition metal compound (CuX, X = Br, Cl) activated by bipyridyl or substituted bipyridyls.

The fact that controlled radical polymerization yields polymers of predetermined molar masses and narrow polydispersity has been successfully applied in macromolecular engineering to synthesize various block and graft copolymers as well as hyperbranched polymers.^{18,22–24} Nevertheless, only few reports are available on the synthesis of star-shaped polymers. Matyjaszewski has mentioned the preparation of hexa-arm stars²² using hexakis(bromomethyl)benzene as the initiator in the ATRP of styrene and Sawamoto has reported the synthesis of a tri-arm poly(methyl methacrylate).²⁵ In their recent paper Pugh and co-workers have described the synthesis of tri-arm liquid-crystalline

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polyacrylates by ATRP using tris(bromomethyl)mesitylene as a trifunctional initiator.²⁶ In all these reports, however, the details pertaining to the characterization of the star polymers have not been presented. Following the nitroxide route, Hawker has synthesized tri-arm polystyrene and characterized them by comparing their molar mass with that of their individual arms, the latter ones being isolated by cleavage of the central core.²⁷

The dearth of information on well-defined stars by a potential "controlled radical polymerization route" prompted us to synthesize a novel multifunctional initiator for the preparation of polystyrene stars of high functionality. Here, we demonstrate the use of a novel calixarene derivative as an effective initiator for ATRP and describe the conditions best suited to the synthesis of well-defined octafunctional polystyrene stars. To the best of our knowledge, this is the first report on the synthesis and characterization of well-defined octa-arm star polymers by a controlled/"living" radical process.

Experimental Section

Materials. Styrene was stirred overnight over CaH₂ and distilled prior to use. CuBr (Aldrich) and 2,2'-bipyridyl (Aldrich) were used as received. 4-*tert*-Butylcalix[8]arene, (5,11-,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene) (TBC-8), 4-*tert*-butylphenol, 2-bromopropionyl bromide and triethylamine, all from Aldrich, were used as received. All other solvents used were purified by standard procedures.

Synthesis of the Octafunctional Initiator 5,11,17,23-,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis-(2-bromopropionyloxy)calix[8]arene (1). In a 250-mL three-neck flask, equipped with a magnetic stirrer, 3 g (2.3×10^{-3} mol) of TBC-8 was suspended in 30 mL of dry THF. Then 7.7 mL of triethylamine (5.52×10^{-2} mol) was added and the mixture became homogeneous upon stirring. The solution was cooled to 0 °C and 5.7 mL (5.52×10^{-2} mol) of 2-bromopropionyl bromide dissolved in 30 mL of THF were added dropwise over a period of 1 h and then the reaction mixture was stirred at room temperature for 48 h. The solution was concentrated and precipitated in ice cold water. The crude solid compound thus obtained was dissolved in diethyl ether and washed successively with dilute K₂CO₃ water solution and dried over anhydrous MgSO₄. Ether was removed and the concentrate precipitated from a mixture of methanol/water (90/10 v/v). The precipitation was repeated two more times to obtain a white powder of **1** in 76% yield. ¹H NMR (CDCl₃) δ: 7.1 (s, 2H, aromatic protons), 4.4 (s, 1H, -CH-), 3.7 (s, 2H, -CH₂-), 1.6 (s, 3H, CH₃-), 1.2 (s, 9H, *tert*-butyl). ¹³C NMR (CDCl₃) δ: 21.4 (CH₃-CH-Br), 30.5 (Ar-CH₂-Ar), 31.2 (-CH₃ of *tert*-butyl), 34.3 (C(CH₃)₃), 39.1 (CH₃-CH-Br), 126.1, 130.8, 144.5, 148.9 (aromatic carbons) and 167.8 (carbonyl). Elemental analysis: (*M_w* calcd for C₁₁₂H₁₃₆O₁₆Br₈, 2377 g·mol⁻¹). Calcd: C, 56.35; H, 5.72; O, 10.77; Br, 26.94. Observed: C, 55.72; H, 5.43; O, 10.76; Br, 27.75.

Synthesis of 4-*tert*-Butylphenyl(2-bromopropionate) (2). In a 250-mL three-neck flask equipped with a magnetic stirrer, 10 g (6.6×10^{-2} mol) of 4-*tert*-butylphenol was suspended in 80 mL of dry THF and 11.2 mL of triethylamine (7.9×10^{-2} mol). The mixture was cooled to 0 °C and 8.4 mL (7.9×10^{-2} mol) of 2-bromopropionyl bromide dissolved in 20 mL of THF was added dropwise over a period of 1 h. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after the solution was concentrated the crude ester was dissolved in diethyl ether. The organic layer was washed successively with dilute K₂CO₃ water solution and dried over anhydrous MgO₄. The crude product was distilled under vacuum (90 °C/2 mmHg) to obtain **2** as a colorless liquid in 80% yield. ¹H NMR (CDCl₃) δ: 7.47 (d, 2H, aromatic protons, a,a'; *J* = 8.47 Hz), 7.10 (d, 2H, aromatic protons, b,b'; *J* = 8.38 Hz), 4.60 (q, 1H, -CH-, *J* = 6.8 Hz), 1.96 (d, 3H, CH₃-, *J* = 6.9 Hz), 1.35 (s, 9H, *tert*-butyl).

ATRP of Styrene. The general procedure is as follows: To a 100-mL three-neck flask which was flamed and dried under vacuum, catalyst, ligand, initiator, and styrene were added, in the order mentioned, under a N₂ atmosphere. The flask was then placed in an oil bath thermostated at the required temperature. After it was stirred for a certain time, the flask was cooled to room temperature and the contents were dissolved in THF and then passed through a column of neutral alumina to remove the metal salts. The polymer was precipitated from an excess of ethanol, filtered, and dried at 50 °C under vacuum for 24 h. The conversion was obtained gravimetrically.

Hydrolysis of the Star Polymer. The octafunctional star polymer, 0.3 g, was dissolved in 20 mL of THF in a 250-mL round-bottomed flask fitted with a condenser and N₂ inlet. Then 10 mL of KOH (1 M solution in ethanol) was added and the charge refluxed for 72 h. The solution was evaporated to dryness, dissolved in THF, and finally precipitated in methanol and dried.

Characterization. NMR spectra were obtained using a Bruker AC200 NMR spectrometer. CDCl₃ was used as a solvent. Apparent molar masses of polystyrene stars were determined using size exclusion chromatography apparatus equipped with a Varian refractive index detector and a JASCO 875 UV/VIS absorption detector, dual detection fitted with three TSK columns (G4000HXL, G3000HXL, and G2000HXL). Calibration in the case of RI detection was performed using linear polystyrene standards. The actual molar masses of the polystyrene stars were calculated from the response of a multiangle laser light scattering detector (Wyatt technology) that was connected to a size exclusion chromatography (MALLS/SEC) line. The *dn/dc* values for polystyrene star were measured in THF, at 25 °C, with a laser source operating at 633 nm and was found to be the same as that of linear polystyrene (*dn/dc* = 0.183 cm³/g).

Results and Discussion

Synthesis of a Novel Octafunctional Initiator for the ATRP of Styrene. The preparation of polystyrene stars consisting of precisely eight arms by the core-first method called for the synthesis of an initiator possessing eight initiating sites. This novel octafunctional initiator was readily synthesized in one step starting from the commercially available TBC-8, whose chemical modification is well-documented.²⁸⁻³²

The bromoester **1** obtained was characterized by ¹H NMR, ¹³C NMR, elemental analysis, and HPLC and was found to be chemically pure. The ¹H NMR spectrum of **1** (Figure 1) showed no signal corresponding to residual phenolic protons of the starting TBC-8, indicating its quantitative esterification. The synthesis of **1** led to a mixture of diastereoisomers which explains the broad proton NMR signals observed. A small peak appearing at 2.7 ppm in the ¹H NMR spectrum was assigned to CH₃-CH(Br) protons based on the two-dimensional COSY (¹³C-¹H) spectrum, and this signal appears in addition to the one at 4.1 ppm for the same protons. The presence of these two peaks (at 4.1 and 2.7 ppm) indicates that **1** exists in more than one conformation at room temperature. The replacement of phenolic protons of the *p*-*tert*-butylcalix[8]arene by a bulky 2-bromopropionyl group makes the calixarene derivative less flexible, and it appears that a particular conformer reflected by a peak at 4.1 ppm for CH₃-CH(Br) proton is in major proportion. It should be noted that the ¹H NMR spectra of calixarene derivatives in general show a temperature dependence and the appearance of complex sets of peaks are, therefore, not surprising. ³¹FAB-MS of **1** showed a molecular ion peak at *m/e* = 2377; however, the most intense peak was that of the ion at *m/e* = 2241 which resulted from the elimination of one

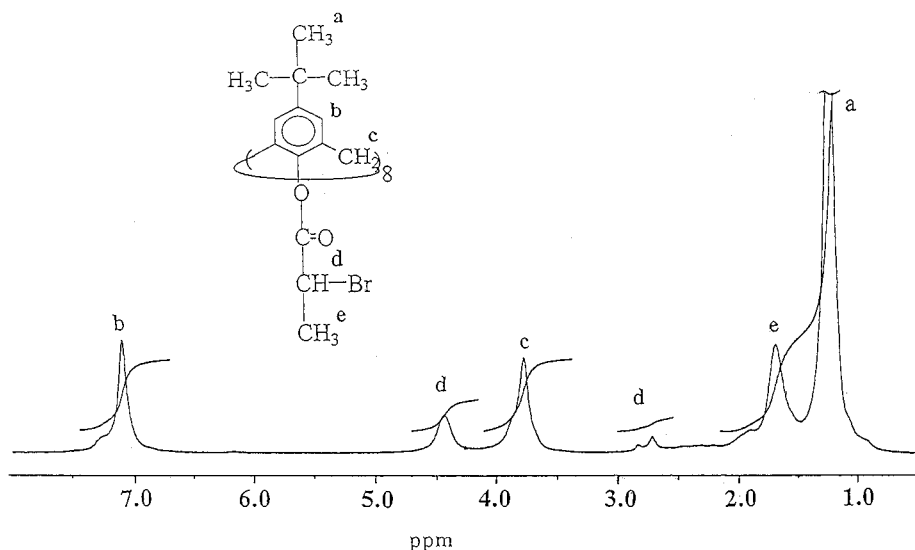
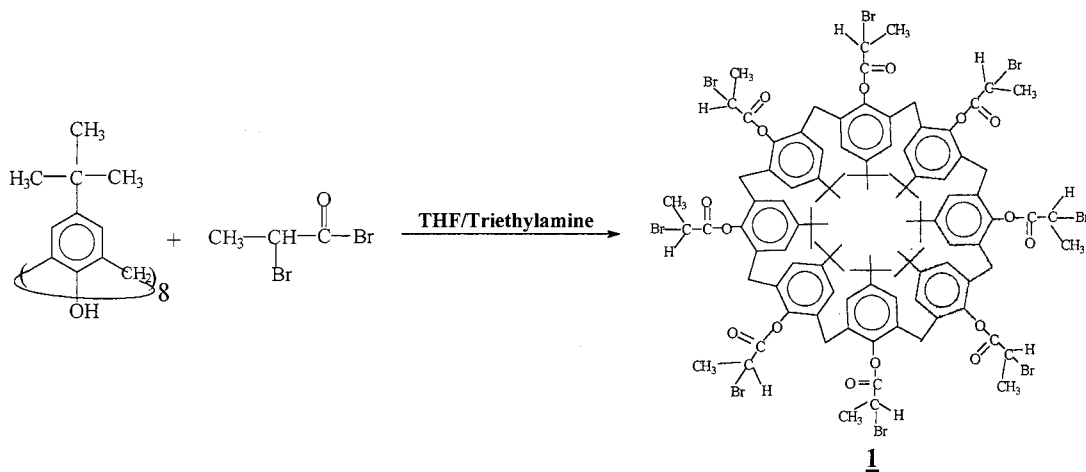


Figure 1. ^1H NMR (CDCl_3) 200 MHz spectrum of 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis(2-bromopropionyloxy)calix[8]arene (**1**).

Scheme 1. Synthesis of the Calixarene-based Octafunctional Initiator (1)

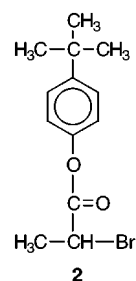


$\text{C}(\text{O})\text{CH}(\text{Br})(\text{CH}_3)_2$ group. The appearance of peaks in the FAB-MS conform to the isotopes of bromine ($\text{Br}^{79}/\text{Br}^{81}$), indicating the presence of eight bromine groups in **1**.

It is worth mentioning that, in the present case, the synthesized initiator is highly soluble in most of the common organic solvents and in monomers such as styrene and methyl methacrylate. In contrast, hexakis(bromomethyl)benzene, which was described by Matyjaszewski as a hexafunctional initiator for the ATRP of styrene,²² was found insoluble in almost all the common organic solvents including monomers such as styrene. **1** was then utilized as an octafunctional initiator for the bulk ATRP of styrene in the presence of $\text{CuBr}/2,2'$ -bipyridyl. The synthetic route is depicted in Scheme 2.

It has been shown that alkyl halides with activated substituents on the α -carbon such as carbonyl can be used efficiently to polymerize styrene.³³ Nevertheless, to establish the precise reaction conditions required for the ATRP of styrene with our novel initiator and also to check the efficiency of an ester-type initiator in this process, model experiments have first been carried out with a monofunctional equivalent of **1**, namely, 4-*tert*-butylphenyl(2-bromopropionate) (**2**).

ATRP of Styrene Using a Monofunctional Initiator, 2. The model monofunctional initiator (**2**) was



synthesized from 4-*tert*-butylphenol and 2-bromopropionyl bromide under similar conditions employed for the preparation of **1**. The results of the bulk polymerization of styrene using **2** as the initiator are given in Table 1.

As illustrated in Figure 2, the plot of $\ln[M_0]/[M]$ versus time is linear for different $[M]/[I]$ ratios (117 and 750), indicating that the apparent propagation rate constant is first-order in the monomer concentration; this implies that the concentration of the growing radicals stays constant during the polymerization regardless of the initial concentration of the initiator. The number average molar mass was found to increase linearly with conversion (Table 1) for the two series of experiments, indicating a negligible contribution of

Scheme 2. "Core-First" Synthetic Strategy for a PS Star by ATRP

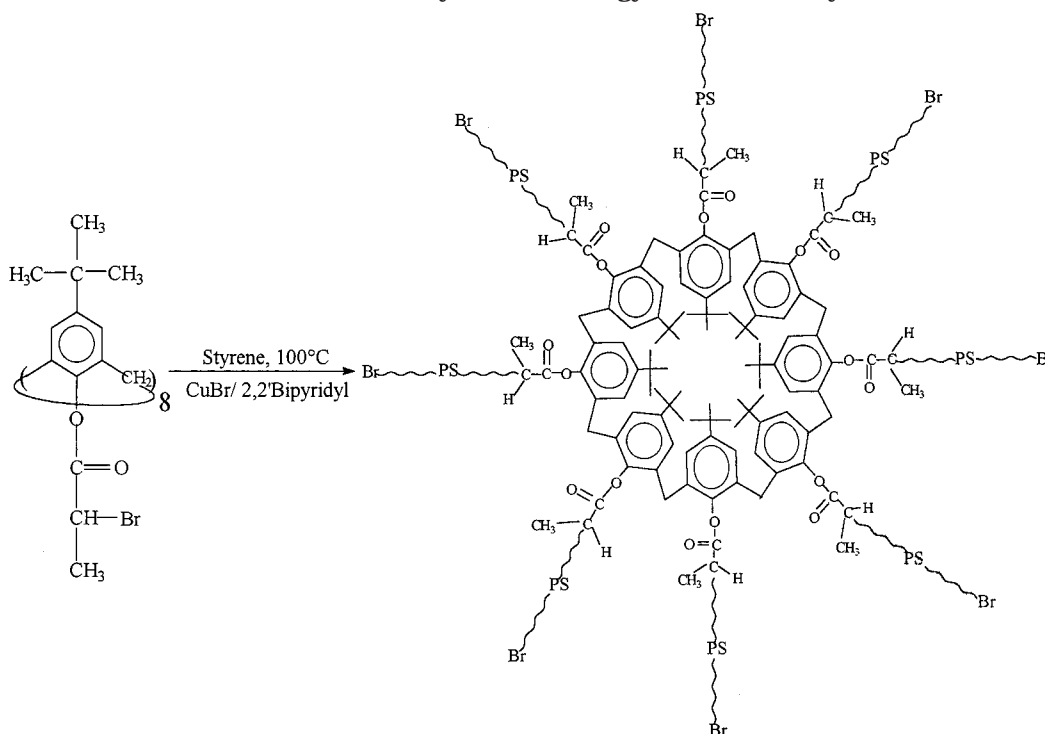


Table 1. Results of the Bulk Polymerization of Styrene, at 100 °C, Using a Monofunctional Initiator (2)^a

run	[M]/[I]	time (h)	conversion (%)	\overline{M}_n (SEC)	\overline{M}_n (theo) ^b	PDI
1	117	1.5	11.5	2000	1700	1.27
2	117	3	20	4600	4200	1.27
3	117	6	53.4	6500	6700	1.25
4	117	7	59.3	7300	7500	1.30
5	117	8	64	8500	8000	1.27
6	750	24	34.1	30000	27000	1.15
7	750	30	44	35600	35500	1.14
8	750	37	47	41800	37200	1.15
9	750	40	53	43600	42500	1.12

^a Stoichiometry of [I]:[CuBr]:[2,2'-bipyridyl] = 1:1:2. ^b \overline{M}_n (theo) = (conversion × [M]/[I] × M_n) + M_i , where M_n and M_i are the molar masses of styrene and the initiator, respectively.

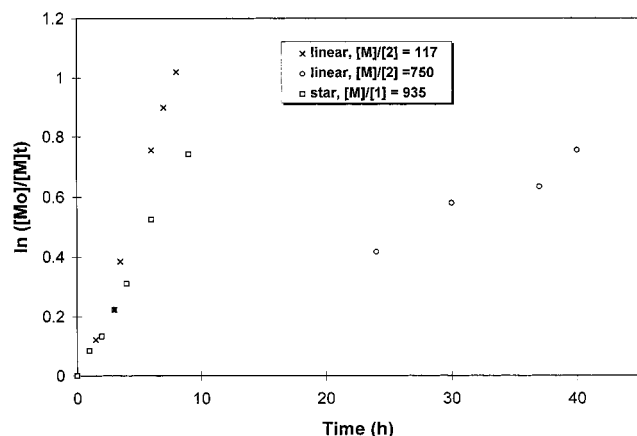


Figure 2. First-order kinetic plot for the bulk polymerization of styrene, using a monofunctional initiator (2) and octafunctional initiator (1), separately, at 100 °C.

transfer reactions under these conditions. The polymers obtained were of low polydispersity and the GPC traces were monomodal. The efficiency of the initiator (f), given by the ratio of the calculated and the experimental

\overline{M}_n values, was found to be close to unity. These results confirm that the bromoester function in 2 is an efficient initiator for the ATRP of styrene.

The polymerization with the higher [M]/[I] ratio (750 as compared to 117) resulted in polymers having relatively narrow polydispersity (Table 1) as expected for "living"/controlled processes. This is not surprising because under the condition of fast initiation the polydispersity index (I) of polymers prepared under controlled conditions is indeed known to decrease with the degree of polymerization (DP_n) according to the following equation:³⁴

$$I = 1 + \frac{\overline{DP}_n}{(\overline{DP}_n + 1)^2}$$

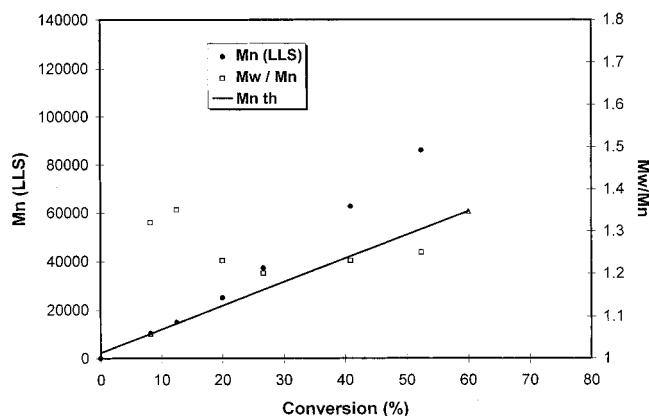
Synthesis of Octa-arm Polystyrene Stars. After the reaction conditions that are best-suited to control the polymerization of styrene are established with the model monofunctional initiator 2, the octafunctional initiator 1 was used to polymerize this monomer. In the first series of experiments the molar mass of each arm targeted was the same as that of linear polymers obtained using 2 as the initiator for synthesizing polystyrene stars; a [M]/[1] ratio of 935 was therefore chosen as compared to the [M]/[2] ratio of 117 for the linear system. The results of the bulk polymerization of styrene using 1 as the initiator, at 100 °C, are listed in Table 2.

It can be seen from Figure 2 that both octafunctional and linear systems exhibit the same kinetics only below 15–20% conversion. As to the experimental \overline{M}_n values, they match the targeted ones only until that range of conversion (Figure 3), the molar mass distribution of the corresponding star samples being all symmetrical and unimodal. Beyond 15–20% conversion the molar mass control is lost and experimental values of molar masses strongly depart from expected ones: concomi-

Table 2. Results of Bulk Polymerization of Styrene, at 100 °C, Using an Octafunctional Initiator (1)^a

run	[M]/[I]	time (h)	conversion (%)	\overline{M}_n (SEC)	\overline{M}_n (LLS)	Mn (theo) ^b	PDI
10	935	1	8.2	8 200	10 600	10 300	1.32
11	935	2	12.5	11 700	15 500	14 500	1.35
12	935	3	20	18 500	29 800 ^c	21 800	1.23
13	935	4	26.7	29 400	37 200 ^c	28 400	1.20
14	935	6	40.9	44 500	62 700 ^c	42 200	1.23
15	935	8.5	52.4	50 500	86 100 ^c	53 400	1.25

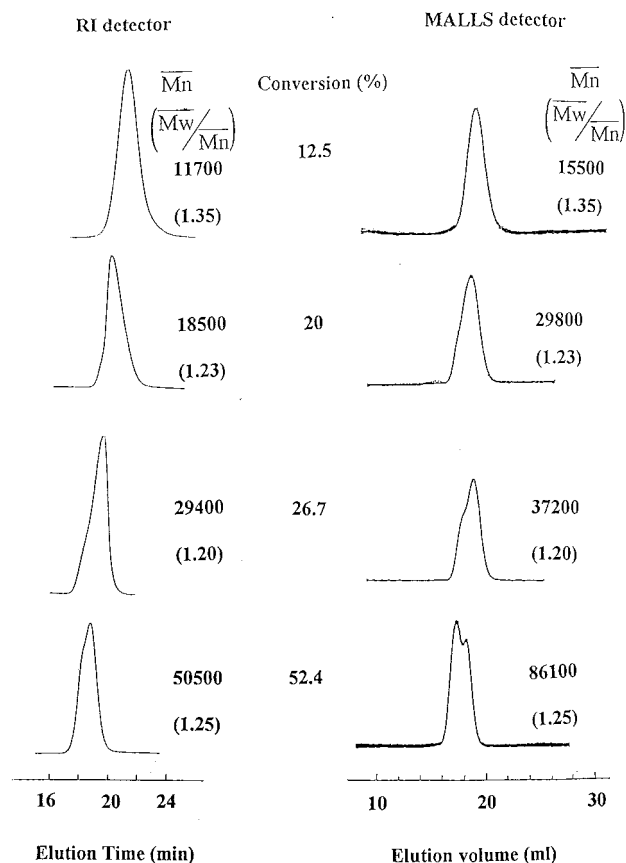
^a Stoichiometry of [I]:[CuBr]:[2,2'-bipyridyl] = 1:1:2. ^b \overline{M}_n (theo) = (conversion × [M]/[I] × M_m) + M_i , where M_m and M_i are the molar masses of styrene and the initiator, respectively. ^c Shoulder in the high molar masses region.

**Figure 3.** Evolution of molar masses and molar mass distribution with monomer conversion for the bulk ATRP of styrene, at 100 °C, using (1) as the initiator.

tantly, a shoulder appears in the high molar mass side of the SEC traces of the stars (Figure 4) which can be attributed to the irreversible coupling of the growing radicals between different stars. Moreover, the shoulder due to intermolecular termination becomes more pronounced with conversion (Figure 4). Nevertheless, all the polymers obtained are completely soluble, and no insoluble material resulting from cross-linking could be detected even at high conversion.

The use of a multiangle laser light scattering (MALLS) detector coupled to a SEC line emphasizes the presence of a separate population in the high molar mass region. The effect of termination on the shape of the eluograms could be detected more clearly then. Moreover, the MALLS/SEC technique allows the determination of the actual molar masses of the stars. The SEC technique, on the other hand, usually underestimates the molar masses of branched macromolecules due to the compact nature of the latter ones, and therefore only gives the apparent values. Figure 4 also shows the eluograms obtained from MALLS/SEC for the polymers prepared at a different conversion with a [M]/[I] ratio of 935. The SEC traces displayed in Figure 4 clearly show the better sensitivity of the light scattering detector with respect to high molar mass population.

The appearance of a second population in the SEC eluogram of stars (Figure 4) and the deviation of \overline{M}_n values after around 15–20% monomer conversion (Figure 3) can be explained as follows. In any of the controlled radical polymerizations reported so far, the bimolecular termination cannot be totally suppressed. In the case of stars both inter- and intramolecular termination of the growing radicals are possible. Coupling reactions between two different stars result in an increase of the

**Figure 4.** SEC traces (RI detector) and SEC traces (LLS detector) of polystyrene stars obtained at different conversions for [M]/[I] = 935.

molar mass; for example, after one intermolecular coupling between two stars the resulting polymer would be constituted of 14 branches instead of the expected octa-arm star. Intramolecular coupling between two branches of the same star molecule, on the other hand, might also occur, but it could not be detected using SEC, owing to its insignificant effect on the molar mass of the stars. Its occurrence should be favored only under dilute conditions, that is, at low conversion. As the kinetics of linear and octafunctional systems with same [M]/[RX] ratios ([RX] being their overall concentration of growing species) are quite comparable, at least at low conversion (<15–20% monomer conversion as shown in Figure 2), the possibility for the star arms to undergo extensive intramolecular termination at such low conversion can be ruled out.

Hence, it is most probable that termination reactions are mainly intermolecular, this being reflected in the shape of the SEC traces, with the appearance of a second population in the high molar mass region. In the case of linear polymers, the dead chains formed by bimolecular termination in a typical ATRP, although present, are usually not detected because the number of chains that undergo termination is insignificant. In contrast, the effects due to termination are certainly much more easier to detect in the case of the preparation of stars of high functionality. Indeed, even though the probability p of chain termination

$$\left(p = \frac{k_t[M^*]}{k_p[M] + k_t[M^*]} \equiv \frac{k_t[M^*]}{k_p[M]} \right)$$

is likely the same for star and linear systems, the

Table 3. Critical Overlap Concentration (C^*) for Polystyrene Stars Obtained at Various Conversions

[M]/[I]	conversion (%)	\bar{M}_n (LLS)	PS star concentration (g/L)	C^* (g/L)
935	8.2	10 600	74.7	191.5
935	12.5	15 500	114	182.6
935	20 ^a	29 800	182	176.8
935	26.7 ^a	37 200	243	83
935	40.9 ^a	62 700	372	71.9
1500	11.5	25 200	104.7	167
1500	17 ^a	31 900	154.7	149
1500	21 ^a	43 900	191.1	92
3000	6	19 700	54.6	218
3000	14.6	60 600	132.9	66.5
3000	20 ^a	76 700	182	63

^a Shoulder in the high molar masses region.

probability for two stars to get coupled should be roughly 8 times higher than that in the case of the monofunctional system described above. If one considers that a fraction x of linear growing radicals are deactivated within time t ($x[\text{RX}]_0 = k_t[\text{M}^*]^2 t$), the fraction of stars that will be affected by termination during the same time will be 8 times the value for linear chains, just because $[\text{RX}]_0$ is equal to $8[\text{stars}]_0$.

With a [M]/[I] ratio of 935 well-defined PS stars could not be synthesized beyond molar masses of $16\,000\text{ g}\cdot\text{mol}^{-1}$. In an attempt to prepare well-defined stars of higher molar masses, a second series of experiments were carried out using quite higher [M]/[I] ratios (1500–12000, Table 3). By increasing the [M]/[I] ratios, one can indeed expect to lower the probability for termination with respect to that of propagation: well-defined stars of higher molar masses could actually be synthesized using this technique until around 15–20% monomer conversion; thereafter, the polymerization was ill-controlled (see Table 3).

The fact that effects due to intermolecular termination appear only above 15% monomer conversion, as observed from the MALLS/SEC traces and Figure 2, may not be coincidental. It is likely that the stars formed in the reaction medium have reached their critical overlap concentration³⁵ C^* (with $C^* = 3\bar{M}_w/4\pi R_g^3 N_a$, where \bar{M}_w is the absolute mass average molar mass of the star obtained by light scattering and R_g is the radius of gyration of a linear PS exhibiting the same hydrodynamic volume as that of the star) and are therefore more inclined to undergo intermolecular termination than are linear chains prepared with the same [M]/[RX] ratio. Table 4 clearly shows that well-defined stars, in terms of molar mass control and polydispersity, could be synthesized provided the actual concentration of stars in the reaction medium is below their C^* . Stars obtained under these conditions of conversion and concentration with relatively high [M]/[I] ratios (1500 and 3000 as compared to 935) indeed show symmetrical and narrow molar mass distribution (Table 3). However, Table 4 also presents the evidence for the occurrence of intermolecular termination in detectable proportion whenever the actual concentration of stars cross their critical overlap concentration. R_g values used in the above formula are those obtained at 25 °C, and the comparison of C^* , thus obtained, to the PS star concentration at 100 °C may involve some error.

The experiments carried out with still higher [M]/[I] ratios (6000 and 12000) indicate that C^* might not be the only factor that controls the occurrence of intermolecular termination between stars. Obviously, the

overall concentration of the chain and thus the instantaneous concentration of growing radicals also plays an essential role. Indeed, well-defined stars of quite high molar masses ($270\,000\text{ g}\cdot\text{mol}^{-1}$) were obtained using such high [M]/[I] ratios (>6000 , Table 3) well-above their overlap concentration. Provided the concentration of radicals is low enough, these experiments show that it is possible to grow star polymers of rather large sizes with a minimized possibility of bimolecular termination.

However, with such high [M]/[I] ratios, the rate of polymerization was very slow and it took longer ($>15\text{ h}$) to achieve a monomer conversion of around 20%. There is another feature that is related to the use of very low concentrations of the initiator: the SEC traces of the corresponding stars exhibited an additional small peak in the low molar mass region that is certainly due to the formation of a linear polymer by the thermal polymerization of styrene. A representative eluogram of the PS star obtained using a [M]/[I] of 12 000 (monomer conversion = 18%) is given in Figure 5. The pure star was then isolated from the linear contaminant by extracting the latter using cyclohexane as follows. The sample was dissolved in cyclohexane by heating and the homogeneous solution was cooled and allowed to stand at room temperature overnight. Two phases were obtained and the lower viscous phase was found to be rich in the star polymer. The lower layer was separated and the operation was repeated two more times to obtain a pure star polymer. SEC traces of the star polymer before and after cyclohexane extraction is given in Figure 5. The extraction procedure followed was rather crude and a small proportion of stars was certainly lost in the cyclohexane extract which is reflected in the slightly increased molar mass of the star after cyclohexane extractions (see Table 3). It should be noted that the presence of these linear chains could be detected only after a reaction time of approximately 15 h, the corresponding peak in the SEC trace becoming more important with the duration of the polymerization. The fact that the molar mass ratio of the two species detected by SEC revolves around the value of 8 indicates that the low molar mass materials are certainly linear chains produced from the beginning of the polymerization by the thermal process. Being created at the earlier stage of the polymerization, these chains whose proportions do not exceed 10% of the total sample grow at the same rate as that of the star arms. This feature would mean that the concentration of radicals formed by the thermal mechanism at the earlier stage of the polymerization is quite small as compared to the amount of radicals produced by the reduction of the secondary bromine bond by Cu(I). As to the chains that are generated by the thermal process throughout the polymerization time, they could not be detected due to their negligible amount. Thus, well-defined octa-arm star polymers as high as $340\,000\text{ g}\cdot\text{mol}^{-1}$ ($I = 1.10$) could be synthesized by this strategy by increasing the initial feed ratio ([M]/[I]) to 12 000 and subsequently eliminating linear contaminants.

Characterization of Polystyrene Star Functionality. The ^1H NMR spectra of the synthesized star polymer ($\bar{M}_n = 8200$) exhibit a signal at 4.5 ppm which can be assigned to the secondary bromine end group ($-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Br}$). As to the signal corresponding to the methine proton of the initiator (at 4.3 ppm), it has completely disappeared, indicating a quantitative initiation.

Table 4. Results of Bulk Polymerization of Styrene, at 100 °C, Using an Octafunctional Initiator (1) at High [M]/[I] Ratios^a

run	[M]/[I]	time (h)	conversion (%)	\overline{M}_n (SEC)	\overline{M}_n (LLS)	\overline{M}_n (theo) ^b	PDI
16	1500	3	11.5	17 800	25 200	20 500	1.23
17	1500	4	17	27 400	31 900	29 000	1.21
18	1500	5	21	33 600	43 900 ^c	35 200	1.14
19	3000	4	6	13 300	19 700	19 000	1.20
20	3000	8	14.6	43 300	60 600	48 000	1.12
21	3000	12.5	20	51 400	76 700 ^c	63 700	1.10
22	6000	15	12.5	56 500	84 000 ^d	80 400	1.10
23	6000	20	19.5	104 900	146 000 ^d	124 300	1.10
24	12000	27	18	175 000	276 000 ^d	227 000	1.10
					340 000 ^e		

^a Stoichiometry of [I]:[CuBr]:[2,2'-bipyridyl] = 1:1:2. ^b \overline{M}_n (theo) = (conversion × [M]/[I] × M_n) + M_i , where M_n and M_i are the molar masses of styrene and the initiator, respectively. ^c Shoulder in the high molar masses region. ^d Additional peak in the low molar masses region. ^e After cyclohexane extraction.

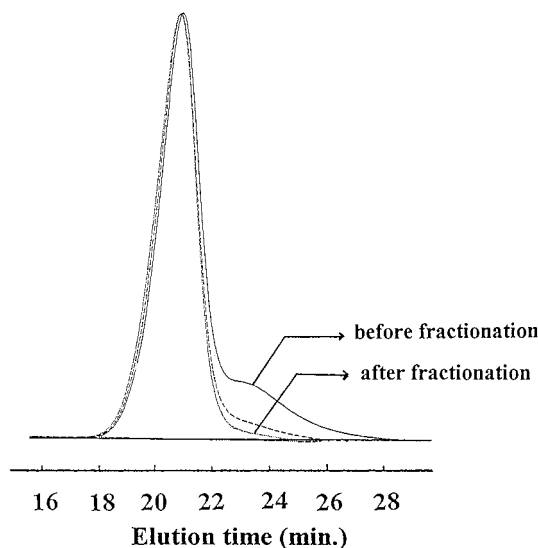


Figure 5. SEC traces (RI detector) of polystyrene stars ($\overline{M}_n = 276\,000$) obtained using [M]/[I] of 12 000, before and after cyclohexane extraction.

SEC molar masses of polystyrene stars are lower than those obtained by MALLS/SEC which clearly demonstrates that the octa-arm PS stars obtained from the calixarene-based initiator exhibit a branched structure. However, to better characterize these stars and to determine their precise functionality, we have envisaged the two following methods.

(i) *Synthesis of Linear and Star Polymers in One Pot Using a Mixture of Mono- and Octafunctional Initiators.* The bulk polymerization of styrene was carried out in the presence of a mixture of initiators **1** and **2** used in equal molar proportions with respect to the initiating site. The aim was to generate both star and linear polymers in the same experiment in order to compare their molar masses and deduce the functionality of the stars. The kinetics of mono- and octafunctional initiators as can be seen from Figure 2 are quite close below 20% monomer conversion, and hence the stars prepared under such experimental conditions should be constituted of arms of the same molar mass as that of the linear polymer concomitantly formed.

Different experiments were then carried out by varying the [M]/[I] ratio and by restricting the conversion below 15–20% in order to obtain well-defined samples. SEC traces exhibited two peaks, the one appearing at lower elution volumes corresponding to the star and the other one to the linear polymer. A typical SEC trace is

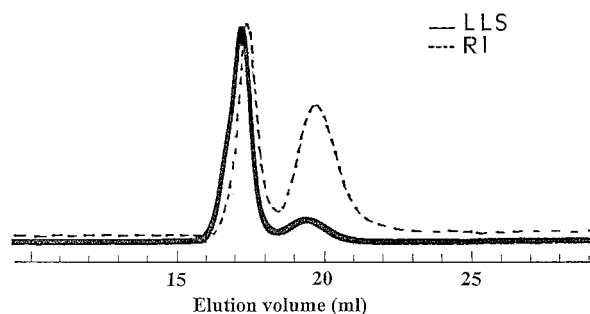


Figure 6. SEC traces (LLS and RI detectors) of the mixture of linear and star polystyrene, obtained by using an equimolar mixture of (**1**) and (**2**) as initiators.

Table 5. Determination of the Actual Functionality of Polystyrene Stars

\overline{M}_n (LLS) of star PS	\overline{M}_n (RI) of linear PS	$f = \overline{M}_n \text{ star (LLS)} / \overline{M}_n \text{ linear (RI)}$
52 000	6 400	8.1
89 000	11 400	7.8
123 000	16 000	7.7
340 000	43 000	7.9

given in Figure 6. The surface areas of the two peaks drawn by the RI detector are approximately equal, and this further substantiates the fact that the rates of polymerization of styrene with respect to **1** and **2** are identical. The actual molar masses of the linear and star species that are listed in Table 5 were obtained by MALLS/SEC. The ratios of the \overline{M}_n of the star to that of the linear polymers were found to be close to the theoretical value of 8, confirming the presence of eight arms attached to the calixarene core.

(ii) *Hydrolysis of the PS Star.* The PS arms are attached to the calixarene core through an ester function that could be cleaved by hydrolysis under basic conditions yielding linear PS. By comparing the molar masses of stars before and after hydrolysis, one can obtain another proof for the star structure. Core destruction has been reported earlier as a useful method to determine the number of branches in star structure.^{10,27} Our star polymers were hydrolyzed using KOH in a mixture of THF and ethanol, and the resulting hydrolyzed polymers were characterized by SEC. The representative SEC traces of the starting well-defined star and the corresponding hydrolyzed polymer are given in Figure 7.

The SEC trace of the linear polymer obtained after hydrolysis is monomodal. It appears also that the

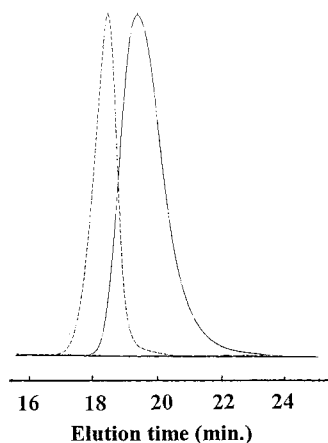


Figure 7. SEC traces (RI detector) (a) before and (b) after hydrolysis of the ester function.

polydispersity of the star polymer is lower than that of their individual arms. This is not surprising since Flory has demonstrated that stars constituted of branches with "the most probable distribution" of chain lengths should exhibit a narrower molar mass distribution corresponding to the relation: $\overline{M}_w/\overline{M}_n = 1 + (1/f)$, where f is the functionality of the star. The ratio between the molar masses obtained before ($\overline{M}_n = 340\,000$) and after hydrolysis ($\overline{M}_n = 43\,000$) was found to be close to 8, confirming that the synthesized stars exhibit the expected functionality.

Hydrolysis of ill-defined stars (in which a shoulder in the high molar mass region could be seen in their SEC trace), on the other hand, resulted in linear polymers, but their SEC traces, unlike the case of well-defined stars, were not monomodal and a shoulder could be seen on the high molar mass region. This can be explained as follows: upon hydrolysis, species corresponding to star-star radical coupling should give rise to the formation of 15 linear chains, out of which one chain should exhibit twice as much as the molar mass of the others. This higher molar mass population appears as a shoulder in the SEC trace of the material obtained after hydrolysis of ill-defined stars. The presence of this shoulder further substantiates the occurrence of coupling between growing stars during the radical process. The corresponding ratios between the molar masses measured before and after hydrolysis were found to be less than 8 for the reasons explained above.

Conclusions

Preparation of octa-arm polystyrenes of precise functionality, by ATRP, has been demonstrated using a novel calixarene-based octafunctional ATRP initiator specifically designed for this purpose. This initiator was synthesized, in one step, starting from commercially available *tert*-butylcalix[8]arene. Well-defined stars could be synthesized by maintaining the monomer conversion below 15–20%, beyond which the molar mass control was lost and the MALLS/SEC traces exhibited a bimodal distribution indicating the occurrence of significant intermolecular termination. To

obtain well-defined stars of high molar mass (up to \overline{M}_n of $340\,000\text{ g mol}^{-1}$), it was found appropriate to use high $[M]/[I]$ ratios (>6000) and slowly grow the star arms. The only drawback that is associated with the use of such large $[M]/[I]$ ratios (>6000) is the contamination of the star samples by some linear chains that are produced by the thermal polymerization of styrene. A last step of fractionation is required in this case to isolate pure star samples.

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