Newly Designed Star-Shaped Polystyrene: Synthesis and Characterization

Eric Cloutet,[†,‡] Jean-Luc Fillaut,[‡] Didier Astruc,*[,‡] and Yves Gnanou*[,†]

Laboratoire de Chimie des Polymères Organiques, ENSCPB-CNRS-Université Bordeaux 1
(UMR 5629), Avenue Pey Berland, B.P. 108, 33402 Talence Cedex, France,
and Laboratoire de Chimie Organique et Organométallique, CNRS-Université Bordeaux 1
(UMR 5802), 351, Cours de la Libération, 33405 Talence Cédex, France

Received April 15, 1998; Revised Manuscript Received July 14, 1998

ABSTRACT: In this study, emphasis is placed on the synthesis of hexaarm star polystyrene obtained via "living" cationic polymerization, using a newly designed hexafunctional initiator (**1**). This hexafunctional initiator (**1**) has been prepared via $[Fe(C_5H_5)]^+$-induced hexabenzylation of hexamethylbenzene, followed by a regiospecific sequence of reactions meant to generate six phenylethyl chloride (PhEtCl) groups on the para position of the outer rings. The conditions that afford a truly controlled polymerization of styrene were first defined using PhEtCl as the monofunctional model of (**1**). Finally, these conditions were used to build hexaarm star polymers from (**1**) as plurifunctional initiator. Well-defined star samples were obtained over a wide range of molar masses (10^3 g/mol ≤ $\bar{M}_n$ ≤ 10^5 g/mol) via this original divergent method.

I. Introduction

Among all branched structures that are known, star-shaped polymers have been certainly the most investigated architectures, attracting much experimental[1] and theoretical[2] interest. Indeed, star polymers represent the simplest model of branched structures, involving only one central branching unit per macromolecule. The best defined among them contain a precise number of arms of equal length. Such species have been very useful in providing further insight into how branching affects the overall properties of polymers in solution or in melt.[2] Some of the applications involving star polymers are the direct result of these structure−property investigations, these branched polymers being now commonly used as viscosity modifiers in paints and coatings or for their improved processability and mechanical properties compared to their linear analogues.[3]

Most of the stars so far obtained have been made by anionic polymerization, via the so-called "arm-first" methodology. This strategy was proved to work particularly well when applied to the deactivation of styryl[4] and dienyl[5] lithium headgroups by chlorosilanes. Polybutadiene stars with not less than 128 arms[6] and the so-called miktoarm stars[7] made of four different types of branches are two recent additions based on this chemistry. The deactivation of cationic "living" chains by plurifunctional nucleophiles was also shown to be an efficient way for the preparation of star-shaped polymers. However, this methodology, which was mainly exploited by the Higashimura team, could only be applied to the synthesis of poly(vinyl ether) stars, multifunctional malonate salts and silyl enol ethers being used in this case as deactivating agents.[8] Star-shaped polymers were also obtained by linking linear "living" chains to a cross-linked core formed by addition of a divinylic molecule at the ultimate step of the process.[9] Such stars are generally ill-defined and exhibit a rather large distribution of functionality. Numerous examples of stars derived by this technique via anionic,[10] cationic,[11] metathesis,[12] or group transfer[13] polymerizations can be found in the literature.

It can be observed that stars prepared by either of the two arm-first methodologies are not designed to participate in further reactions; they generally do not carry a reactive function at the external tip of their arms, unless protected initiators were purposely used. Though quite attractive, the concept of protected initiators entails some limitations due to the fact that functional initiators are not readily available and are generally poorly soluble in hydrocarbon solvents. An alternative procedure for the preparation of end-functionalized star polymers is to resort to the so-called core-first approach. The main limitation associated with this methodology is the paucity of initiators that exhibit high and yet precise functionality. In anionic polymerization, all plurifunctional initiators that have been described[14] are ill-defined, showing a broad distribution of functionality. In contrast to this situation, several well-defined plurifunctional initiators have been developed and successfully used in cationic polymerization. Kennedy et al. have prepared three-, four-, and eight-arm polyisobutylene (PIB) stars from initiators containing three, four, and eight cumyl methyl ether initiating groups,[15] respectively. The same team recently showed how to end functionalize such eight-arm PIB stars with allyl functions.[16] Higashimura[17] and Deffieux[18] have prepared three-arm poly(vinyl ether) stars from trifunctional initiators. One can infer from these examples that cationic processes are particularly well suited to the core-first methodology, affording star samples that can be post functionalized

Surprisingly, no attempt has been made as yet to prepare polystyrene (PS) stars by cationic polymerization using a plurifunctional initiator. The recent disclosure by Higashimura[19] and Matyjaszewski[20] that styrene can be cationically polymerized under "living" conditions incited us first to elaborate a plurifunctional molecule fitted with the same initiating sites as that

---

* To whom all correspondence should be addressed.

[†] ENSCPB-CNRS-Université Bordeaux 1 (UMR 5629).

[‡] CNRS-Université Bordeaux 1 (UMR 5802).

S0024-9297(98)00587-7 CCC: $15.00

used by these authors and then to grow PS stars from this initiator. Advantage was taken of the opportunities granted by Fe(η-C_5H_5)$^+$-induced perfunctionalization of methyl aromatics[21] to devise a novel hexafunctional initiator containing not less than six phenyl ethyl chloride (PhEtCl) functions.[22] In this study, emphasis is placed on the synthesis of this original compound and above all on its use as initiator of the controlled carbocationic polymerization of styrene. The hexafunctionality of the PS stars obtained in this way was carefully checked using appropriate methods of characterization.

II. Experimental Section

A. Materials. All reactions were carried out under dry Argon atmosphere and were kept safe from light for the iron sandwich complexes, using Schlenk techniques. Dimethoxy-1,2-ethane (DME) was distilled from sodium/benzophenone. Methanol was refluxed over Mg for 24 h and distilled before use. All other reagents were purchased from Aldrich and were used after distillation for the liquids or drying for the solids. All anhydrous solvents were deaerated before use. Tetrahydrofuran was distilled from sodium/benzophenone; $SnCl_4$ (Aldrich, purity > 99,9%, 1.0 M solution in CH_2Cl_2) was used as received and handled under dry Argon. Commercial styrene and 1-phenylethyl chloride (PhEtCl) were distilled twice over calcium hydride (CaH_2) under reduced pressure, the last distillation being achieved just before use; 2,6-di-*tert*-butylpyridine (DTBP) was stirred over KOH for 1 day and distilled just before use. Tetra-*n*-butylammonium chloride (n-$Bu_4N^+Cl^-$) salts were dissolved in CH_2Cl_2 and dried over CaH_2 for 2 days, filtered under dry Argon and, after removal of solvent under vacuum, dried under vacuum at 90 °C. 1,4-Dioxane was purified by distillation from sodium/benzophenone. Polymerizations were performed in a 500 mL-reaction vessel equipped with six outlets and a magnetic stirrer, under dry argon, and quenched with prechilled methanol containing a small amount of ammonia (10% in volume of 6 N ammonia).

B. Preparation of the Hexafunctional Initiator 1. Compound **2** was prepared as described in reference (21).

(a) $C_6[(CH_2)_2C_6H_4COCH_3]_6$, 3. To a 250 mL three-necked flask containing 500 mg (0.7 mmol) of **2** were added 1 mL (14 mmol) of freshly distilled acetyl chloride and 50 mL of CH_2Cl_2. After addition of 1.85 g (14 mmol) of aluminum trichloride (Al_2Cl_6) by means of a bulb for solids, the mixture was stirred at room temperature for 12 h. The excess Al_2Cl_6 was hydrolyzed by addition of water, and the product was extracted with CH_2Cl_2. The extract was washed with water, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure using a rotary evaporator. Recrystallization from heptane gave 582 mg (0.6 mmol) of white crystals of **3** in 86% yield. ^1H NMR: ($CDCl_3$, δ ppm) 7.3 (m, AA′BB′system, C_6H_4, 24H), 3.0 and 2.9 (unresolved m, CH_2, 24H), 2.6 (s, CH_3, 18H). ^{13}C NMR ($CDCl_3$, δ ppm): 197.7 (C=O), 147.3 (Cq−C=O), 136.4 (CH_2−Cq), 135.5 (Cq−CH_2), 128.9 and 128.3 (CH of C_6H_4), 37.8 and 32.2 (CH_2), 26.7 (CH_3). Anal. Calcd for $C_{66}H_{66}O_6$: C, 83.02; H, 6.92. Found: C, 82.90; H, 7.00. Mp = 227−229 °C.

(b) $C_6[(CH_2)_2C_6H_4CH(CH_3)OH]_6$, 4. A 0.45 g (12 mmol) sample of $NaBH_4$ was dissolved in a mixture of solvents $MeOH/CH_2Cl_2$ (40/30 mL), and stirred for 5 min at room temperature. To this solution, was added 0.38 g (0.4 mmol) of **3** dissolved in 10 mL of CH_2Cl_2 through a steel cannula (under an argon flow), and the solution was stirred at room temperature for 16 h. The reaction mixture was hydrolyzed by addition of 1 M NaOH. The product was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and filtered. After concentration of the solvent by means of a rotary evaporator, recrystallization from hexane yielded 279 mg (0.29 mmol) of the hexa secondary alcohol **4** as a white powder in 72% yield. IR (FT): $\nu_{OH} = 3100-3700\ cm^{-1}$ (KBr). ^1H NMR (CD_3OD, δ ppm): 7.1 (m, AA′BB′system, C_6H_4, 24H), 4.8 (q, CH(CH_3)OH, 6H), 3.3 (s, OH, 6H), 2.8 and 2.7 (unresolved m, $(CH_2)_2$, 24H), 1.4 (d, CH(CH_3)OH, 18H. ^{13}C NMR (CD_3OD, δ ppm): 145.4 (CH_2−Cq), 142.3 (Cq−CH(CH_3)OH), 137.7 (Cq−$(CH_2)_2$), 129.3 and 126.7 (CH of C_6H_4), 70.8 (CH(CH_3)OH), 38.6 and 33.4 $(CH_2)_2$), 25.8 (CH_3). Anal. Calcd for $C_{66}H_{78}O_6$, C, 80.49; H, 8.13. Found: C, 80.29; H, 8.22.

(c) $C_6[(CH_2)_2C_6H_4CH(CH_3)Cl]_6$, 1. A 20 mL aliquot of thionyl chloride ($SOCl_2$) was slowly added in a Schlenk flask to 375 mg (0.39 mmol) of **4** at 0 °C. The reaction mixture was allowed to warm and was stirred for 4 h at room temperature. After $SOCl_2$ was removed under vacuum, the gray solid residue was washed several times with dry pentane under argon, affording 375 mg (0.34 mmol, 95% yield) of product **1** as a white powder. ^1H NMR ($CDCl_3$, δ ppm): 7.3 (m, AA′BB′ system, C_6H_4, 24H), 5.2 (q, CH(CH_3)Cl, 6H) 3.0 (unresolved m, $(CH_2)_2$, 24H), 1.9 (d, CH(CH_3)Cl, 18H). ^{13}C NMR ($CDCl_3$, δ ppm): 142.2 ($(CH_2)_2$−Cq), 140.9 (Cq−CH (CH_3)Cl, 136.6 (Cq−$(CH_2)_2$), 128.4 and 126.9 (CH of C_6H_4), 58.6 (CH(CH_3)Cl, 37.5 and 32.6 ($(CH_2)_2$), 26.6 (CH_3). Anal. Calcd for $C_{66}H_{72}Cl_6\cdot 1.5H_2O$: C, 71.74; H, 6.79; Cl, 19.29. Found: C, 71.71; H, 6.67; Cl, 19.52.

C. Controlled Cationic Polymerization of Styrene Using the New Hexafunctional Initiator 1 ($\bar{M}_{n,th} = 7200$ g/mol). To improve the controlled character of the cationic polymerization of styrene, the temperature was varied between −15 and −50 °C (see text). The typical experimental conditions with **1**/$SnCl_4$/n-$Bu_4N^+Cl^-$/DTBP/CH_2Cl_2 as hexafunctional initiating system at −15 °C were as follows. Prior to the polymerization, a mixture of 200 mg (0.2 mmol) of **1** (the hexafunctional initiator) and 667 mg (2.4 mmol) of n-$Bu_4N^+Cl^-$ salts were freeze-dried from their 1,4-dioxane solution (20 mL). After dissolution of the mixture in 116 mL of CH_2Cl_2, 0.25 mL (1.1 mmol) of DTBP and 15 mL (131 mmol) of styrene were subsequently introduced. The reaction mixture was stirred for 5 min, and then the polymerization was initiated by adding a solution of $SnCl_4$ in CH_2Cl_2 (5.5 mL, 5.5 mmol). After a given time, the polymerization was quenched with prechilled methanol (20 mL) containing 2 mL of 6 N ammonia. The quenched reaction mixture was diluted with CH_2Cl_2, filtered, concentrated, and precipitated twice from methanol. The polystyrene (PS) sample was dried and purified by freeze-drying from its 1,4-dioxane solution before characterization and further use.

D. Characterization. ^1H NMR spectra were recorded in solution in $CDCl_3$ with a Bruker AC 250 (250 MHz, for the hexafunctional initiator) or AC 200 (200 MHz, for the star polymers) spectrometer; all chemical shifts are reported in parts per million (δ in ppm) with reference to tetramethylsilane (Me_4Si) and were measured relative to Me_4Si as internal standard. ^{13}C NMR spectra were recorded at 62.90 MHz on a Bruker AC 200 spectrometer with the solvent carbon signal as internal standard.

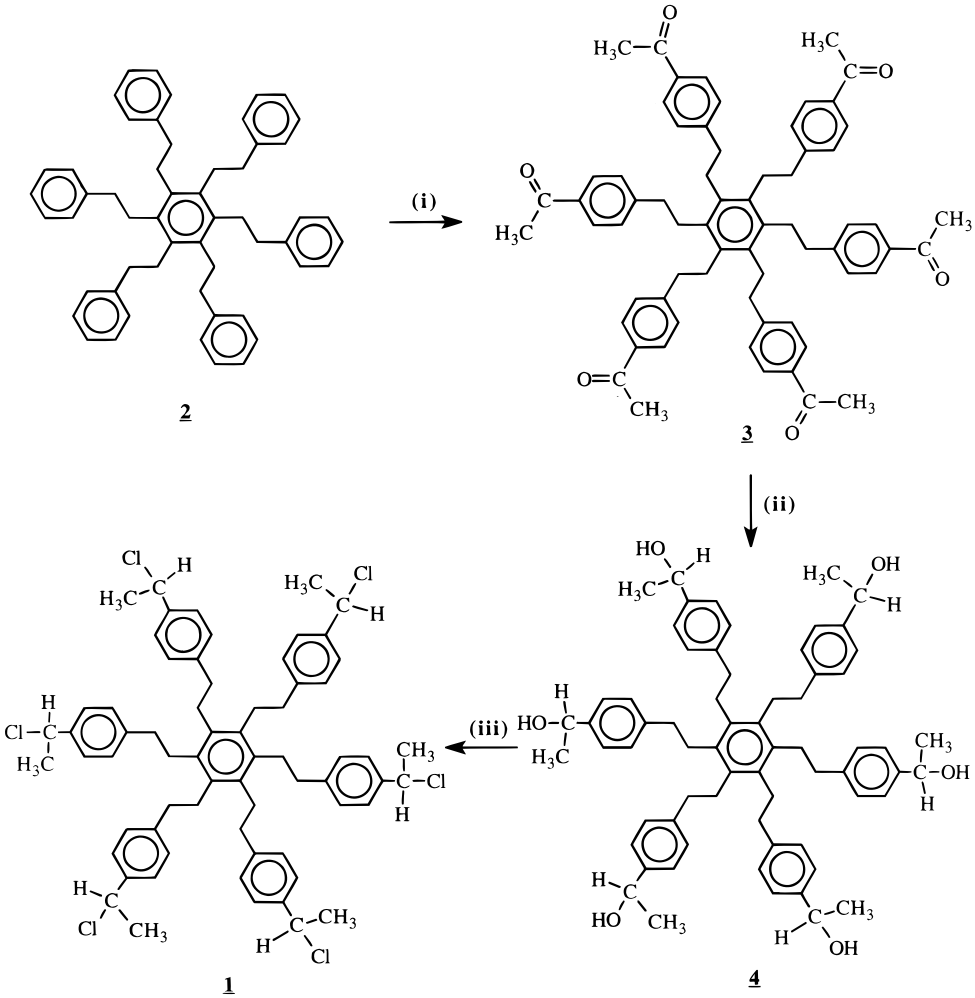
Molar masses were determined by size exclusion chromatography (SEC) using a JASCO HPLC-pump type 880-PU, a Varian 5500 apparatus equipped with refractive index/UV dual detection, and three TSK gel columns calibrated with PS standards. The flow rate of THF (used as eluent) was 0.7 mL/min. The columns were calibrated using narrowly distributed PS standards. Absolute molar masses of star polymers were obtained by SEC coupled with a multi-angle laser light scattering (MALLS) detector (DAWN−F laser photometer, Wyatt Technology Inc.). The refractive index increment ($dn/dc = 0.185$ mL/g) was found to be the same for PS linear samples and for stars.

III. Results and Discussion

The goal of this research was the synthesis of novel well-defined hexaarm polystyrene (PS) stars; following the reasons given in the Introduction, we chose to use the divergent route that is based on the growth of the star arms from a central core. The latter has to be perfectly well-defined to be used as multifunctional initiator.

In a first step, a new hexafunctional initiator **1** containing six phenylethyl chloride (PhEtCl) groups was

Scheme 1. Synthesis of the Hexafunctional Initiator 1: (i) CH_3COCl, $AlCl_3$, CH_2Cl_2, room temperature, 16 h; (ii) $NaBH_4$, $MeOH-CH_2Cl_2$ (50/50; v/v), room temperature, 16h; (iii) $SOCl_2$, room temperature, 3−4 h



synthesized; these groups were introduced in **1** because they were shown to bring about the "living" cationic polymerization of styrene in the presence of appropriate Lewis acid and ammonium salts.[19,20,22]

In a second step, attempts to improve the controlled character of the cationic polymerization of styrene using a monofunctional model of our hexafunctional initiator (**1**) were made. The conditions that were found appropriate to generate linear PS chains of controlled structure were then applied to the preparation of star samples. As the cationic polymerization of styrene does not proceed via a "truly" "living" process even in the presence of ammonium salts, one cannot expect to obtain stars of perfectly defined structure in an unlimited range of molar masses.

One of the objectives of this study was to accurately explore the domain of molar masses that is the most appropriate for the synthesis of stars under controlled conditions. Along with the careful characterization of the star samples, special attention was also given to the determination of their actual functionality.

A. Synthesis of the Hexafunctional Initiator 1 (Scheme 1). Following a known procedure developed by one of us,[21] molecule **2** was prepared upon one-pot perbenzylation of the organo-iron complex $[Fe(\eta\text{-}C_5H_5)\{C_6Me_6\}]^+PF_6^-$ and subsequent removal of the $[Fe(\eta\text{-}C_5H_5)]^+PF_6^-$ moiety by photodecomplexation.

To obtain the targeted hexafunctional initiator **1**, the only possibility was to para-functionalize the six outer phenyl rings of **2**. This was effected through a classic Friedel−Crafts acetylation reaction of **2** using acetyl chloride and aluminum trichloride in CH_2Cl_2; the pure hexaacetylated derivative **3** was isolated in good yield (86%). The reduction of **3** by an hydride such as $NaBH_4$ in 1/1 $MeOH/CH_2Cl_2$ (this solvent mixture is inspired by the work of Ward and Rhee[23]) gave the hexol **4**, which was subsequently chlorinated by $SOCl_2$ (neat) to afford the targeted hexaphenylethyl chloride compound **1**. The overall yield of **1** from **2** after these four straighforward steps is 59%. As expected, two signals at 5.2 ppm and at 1.9 ppm are visible in ^1H NMR spectra; they are respectively due to the resonance of the methine and the methyl protons, all adjacent to the chlorine atoms in the initiator **1** $[-CH_2PhC\mathit{H}(C\mathit{H}_3)Cl]$. The ^{13}C spectrum of **1** is given in Figure 1. The nature of **1** is also ascertained by elemental analysis and FAB^+ mass spectroscopy which shows peaks at $MH^+ - HCl$, $MH^+ - 2HCl$, $M^+ - 3HCl$, etc. in agreement with the proposed structure (Scheme 1).

B. Optimization of the Linear Controlled Cationic Polymerization of Styrene Using PhEtCl as a Model of the Hexafunctional Initiator. To establish the best conditions for the synthesis of PS stars using **1**, it was necessary to optimize in a preliminary study the polymerization process on a monofunctional model. Higashimura[18] and Matyjaszewski[19] were the first to report on the "living" cationic polymerization of styrene using $[PhEtCl/SnCl_4/n\text{-}Bu_4N^+Cl^-]$ as initiating

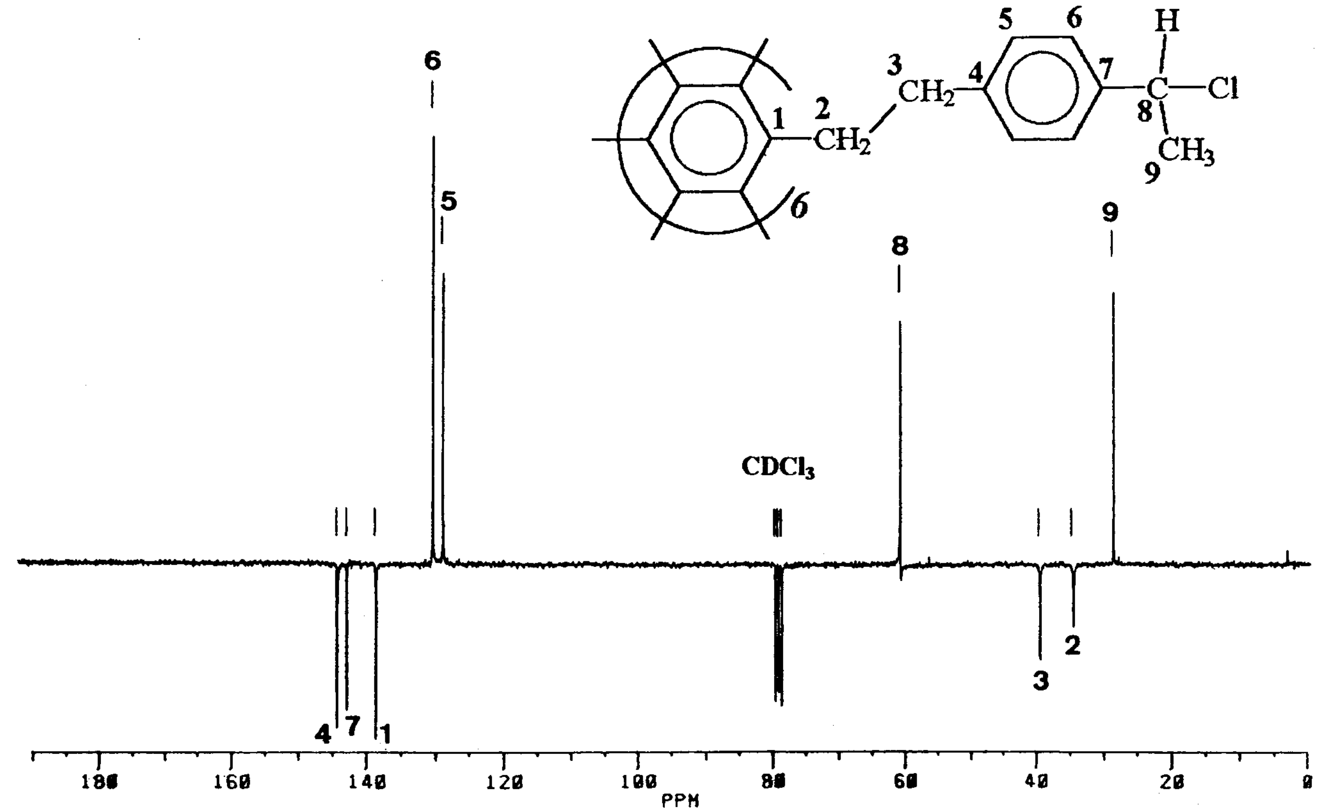
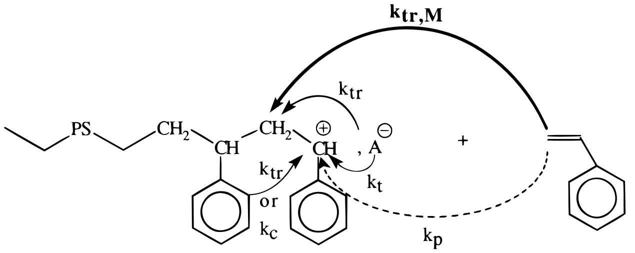


Figure 1. ^{13}C NMR spectrum of **1** (62.90 MHz, $CDCl_3$).

Scheme 2. Mechanism of the Cationic Polymerization of Styrene[24]



system. Considering all the side reactions that usually occur (see Scheme 2,[24] where k_p, k_t, k_{tr}, $k_{tr,m}$, and k_c are respectively the rate constants of propagation, termination, intramolecular transfer, transfer to monomer, and intramolecular cyclization) in the cationic polymerization of styrene, these two contributions[19,20] can be viewed as a major step forward in the control of this system. However, PS samples of predetermined size and narrow distribution could only be obtained in a limited domain of molar mass ($\bar{M}_n = \leq 5000$ g/mol).

In Scheme 2 one can see the complexity of the growing polystyryl system with its two electrophilic centers (Cα and Cβ) and three nucleophilic sites (double bond of the monomer, counterions, and aromatic rings). While studying the cationic polymerization of styrene initiated by triflic acid, Vairon et al.[25] determined through kinetic measurements the rate constants of the various reactions that occur in such process and established the following reactivity order: $k_p > k_{tr} > k_{trM} > k_c$ at low temperatures. Because the reactions of elimination and transfer exhibit a higher activation energy than that of the propagation, the ratio k_p/k_{tr} is supposed to increase upon lowering the temperature; but a decrease in temperature cannot by itself totally suppress these side reactions. Higashimura et al.[19a] showed the importance of ammonium salts (n-$Bu_4N^+Cl^-$) and their role in such systems. These salts were found to modify the equilibrium existing between free ions and ion pairs in favor of the latters, behaving as free ion scavengers. In the presence of these salts, the Lewis acid $SnCl_4$ is converted into pentachlorostannate anions (n-Bu_4N^+-$SnCl_5^-$) which has a much lower ionizability than that of $SnCl_4$: most of the polymer termini exist as dormant covalent C−Cl species rather than active carbocations.[19] On the other hand, Kennedy et al.[26] have shown that certain sterically hindered amines such as 2,6-di-*tert*-butylpyridine (DTBP) not only scavenge protons produced by transfer but can also curb undesirable reactions.

A first series of experiments was carried out at −15 °C, using the same conditions as those described by Higashimura.[19] As long as the targeted molar masses were chosen below 5000 g/mol, the system was able to produce chains of controlled size and narrow molar mass distribution (MMD). When larger molar masses were targeted, the effects due to the elimination of protons and transfer to monomer became detectable, and the control of the chain growth was lost above the foregoing value of molar mass. This was also noticed by Matyjaszewski and Higashimura.

In a second series of experiments which were aimed at producing chains of higher molar mass 20 000 g/mol, a proton trap, namely 2,6-di-*tert*-butylpyridine (DTBP), was used in addition to ammonium salts and under the following conditions: $[DTBP]_0/[PhEtCl]_0 = 1/1$ in CH_2Cl_2 at −15 °C. In the latter case $\bar{M}_n$ was found to increase linearly up to 6000 g/mol, that is below 40% of monomer conversion: the samples obtained were well-defined with low molar mass dispersities (MMD < 1.1). Above 40% conversion, the eluograms of the samples exhibited a shoulder of weak intensity next to the main peak at low retention times. This indicates the forma-

Table 1. Linear Samples Obtained Using the Initiating System $PhEtCl/SnCl_4/n\text{-}Bu_4N^+Cl^-/CH_2Cl_2$ at $T = -30$ °C and $T = -50$ °C

samples	$[M]_0$ (mol/L)	T (°C)	conversion (%)	$\bar{M}_n$,exp[a] (g/mol)	MMD = $\bar{M}_w/\bar{M}_n$	Q_1[b]	Q_2[c]
PS 49	4.6	−50	40	15 000	1.5	5	0.4
PS 50	4.6	−30	50	19 500	1.2	5	0.4
PS 51	4.4	−30	50	20 000	1.3	10	0.4
PS 53	3	−30	60	22 000	1.2	10	0.4
PS 54	1.5	−30	60	21 000	1.2	10	0.4
PS 55	1.5	−30	60	26 000	1.3	20	0.2
PS 57	1.5	−50	50	20 000	1.2	20	0.2

[a] Average molar masses determined by SEC equipped with refractive index (RI)/UV dual detections, the molar mass distributions being of Poisson type. [b] $Q_1 = [SnCl_4]_0[PhEtCl]_0$. [c] $Q_2 = [Bu_4N^+Cl^-]_0/[SnCl_4]0$.

tion of end-standing unsaturations by β-elimination of protons and their attack by growing carbocations. No species were detected in the low molar mass region: the protons resulting from β-elimination were indeed trapped by DTBP and were therefore unable to initiate new chains.

The temperature was the last parameter to be varied. To avoid a too sluggish polymerization, the overall concentration of monomer and also the ratio of Lewis acid concentration to that of the initiator were increased (Table 1).

As observed by SEC, the best results were obtained at −30 °C with a monomer concentration of 1.5 M, and with the following experimental conditions: $[SnCl_4]_0/[PhEtCl]_0 = 20$ and $[n\text{-}Bu_4N^+Cl^-]/[SnCl_4] = 0.2$. Various unimodal PS samples were indeed synthesized in a controlled manner in the range 2000−25000 g/mol as molar mass.

In conclusion, one can infer from these experiments on a linear model that the system $PhEtCl/SnCl_4/n\text{-}Bu_4N^+Cl^-/DTBP/CH_2Cl_2$ operating at − 15 °C can be only used for the preparation of linear PS samples of low molar mass ($M_n = 8000$ g/mol) whereas the system $PhEtCl/SnCl_4/n\text{-}Bu_4N^+Cl^-/CH_2Cl_2$ operating at − 30 °C is well suited to the controlled synthesis of PS samples in a wider range of molar masses ($\bar{M}_n = 2000$ g/mol to $\bar{M}_n = 30\,000$ g/mol).

C. Synthesis of Hexaarm Star-Shaped Polystyrenes. The scheme for the synthesis of the polystyrene stars is shown in Scheme 3.

Subsequent to the study on the monofunctional model (Part B), two systems have been investigated to make PS stars.

(a) Polymerization of Styrene using the Hexafunctional Initiator 1 in Conjunction with Added DTBP. The first system consisted of **1**:$C_6[(CH_2)_2C_6H_4\text{-}CH(CH_3)Cl]_6$, $SnCl_4$, $n\text{-}Bu_4N^+Cl^-$, and DTBP. The polymerization was carried out in CH_2Cl_2 at − 15 °C under conditions similar to those described for the linear model. As it was previously shown, above a targeted $\overline{DP}_n$ of 80 per arm, the preparation of samples of controlled size and unimodal distribution is difficult to achieve; it was therefore not attempted to derive stars $\bar{M}_n$'s larger than 50 000 g/mol which for this value corresponds roughly to a $\overline{DP}_n \approx 80$ for each individual arm (Table 2).

Characterization by SEC equipped with a light-scattering detector (SEC/MALLS) has been used to obtain absolute molar masses for these star materials (entry 3). The refractive index increment (dn/dc) of the PS stars was found to be equal to that determined for linear PS, which is known to be 0.185 mL/g. The molar masses values provided by the usual RI/UV dual detection (entry 2) are misleading since they are based on a calibration curve established with linear PS standards. The discrepancy which is found between the data given by LS detection and those drawn from RI detection (entries 2 and 3) reflects the fact that branched macromolecules exhibit a lower hydrodynamic volume than their linear homologues of same molar mass ($V_{H,star} < V_{H,linear\ of\ same\ molar\ mass}$).

It can be stressed that with this first system (**1**/$SnCl_4/n\text{-}Bu_4N^+Cl^-/DTBP/CH_2Cl_2$ operating at 15 °C), samples exhibiting narrow MMD's and controlled sizes could only be obtained below molar mass values of 32 000 g/mol. The SEC traces of star samples of higher molar mass (51 000 g/mol) showed a shoulder in the high molar mass region indicating the occurrence of coupling reaction between stars; in contrast no linear population was detected at larger elution volumes which means that all released protons were trapped by DTBP. Whereas the effect due to β-elimination of protons could only be detected above a critical $\overline{DP}_n$ value of 80 for the linear system, the upper limit seems not to exceed a $\overline{DP}_n$ of 50 for each arm in the case of hexaarmed stars. This can be accounted for by considering that the probability for two star molecules to get coupled through a reaction between a terminal unsaturation and a growing carbenium is higher than in the homologous monofunctional case.

(b) Polymerization of Styrene using the Hexafunctional Initiator 1 at −30 °C. The second initiating system that was studied consisted of **1**:$C_6[(CH_2)_2C_6H_4\text{-}CH(CH_3)Cl]_6$, $SnCl_4$, and $n\text{-}Bu_4N^+Cl^-$, the polymerization being carried at −30 °C and in CH_2Cl_2 as usual—as DTBP is not essential at such a low temperature it was not used. As in the case of the analogous monofunctional system, we added larger quantities of $SnCl_4$ ($[SnCl_4]_0/[PhEtCl]_0 = 20$) in order to increase the ionization and exchange rates. Star-shaped polymers with arms of larger size were therefore targeted: $\overline{DP}_n$'s of 500 for each individual arm were chosen which corresponds to $\bar{M}_n$'s of 3×10^5 g/mol, even though it was known to us that above an observed $\overline{DP}_n$ of 300, the precise control of the sample size and its MMD are difficult to achieve—according to our study on the monofunctional model (Table 3).

$\bar{M}_n$'s up to 110 000 g/mol were obtained with a Poisson-type distribution and without detecting any side peak. However, samples that correspond to larger conversion and higher molar mass were found to be contaminated with a small fraction of linear chains that likely arose from transfer to monomer. Star samples that exhibit a molar mass of 10^5 g/mol and a sharp distribution (MMD ≤ 1.2) are hence accessible upon using the initiating system constituted of **1**, $SnCl_4$, and $n\text{-}Bu_4N^+Cl^-$ in CH_2Cl_2 at −30 °C. The system based on DTBP in conjunction with **1**, $SnCl_4$, and $n\text{-}Bu_4N^+Cl^-$ in CH_2Cl_2 at −15 °C appears more suitable to prepare star samples with $\bar{M}_n$ ranging from 6×10^3 to 3×10^4 g/mol (MMD = 1.1).

(c) Determination of the Actual Number of Arms of Star Polymers. To check whether the six PhEtCl groups of **1** have indeed initiated polymerization and given rise to six PS arms, another series of polymerizations was carried out, in which linear chains (from the monofunctional initiator PhEtCl) and star-shaped PS (from the hexafunctional initiator **1**) were grown con-

Scheme 3. Synthesis of Hexaarm PS Star Molecules from the New Hexafunctional Initiator 1

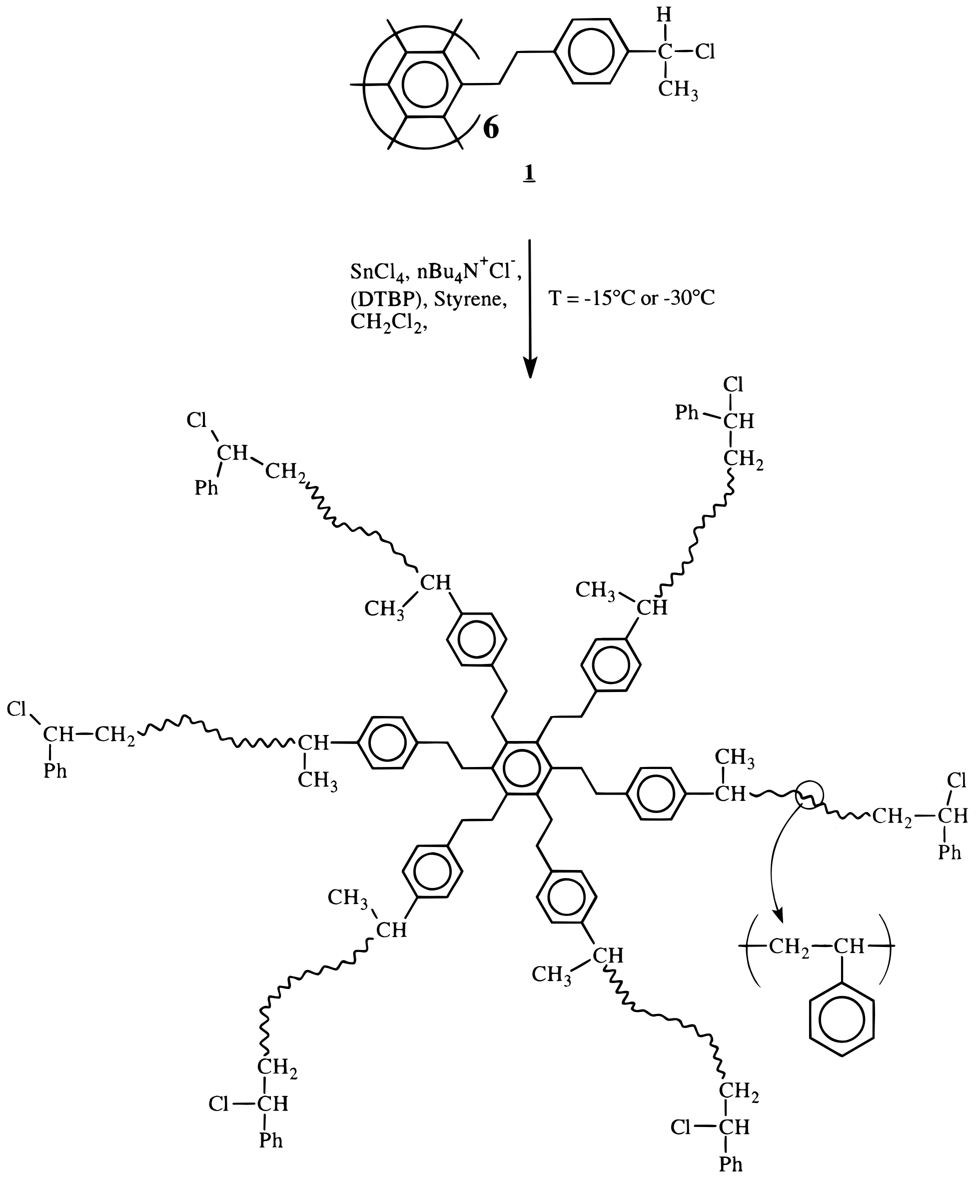


Table 2. Hexaarm PS Stars Obtained Using the Initiating System 1/$SnCl_4$/n-$Bu_4N^+Cl^-$/DTBP/CH_2Cl_2 at T = −15 °C and the Following Conditions: $[M]_0 = 1$ M, $[SnCl_4]/[PhEtCl] = 5$, and $[SnCl_4]/[n\text{-}Bu_4N^+Cl^-] = 2.5$

conversion (%)	$\bar{M}_{n,RI}$ (g/mol)	$\bar{M}_{n,LS}$ (g/mol)	MMD = $\bar{M}_w/\bar{M}_n$
60	7000	8500	1.05
50	9200	11500	1.08
50	12800	17500	1.09
60	25000	35000	1.07
60	40500[a]	51000[a]	1.25[a]

[a] Bimodal distribution: on the various chromatograms, the presence of a shoulder is noted at the basis of the main peak in the region of high molar masses. No peak corresponding to linear chains was detected.

Table 3. Hexaarm PS Stars Obtained Using the Initiating System 1/$SnCl_4$/n-$Bu_4N^+Cl^-$/CH_2Cl_2 at T = −30 °C and the Following Conditions: $[M]_0 = 1.5$ M, $[SnCl_4]/[PhEtCl] = 20$, and $[SnCl_4]/[n\text{-}Bu_4N^+Cl^-] = 5$ ($\bar{M}_{n,th} \approx$ 50 000 g/mol per branch)

conversion (%)	$\bar{M}_{n,RI}$ (g/mol)	$\bar{M}_{n,LS}$ (g/mol)	MMD = $\bar{M}_w/\bar{M}_n$
10	23 000	32 000	1.18
20	34 000	48 000	1.11
40	80 000	110 000	1.17
50	115 000[a]		

[a] Double distribution: presence of a population of smaller molar mass.

comitantly. For these polymerizations, the experimental conditions were chosen so as to generate linear chains and star arms whose molar mass would not exceed the limit of detection of side reactions. The two systems that were found well fitted for the preparation of low molar mass samples ($T = -15$ °C and presence of DTBP) and of higher ones ($T = -30$ °C) were used for this purpose (Table 4).

Provided the initiation and chain growth occur similarly whether the carbenium is carried by the mono- or the hexafunctional species, the molar masses of the linear chains should be identical to that of the individual arm of the stars. On the other hand the ratio of the average molar mass of the stars to that of the linear chains should give access to the actual functionality of the stars formed whether the initiation by the PhEtCl functions of **1** is indeed quantitative or uncomplete. The characterization of the samples by SEC/MALLS showed two well-separated peaks corresponding to the two species present in the reaction medium (Figure 2). The comparison of their respective average molar masses

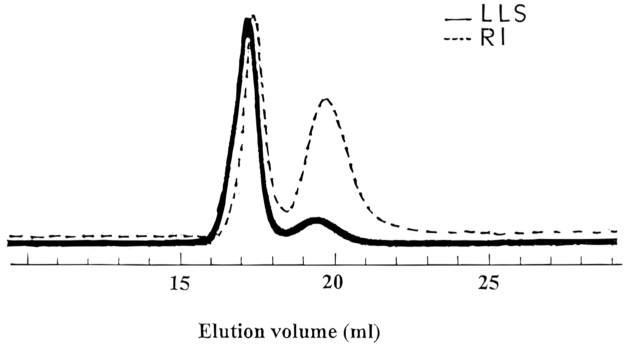


Figure 2. SEC/MALLS traces of a mixture of star and linear PS prepared from a mixture of mono- and hexafunctional initiators used in conjunction with $SnCl_4$/DTBP/n-$Bu_4N^+Cl^-$ at T = −15 °C.

Table 4. Determination of the Average Number of Arms (*f*) of the PS Star Samples Obtained from the Following Initiating Systems: 1/$SnCl_4$/n-$Bu_4N^+Cl^-$/DTBP/CH_2Cl_2 at *T* = −15 °C (Lines 1−3) and 1/$SnCl_4$/n-$Bu_4N^+Cl^-$/CH_2Cl_2 at *T* = −30 °C (Lines 4 and 5)

$\bar{M}_{n,linear\ (RI)}$ (g/mol)	$\bar{M}_{n,star\ (LS)}$ (g/mol)	$f = \bar{M}_{n,star}/\bar{M}_{n,lin}$
2700	15700	5.8
3300	19000	5.9
4500	25000	5.6
8400	48300	5.8
14000	78400	5.6

was easy and accurate; it was effected by simple integration of the area of each peak.

In each case, the SEC/MALLS traces exhibited Poisson-type distributions and showed a narrow MMD, which confirmed that polymerization occurred under controlled conditions. The values obtained for the ratios of the star molar mass to that of the linear chains indicate that **1** has effectively functioned as a true hexafunctional initiator. Indeed, the actual functionality of the star appears to fall in close agreement with the expected value of six: for all the samples checked the number of branches of the PS stars was found to revolve in the range 5.6−5.9 (from SEC measurements). It can be inferred from these experiments that six chains have effectively grown concomitantly from **1**.

Conclusion

A novel polyfunctional molecule **1** fitted with six phenyl ethyl chloride groups (PhEtCl) and designed to serve as initiator for the cationic polymerization of styrene has been synthesized by $Fe(C_5H_5)^+$-induced hexabenzylation of hexamethylbenzene followed by regiospecific acylation, reduction, and chlorination. In a preliminary study, the cationic polymerization of styrene has been optimized on a monofunctional initiator model (PhEtCl). Linear samples with controlled structure and $\bar{M}_n$ of about 30 000 g/mol could be obtained using low temperatures (T = −30 °C), 1.5 M as monomer concentration, and the following ratios of Lewis acid to initiator and ammonium salts: $[SnCl_4]_0/[PhEtCl]_0 = 20$; $[n\text{-}Bu_4N^+Cl^-]/[SnCl_4] = 0.2$. Well-defined polystyrenes of lower molar mass and sharper distribution (MMD < 1.1) were also obtained by using a second system at −15 °C in the presence of 2,6-di-*tert*-butylpyridine (DTBP) used as proton trap. Finally, well-defined star-shaped PS molecules were synthesized over a broad range of molar masses using the hexafunctional compound **1** as initiator and experimental conditions close to those engineered for the linear system. Indeed, this plurifunctional initiating system was shown to afford PS stars with expected size and sharp distribution up to 10^5 g/mol as molar mass. The actual number of branches of these PS stars, which was determined by simultaneously polymerizing linear and star polymers, was found to be in good agreement with the expected value of six. One of the possible extensions of this work would be to utilize this hexafunctional system of polymerization to make star block copolymers and end-functionalized stars.

References and Notes

(1) Grest, G. S.; Fetters, L. J.; Huang, J. S.; Richter, D. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1996; Vol. XCIV, p 67.

(2) (a) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301. (b) Stockmayer, W. H.; Fixman, M. *Ann. N.Y. Acad. Sci.* **1953**, *57*, 334. (c) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19. (d) Orofino, T. A. *Polymer* **1962**, *2*, 305. (e) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531. (f) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453.

(3) Simms, J. A.; Spinelli, H. J. *J. Coat. Technol.* **1987**, *59*, 126.

(4) Morton, M., Helminiak, T. E., Gadkary, S. D., Bueche, F. *J. Polym. Sci.* **1962**, *57*, 471.

(5) Zelinski, R. P.; Woffard, C. F. *J Polym. Sci.: Polym. Chem.* **1965**, *3*, 93.

(6) (a) Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; Van der Zwan, M.; Iatrou, H.; Hadjichristidis, N.; *Macromolecules* **1993**, *26*, 4324. (b) Zhou, L.-L.; Hadjichristidis, N.; Toporowski, P. M.; Roovers, J. *J. Rubber Chem. Technol.* **1992**, *65*, 603.

(7) (a) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 2479. (b) Iatrou, H.; Siakali-Kioulala, E.; Hadjichristidis, N.; Roovers, J.; Mays, J. *J Polym. Sci.: Polym. Phys.* **1995**, *33*, 1925.

(8) (a) Fukui, H.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci.: Polym. Chem. Ed.* **1993**, *31*, 1531. (b) Fukui, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 7315. (c) Fukui, H.; Sawamoto, M.; Higashimura, T.; *Macromolecules* **1994**, *27*, 1297. (d) Fukui, H.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci.: Polym. Chem. Ed.* **1994**, *32*, 2699. (e) Fukui, H.; Deguchi, T.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1996**, *29*, 1131.

(9) (a) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309. (b) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 5741. (c) Kanaoka, S.; Omura, T.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6407. (d) Deng, H.; Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1996**, *29*, 1772.

(10) (a) Decker, D.; Rempp, P. *C. R. Acad. Sci. Paris* **1965**, *261*, 1977. (b) Zilliox, J. G.; Rempp, P.; Parrod, J. *J. Polym. Sci., Part C* **1968**, *22*, 165. (c) Bi, L.-K.; Fetters, L. J. *Macromolecules* **1975**, *8*, 90. (d) Bi, L.-K.; Fetters, L. J. *Macromolecules* **1976**, *9*, 732. (e) Tsitsilianis, C.; Graff, S.; Rempp, P. *Eur. Polym. J.* **1991**, *27*, 243 and references cited therein. (f) Teyssié, Ph.; Fayt, R.; Jacobs, C.; Jérome, R.; Leemans, L.; Varshnay, S. K. *Polym Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29* (2), 52. (g) Tsitsilianis, C.; Papanagopoulos, D.; Lutz, P. *Polymer* **1995**, *36*, 3745.

(11) (a) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309. (b) Kanaoka, S.; Omura, T.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6407. (c) Deng, H.; Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1996**, *29*, 1772 and references cited therein. (d) Marsalko, T. M.; Majoros, I.; Kennedy, J. P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1996**, *37* (1), 581 and refs cited.

(12) (a) Bazan, G. C.; Schrock, R. R. *Macromolecules* **1991**, *24*, 817. (b) Saunders: R. S.; Cohen, R. E.; Wong, S. J.; Schrock, R. R. *Macromolecules* **1992**, *25*, 2055.

(13) Simms, J. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992**, *33* (1), 164.

(14) (a) Nagasawa, M.; Fujimoto, T. *Prog. Polym. Sci. Japan* **1972**, *2*, 263. (b) Fujimoto, T.; Tani, S.; Takano, K.; Ogawa, M.; Nagasawa, M. *Macromolecules* **1978**, *11*, 673. (c) Eschwey, H.; Hallensleben, M. L.; Burchard, W. *Makromol. Chem.* **1973**, *173*, 235. (d) Lutz, P.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 1051. (e) Tsitsilianis, C.; Lutz, P.; Graff, S.; Lamps, J.-P.; Rempp, P. *Macromolecules* **1991**, *24*, 5897. (f) Rein, D.; Lamps, J.-P.; Rempp, P.; Lutz, P.; Papanagopoulos, D.; Tsitsilianis, C. *Acta Polym.* **1993**, *44*, 225.

(15) (a) Mishra, M. K.; Wang, B.; Kennedy, J. P. *Polym. Bull.* **1987**, *17*, 307. (b) Huang, K. J.; Zsuga, M.; Kennedy, J. P. *Polym. Bull.* **1988**, *19*, 43. (c) Chen, C. C.; Kaszas, G.; Puskas, J. E.; Kennedy, J. P. *Polym. Bull.* **1989**, *22*, 463. (d) Ivan, B.; Kennedy, J. P. *J. Polym. Sci.*: *Polym. Chem. Ed.* **1990**, *28*, 89. (e) Jacob, S.; Majoros, I.; Kennedy, J. P. *Macromolecules* **1996**, *29*, 8631.

(16) Jacob, S.; Majoros, I.; Kennedy, J. P. *Polym. Bull.* **1998**, *40*, 127.

(17) Shohi, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 4926.

(18) Schappacher, M.; Deffieux, A. *Macromolecules* **1992**, *25*, 6744.

(19) (a) Ishihama, Y.; Sawamoto, N.; Higashimura, T. *Polym. Bull.* **1990**, *24*, 201. (b) Higashimura, T.; Ishihama, Y.; Sawamoto, N. *Macromolecules* **1993**, *26*, 744.

(20) Lin, C. H.; Xiang, J.S.; Matyjaszewski, K. *Macromolecules* **1993**, *26*, 2785.

(21) (a) Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; McGlinchey, M.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549. (b) review: Astruc, D. *Top. Curr. Chem.* **1991**, *160*, 47. (c) Astruc, D. *Tetrahedron* **1983**, *39*, 4027.

(22) Cloutet, E.; Fillaut, J.-L.; Astruc, D.; Gnanou, Y. In *Macromolecular Engineering Recent Advances*; Mishra, M. K., Nuyken, O., Kobayashi, S., Yagci, Y., Sar, B., Eds: Plenum Press: New York, 1995; p 47.

(23) Ward, D. E.; Rhee, C. K. *Can. J. Chem.* **1989**, *67*, 1206.

(24) Matyjaszewski, K.; Lin, C.-H.; Bon, A.; Xiang, J. S. *Macromol. Symp.* **1994**, *85*, 65−78.

(25) Vairon, J.-P.; Rives, A.; Bunel, C. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 97−105.

(26) Kennedy, J. P.; Chou, R. T. *J. Macromol. Sci.−Chem.* **1982**, *A18*, 3(1).

MA980587Q