Synthesis of Poly(chloromethylstyrene-\textit{b}-styrene) Block Copolymers by Controlled Free-Radical Polymerization

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ABSTRACT: The controlled free-radical polymerization of styrene and chloromethylstyrene monomers in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) has been studied with the aim of synthesizing block copolymers with well-defined structures. First, TEMPO-capped poly(chloromethylstyrene) was prepared. Among several initiating systems [self-initiation, dicumyl peroxide, and 2,2’-azobis(isobutyronitrile)], the last offered the best compromise for obtaining a good control of the polymerization and a fast polymerization rate. The rate of the TEMPO-mediated polymerization of chloromethylstyrene was independent of the initial concentration of TEMPO but unexpectedly higher than the rate of the thermal self-initiated polymerization of chloromethylstyrene. Transfer reactions to the chloromethyl groups were thought to play an important role in the polymerization kinetics and the polydispersity index of the resulting poly(chloromethylstyrene). Second, this first block was used as a macroinitiator in the polymerization of styrene to obtain the desired poly(chloromethylstyrene-\textit{b}-styrene) block copolymer. The kinetic modeling of the block copolymerization was in good agreement with experimental data. The block copolymers obtained in this work exhibited a low polydispersity index (weight-average molecular weight/number-average molecular weight < 1.5) and could be chemically modified with nucleophilic substitution reactions on the benzylic site, opening the way to a great variety of architectures.


Keywords: block copolymers; nitroxide; controlled free-radical polymerization; chloromethylstyrene

INTRODUCTION

Block copolymers are useful for a wide range of applications, such as the compatibilization of nonmiscible polymers, the dispersion of mineral fillers in a polymer matrix, and the stabilization of colloids. Anionic\textsuperscript{1} and cationic\textsuperscript{2} polymerizations allow the synthesis of such polymers, but the purity of the reagents is often restrictive and the variety of monomers polymerizable in this manner is rather limited. Free-radical polymerization can be applied to a wide range of monomers; however, it does not permit the synthesis of block copolymers because of the predominance of termination reactions over propagation ones. Nevertheless, a few methods have been developed to obtain block copolymers by radical polymerization,\textsuperscript{3} including the use of multifunctional initiators\textsuperscript{4–7} or macroinitiators,\textsuperscript{8,9} the bis-telomerization technique\textsuperscript{10} or telomerization with chemical modification\textsuperscript{11,12} and, more recently, living or controlled free-radical polymerization.\textsuperscript{13} For nitroxide-mediated polymerization, a thermally re-
versible primary termination between propagating radicals $P^*$ and the stable nitroxide $T^*$ occurs (Scheme 1) and allows the polymerization to be controlled, opening the door to smart architectures such as block copolymers.

A recent survey on chloromethylstyrene (CMS), its homopolymer (PCMS), and its copolymers shows that it is probably one of the most important functional monomers. A large number of nucleophilic substitutions on benzylic chlorine are indeed feasible. For example, poly(chloromethylstyrene-b-styrene) block copolymers appear to be good candidates for a versatile route toward the synthesis of polymeric surfactants.

Several studies have been dedicated to the synthesis of poly(chloromethylstyrene-b-styrene) block copolymers. 22,25–27 Bertin and Boutevin 25 studied the TEMPO-mediated polymerization of CMS, and some trends on the substituent effects of styrenic monomers have been reported. 15–17 It appears that the TEMPO-mediated polymerization of CMS is faster than the TEMPO-mediated polymerization of CMS, as for styrene, it was not established if the rate of the TEMPO-mediated polymerization of CMS (without CSA) was the same as the rate of the thermal self-initiated polymerization of CMS. 22 Otherwise, the occurrence of chain termination by chain transfer was pointed out to explain the higher polydispersity index for PCMS in comparison with polystyrene as well as the substantial decrease of the rate of the polymerization above about a 60% conversion of the monomer. 22 Indeed, chain transfer in the polymerization of CMS is favored by the presence of chloromethyl groups (benzylic sites), as reported in previous studies. 23,24 Nevertheless, the transfer reaction to the chloromethyl groups has not been discussed in detail, and the related side reactions with the mediator (TEMPO) have not been suggested in previous studies. Finally, only a few works have been devoted to the synthesis of poly(chloromethylstyrene-b-styrene) block copolymers. 22,25–27

This work aims at investigating the synthesis of poly(chloromethylstyrene-b-styrene) block copolymers by controlled free-radical polymerization in the presence of a stable nitroxide radical (TEMPO). This study focuses on the influence of the nature of the initiator and the use of accelerating agents on the kinetics and living character of the polymerization of CMS. We discuss the kinetics, taking into account the possible side reactions with the mediator (TEMPO) related to the transfer reactions to the chloromethyl groups. Then, the synthesis of well-defined poly(chloro-
methylstyrene-b-styrene) block copolymers is reported.

EXPERIMENTAL

Materials
Styrene (99%; Aldrich) and CMS (ca. 60/40 meta/para-isomer mixture; 97%; Aldrich) were distilled under reduced pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN; 98%; Aldrich) was recrystallized from ethanol. TEMPO (99%; Aldrich), DCP (98%; Aldrich), and the solvents were used as received.

Polymerization of CMS
In a typical run, 52.7 mg of AIBN (321 μmol), 100.3 mg of TEMPO (642 μmol), and 25 g of CMS (163.8 mmol) were incorporated in a Schlenk reactor. The reactor was sealed with a septum. After three freeze–thaw–pump cycles, the reactor was immersed in an oil bath at 125 °C. The polymerization was conducted under an argon atmosphere with magnetic stirring. For kinetic analyses, samples were withdrawn from the reactor with a glass syringe, through a septum, and under a positive argon purge. Conversion was determined by 1H NMR analysis on crude samples in CDCl₃. The conversion of the CMS monomer was calculated from the intensity $I₁$ of the signal of the vinylic protons corresponding to the residual CMS monomer (2H, 2d at 5.35 and 5.85 ppm) in comparison with the intensity $I₂$ of the signal for the benzylic protons (2H, 1s for the residual CMS monomer at 4.6 ppm and a broad peak for PCMS polymer at 4.3–4.7 ppm). The fractional monomer conversion was given by $1 - I₁/I₂$.

RESULTS AND DISCUSSION

Effect of the Nature of the Initiator
The TEMPO-mediated polymerization of CMS was carried out in bulk in the absence of initiator (thermal self-initiation) at 130 °C and in the presence of peroxide initiator (DCP) or azo initiator (AIBN) at 125 °C. The DCP or AIBN initiators were used in a stoichiometric proportion versus TEMPO. Benzoic peroxide initiator was not considered in this work because the ester bond could be hydrolyzed during a subsequent nucleophilic

Characterizations
Molecular weights were determined by SEC calibrated with polystyrene standards. SEC was performed with a Spectra Physics Instruments SP8810 pump and a Shodex RIse-61 refractometer detector (with tetrahydrofuran as the eluent at 30 °C and 1 mL/min; two columns of PL gel mixed D).

1H NMR was conducted on a Bruker spectrometer at 200 MHz in CDCl₃. The conversion of the CMS monomer was calculated from the intensity $I₁$ of the signal of the vinylic protons corresponding to the residual CMS monomer (2H, 2d at 5.35 and 5.85 ppm) in comparison with the intensity $I₂$ of the signal for the benzylic protons (2H, 1s for the residual CMS monomer at 4.6 ppm and a broad peak for PCMS polymer at 4.3–4.7 ppm). The fractional monomer conversion was given by $1 - I₁/I₂$.

Polymerization of Styrene with PCMS-TEMPO Alkoxyamine as the Macroinitiator
In a typical run, 2 g of PCMS-TEMPO ($M_n = 26100$; polydispersity index, $I_p = 1.44$; 76.6 μmol) and 14.4 g of styrene (138.2 mmol) were introduced in a Schlenk reactor. After three freeze–thaw–pump cycles, the reactor was immersed in an oil bath at 125 °C. The polymerization was conducted as the aforementioned polymerization. The resulting poly(chloromethylstyrene-b-styrene) was recovered by precipitation in cold methanol and dried at 35 °C under reduced pressure ($10^{-1}$ mmHg) (Scheme 3).

Scheme 2. Structure of TEMPO-capped PCMS.

substitution reaction involving the PCMS (chemical modification of the PCMS) and, therefore, would possibly produce crosslinking. Polymerization data are shown in Table I. Experimental and theoretical molecular weights are in good agreement. From runs 2 and 3 (without an initiator), a linear variation of the molecular weight of PCMS versus conversion can be deduced. It confirms the ability of TEMPO to control the polymerization of CMS. From run 1, it can be seen that polymerization is controlled even in the presence of an inhibitor (50–100 ppm of tert-butyl catechol), although it takes a longer time to reach a high monomer conversion. The fastest polymerization is obtained with DCP as the initiator, but this rate enhancement is accompanied by a significant broadening of the molecular weight distribution [weight-average molecular weight/number-average molecular weight ($M_w/M_n$) = 1.73; run 4], as anticipated by Smirnov. 28 Finally, the best compromise between the control of the polymerization (low $M_w/M_n$) and the rate of the polymerization was obtained with AIBN as the initiator (run 5).

### Effect of the Use of an Accelerating Agent

Hawker et al. 29 reported the efficiency of acylating agents as accelerating additives for the TEMPO-mediated polymerization of styrene, whereas it was shown that the use of such additives (e.g., benzoic anhydride) did not lead to any enhancement of the polymerization rate for other nitroxides. 30 In this respect, we tested the effect of benzoic anhydride on the TEMPO-mediated polymerization of CMS initiated by AIBN and found that the polymerization was indeed faster in the presence of the acylating agent (Table I, run 6). However, as for run 4 with DCP as the initiator, the polydispersity index ($I_p = 1.61$) is slightly higher in comparison with the blank experiment (run 5, $I_p = 1.44$).

### Kinetics of the TEMPO-Mediated Polymerization of CMS

Kazmaier et al. 22 studied the kinetics of the TEMPO-mediated polymerization of CMS initiated by BPO and found that the plot of $\ln([M]/[M])$ versus time showed a substantial curvature (at a high conversion, above about a 60% conversion) that was ascribed to chain termination by chain transfer to CMS monomer and PCMS polymer. We also investigated the kinetics of the polymerization in the absence and presence of the initiator (AIBN). Figure 1 shows the evolution of the molecular weight versus conversion in both

![Figure 1. Evolution of $M_n$ versus conversion for the polymerization of CMS at 130 °C for [CMS]/[TEMPO] = 220, without an initiator (■) or in the presence of AIBN ([AIBN]/[TEMPO] = 0.5) as the initiator (△). The dashed line represents the theoretical $M_n$ (mass of monomer × conversion/[TEMPO]).](image-url)
cases. The linear character of these plots and the good agreement with the theoretical molecular weights confirm the living character of the polymerization.

As shown on Figure 2, the plots of $\ln([M]_0/[M])$ versus time remained linear in the range of monomer conversions ($\leq 65\%$ conversion), in accordance with the results of Kazmaier et al., who observed a linear portion of the plot up to about a 60% monomer conversion. For AIBN, the inhibition period is unexpected because the half-life of AIBN at 130 °C is very short, so that the polymerization should start early ($t_{1/2,\text{AIBN}} < 30 \text{ s}$ at 130 °C). This feature would reflect a strong cage effect for AIBN in these conditions, leading to a low efficiency of the initiator. After the inhibition period, the polymerization rate (the slope of the plot) was the same with or without the initiator. Moreover, the polymerization rate was much faster than for styrene, as previously noticed.

For styrene, it has been established that the rate of the TEMPO-mediated polymerization is the same as the rate of the autopolymerization (self-initiation without an initiator). The autopolymerization of CMS was studied in the absence of TEMPO (Fig. 2). Unexpectedly, the rate of the autopolymerization of CMS was twice as slow as the rate of the TEMPO-mediated polymerization of CMS. This behavior was checked with another commercial sample of CMS (meta/para isomeric mixture, 96%, distilled; Acros), and the results were similar. The possible reasons for this unusual feature are discussed later. Otherwise, in Figure 3 it is shown that for CMS with TEMPO, the polymerization rate does not depend on the initial concentration of TEMPO (i.e., on the targeted molecular weight of the PCMS), as anticipated for systems where the monomer is able to autopolymerize and where the equilibrium constant $K$ between dormant and active species is very low ($32,33$). However, the reasons for the deviation from the expected kinetic behavior ($\ln([M]_0/[M]) = (R_i/2k_t)^{1/2}t$, where $R_i$ is the rate of thermal self-initiation) that holds for styrene ($32,33$) need further explanation. It is thought by the authors that the transfer reactions to the chloromethyl groups could be responsible for this unusual behavior.

Transfer Reaction to the Benzylic Site

The polydispersity indexes obtained with CMS are larger than those reported for styrene poly-

![Figure 2](image2.png)

**Figure 2.** Kinetic plot of $\ln([M]_0/[M])$ for the polymerization of CMS at 130 °C for $[\text{CMS}]/[\text{TEMPO}] = 220$, without an initiator (▲) or in the presence of AIBN ($[\text{AIBN}]/[\text{TEMPO}] = 0.5$) as the initiator (■). The autopolymerization of CMS at 130 °C without TEMPO is also shown (●).

![Figure 3](image3.png)

**Figure 3.** Kinetic plot of $\ln([M]_0/[M])$ for the polymerization of CMS at 130 °C in the presence of AIBN ($[\text{AIBN}]/[\text{TEMPO}] = 0.5$ for (■) $[\text{CMS}]/[\text{TEMPO}] = 220$ or (▲) $[\text{CMS}]/[\text{TEMPO}] = 77$) as the initiator.
merization with TEMPO. In the TEMPO-mediated copolymerization of styrene with CMS in the absence of initiator, Devonport et al.\textsuperscript{17} also noticed that the polydispersity index increased with the molar feed ratio of CMS to styrene. Similar results were also reported by Kazmaier et al.\textsuperscript{22} with benzoyl peroxide as the initiator. The benzylic site of CMS monomer is prone to transfer reactions because of possible conjugation with the aromatic ring.\textsuperscript{23,24} This side reaction could explain the higher polydispersity index of polymers obtained for CMS in comparison with styrene. To support this idea, benzyl chloride was chosen as a model for a transfer agent in the TEMPO-mediated polymerization of styrene. As shown in Table II, the polydispersity index of the resulting polystyrene slightly increased with the addition of benzyl chloride. Nevertheless, the transfer reaction was not significant enough to be detected by $^1$H NMR analysis; indeed, after polymerization, the intensity of the signal of the benzylic protons of benzyl chloride was consistent with the initial feed ratio of benzyl chloride to styrene in runs 2 and 3 (crude samples). Also, the molecular weight of polystyrene (PS) was not modified with benzyl chloride as can be expected with a transfer agent. The reactions related to the transfer process in the polymerization of CMS are summarized in Scheme 4. First, the chloromethyl groups can react with a carbon-centered radical to yield a benzyl or chlorobenzyl radical (eqs 2 and 3),\textsuperscript{23,24} which would then possibly react with TEMPO to form the related benzylic alkoxyamine (eq 4). The primary benzylic alkoxyamine is known to be quite stable (low dissociation rate)\textsuperscript{34} and, therefore, leads to polydisperse polymers for styrene.\textsuperscript{17} Because TEMPO is known to be a good hydrogen abstractor,\textsuperscript{35–37} it can react with chloromethyl groups to yield the corresponding hydroxylamine (eq 7; $k_7 = 35$ mol$^{-1}$L$^{-1}$s$^{-1}$ at 125 °C, as estimated by Fukuda et al.\textsuperscript{41}) Also, it is known that TEMPOH can react with styrenic monomers to yield an alkoxyamine (which is formally the product of the phenylethyl radical coupling with TEMPO), although this is controversial (eq 8).\textsuperscript{17,42} Lastly, Priddy et al.\textsuperscript{43,44} recently showed that TEMPOCl is able to initiate new controlled polymer chains for styrene (eq 9). From these reactions, the transfer process between TEMPO and the chloromethyl groups leads to a decrease in the concentration of TEMPO and to an increase in the number of initiated polymer chains. Consequently, the side reactions mentioned in Scheme 4 could be the reasons why the polymerization goes faster than the autopolymerization of CMS and the polydispersity index of PCMS is rather large. Thus, it appears from Scheme 4 that the transfer process involved in the nitroxide-mediated polymerization of CMS is quite complex and should be investigated in detail in further studies.

### Synthesis of PCMS-b-PS Block Copolymers

TEMPO-capped PCMS was used as a macroinitiator in the controlled radical polymerization of styrene. The results are presented in Table III. Runs 1 and 2 indicate that a large ratio of styrene to PCMS is preferred to obtain block copolymers with a narrow distribution of the molecular

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<th>Table II. TEMPO-Mediated Bulk Polymerization of Styrene in the Presence of Benzyl Chloride$^a$</th>
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$^a$ $T = 125$ °C; $t_{\text{polymerization}} = 6$ h 30 min; [DCP]/[TEMPO] = 0.5; [styrene]/[TEMPO] = 625–660; BzCl = benzyl chloride.  
$^b$ $^1$H NMR analysis of the crude samples.  
$^c$ Calculated with $M_n = \text{mass of monomer} \times \text{conversion}/[\text{TEMPO}]$.  

(BDE) for C$\text{C}_6\text{H}_5$—CH$_2$—Cl = 68 kcal/mol, BDE for C$\text{C}_6\text{H}_5$—CH$_2$—H = 85 kcal/mol),\textsuperscript{38} the chloromethyl groups could also react with TEMPO to yield the corresponding oxoaminium chloride TEMPOCl (eq 6).\textsuperscript{39,40} TEMPOH is a rather good transfer agent for polystyryl-type propagating radicals (eq 7; $k_7 = 35$ mol$^{-1}$L$^{-1}$s$^{-1}$ at 125 °C, as estimated by Gridnev\textsuperscript{36}), but this reaction is kinetically much less favored than the reversible coupling of these radicals with TEMPO (Scheme 1, eq 1; $k_c = 7.6 \times 10^7$ mol$^{-1}$L$^{-1}$s$^{-1}$ at 125 °C, as estimated by Fukuda et al.\textsuperscript{41}) Also, it is known that TEMPOH can react with styrenic monomers to yield an alkoxyamine (which is formally the product of the phenylethyl radical coupling with TEMPO), although this is controversial (eq 8).\textsuperscript{17,42} Lastly, Priddy et al.\textsuperscript{43,44} recently showed that TEMPOCl is able to initiate new controlled polymer chains for styrene (eq 9). From these reactions, the transfer process between TEMPO and the chloromethyl groups leads to a decrease in the concentration of TEMPO and to an increase in the number of initiated polymer chains. Consequently, the side reactions mentioned in Scheme 4 could be the reasons why the polymerization goes faster than the autopolymerization of CMS and the polydispersity index of PCMS is rather large. Thus, it appears from Scheme 4 that the transfer process involved in the nitroxide-mediated polymerization of CMS is quite complex and should be investigated in detail in further studies.
weights ($M_w/M_n < 2$). Runs 2–4 show that high molecular weight block copolymers can be easily produced in this manner.

However, we were interested in producing block copolymers containing a smaller PS block to tailor polymeric surfactant precursors with a
practical anchor to soluble balance. For low molecular weight PS blocks, a kinetic study of the block polymerization was useful to stop the reaction at the proper time. The kinetic plot at 125 °C is depicted in Figure 4 together with a simulation curve from commercially available software for integration of chemical kinetic equations, GEAR iterator (from QCPE). For modeling, the following classical kinetic scheme was used, where T* represents the nitroxyl counter radical, PS* represents the polystyryl macroradical, M represents the monomer, and R* represents the radicals produced by the self-initiation of styrene (third-order model, global reaction 14):

\[
\begin{align*}
\text{PS-T} & \rightarrow \text{PS* + T*} & k_d (10) \\
\text{PS* + T*} & \rightarrow \text{PS-T} & k_c (11) \\
\text{PS* + PS*} & \rightarrow \text{PS-PS} & k_t (12) \\
\text{PS* + M} & \rightarrow \text{PS*} & k_p (13) \\
\text{M + M + M} & \rightarrow \text{R* + R*} & k_{th} (14) \\
\text{R* + T*} & \rightarrow \text{R-T} & k_c (15) \\
\text{R-T} & \rightarrow \text{R* + T*} & k_d (16) \\
\text{R* + R*} & \rightarrow \text{R-R} & k_i (17) \\
\text{R* + M} & \rightarrow \text{PS*} & k_p (18)
\end{align*}
\]

The rate constants for dissociation \((k_d)\), coupling \((k_c)\), propagation \((k_p)\), bimolecular termination \((2k_t)\), and autoinitiation \((k_{th})\) were obtained from the literature: \(k_p = 10^{7.63} \times \exp(-32.5 \text{ kJ} \cdot \text{mol}^{-1}/\text{RT})\), \(k_t = \frac{2.8 \times 5.5 \times 10^{-6}}{\exp(52.1 \text{ kJ} \cdot \text{mol}^{-1}/\text{RT})}\), \(k_{th} = 2.2 \times 10^5 \exp(-114.8 \text{ kJ} \cdot \text{mol}^{-1}/\text{RT})\) [at 125 °C, \(k_d = 1.6 \times 10^{-3} \text{ s}^{-1}\) and \(k_i = 7.6 \times 10^{-7} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}\)], \(k_{th} = 2.0 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}\); \(k_p = 2300 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}\); \(k_{th}\) (third order) = \(1.9 \times 10^{-10} \text{ mol}^{-2} \cdot \text{L}^2 \cdot \text{s}^{-1}\). The agreement between the experimental points and the simulation curve is rather good. In this respect, the simulation can be used in a first approximation to predict the molecular weight of the PS block at a given time of the polymerization. This tool was successfully applied for the synthesis of well-defined PCMS-b-PS block copolymers (Table IV). Thus, PCMS-b-PS block copolymers with molecular weights of 26,100/4300 and 26,100/9800 with a low polydispersity index \(I_p < 1.5\) were prepared.

**CONCLUSIONS**

The controlled free-radical polymerization of styrene and CMS monomers in the presence of TEMPO has been studied with the aim of synthesizing block copolymers with well-defined structures. First, TEMPO-capped PCMS was pre-

![Figure 4](image-url)

**Figure 4.** Kinetic plot of ln([M]/[M]) for the bulk polymerization of styrene initiated by a PCMS macrolkoxamine of TEMPO, PCMS-T \((M_n = 24,040 \text{ g/mol}, M_w/M_n = 1.47)\), for the initial ratio [styrene]/[PCMS-T]_0 = 1668 at 125 °C (■) and a simulation curve (solid line).
pared. Among several initiating systems (self-initiation, DCP, and AIBN), the last one offered the best compromise for obtaining a good control of the polymerization and a fast polymerization rate. Benzoic anhydride as an additive was able to accelerate the polymerization, but it was accompanied with a broadening of the molecular weight. For CMS, the rate of the TEMPO-mediated polymerization was independent of the initial concentration of TEMPO but unexpectedly higher than the rate of the thermal self-initiated polymerization. This unusual feature is thought to be due to the transfer process to chloromethyl groups, accompanied by the formation of hydroxylamine of TEMPO (TEMPOH) and/or the corresponding oxoaminium chloride (TEMPOCl, which is able to initiate new controlled PCMS chains). These side reactions could also explain the rather high polydispersity index obtained for the resulting PCMS.

Second, the TEMPO-capped PCMS was used as a macroinitiator in the polymerization of styrene to obtain the desired poly(chloromethylstyrene-b-styrene) block copolymer. Our results complete those of Bertin and Boutevin 25 (peroxide initiator), Kazmaier et al. and 22 Listigovers et al.26 (perester initiator), and Devonport et al.17 (gradient copolymers). Kinetic modeling of the block copolymerization was in good agreement with experimental data. The block copolymers obtained in this work exhibited a low polydispersity index ($M_p/M_n < 1.5$) and could be chemically modified with nucleophilic substitution reactions on the benzylic site, opening the way to a wide range of architectures. We are now working on the modification of the PCMS block (nucleophilic substitution) to obtain a variety of polymeric surfactants that could be useful in water media26,47 (substitution with hydrophilic compounds) or in supercritical carbon dioxide48 (substitution with fluorine-based or silicone-based compounds).

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REFERENCES AND NOTES


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<th>Run</th>
<th>$m_{\text{styrene}}/m_{\text{PCMS}}$ (g/g)</th>
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* Polymerization at $T = 125^\circ$C with an [styrene]/[PCMS-T]$_0$ initial ratio of 1804.

* Determined by $^1$H NMR analysis of the block copolymer.

* Initial PCMS block.

* PCMS-b-PS copolymer.

* Calculated with $M_n = (\text{mass of styrene} \times \text{conversion})/\text{[PCMS]} + M_n(\text{PCMS})$. 

Table IV. Synthesis of Poly(chloromethylstyrene-b-styrene) Copolymers Containing a Low Molecular Weight Polystyrene Block*