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Nitroxide-Mediated “Living” Free Radical Polymerization: A Rapid Polymerization of (Chloromethyl)styrene for the Preparation of Random, Block, and Segmental Arborescent Polymers[†]

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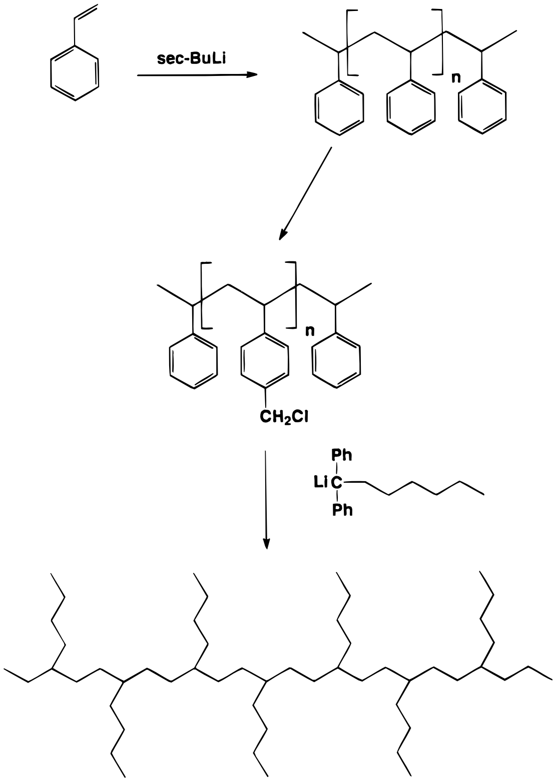
ABSTRACT: The bulk, living polymerizations of 3/4-(chloromethyl)styrene (CMS) in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) gave rise to rapid reaction. The CMS polymerization (no accelerant) proceeded at a rate similar to living styrene polymerizations accelerated with camphorsulfonic acid under comparable reaction conditions. The living nature of the CMS polymerization was confirmed by NMR evidence for TEMPO termination and by chain extension studies on TEMPO-terminated CMS homopolymer. Block and random copolymer synthesis was also demonstrated for this system. Styrene and CMS can interchangeably be used in the block formation.

Introduction

Narrow polydispersity polymers of 4-(chloromethyl)styrene (**1**) are important precursors in the synthesis of arborescent polymers.[1−3] Generally these compounds are made by anionic polymerization of styrene, followed by the reaction of the polymer with chloromethyl methyl ether to functionalize the backbone with the required chloromethyl groups, enabling branching (Scheme 1).[1] Random branching allows the formation of simple (G0) arborescent polymers. If one had a method for controlling the chloromethylation reaction, more complex arborescent polymers, such as block and segmental polymers (Figure 1), would be possible.

The nitroxide-mediated “living” free radical polymerization of styrene can be used to produce random[4−6] and block[5−9] copolymers. If this reaction could be conducted in the presence of the chloromethyl moiety without reaction at the chloromethyl site, then control over (chloromethyl)styrene incorporation would be attained and block and segmental arborescent polymers could be achieved.

Scheme 1



Experimental Section

Bulk polymerizations (Scheme 2) were carried out on purified commercial grade samples of 3/4-(chloromethyl)styrene (CMS) (approximately a 2:1 mixture of *meta* and *para* isomers). Typically a 50 mL, 3-necked flask, purged with argon and equipped with a reflux condenser, was charged with freshly distilled (chloromethyl)styrene (9.16 g), benzoyl peroxide (BPO) (56.0 mg), and 2,2,6,6-tetramethyl-1-piperindinyloxy (TEMPO) free radical (47.7 mg) and heated to 130 °C in an oil bath. Aliquots were taken every hour, and the molecular weights were determined by gel permeation chromatography (GPC) on the crude samples *without precipitation into nonsolvent* on a Waters/Millipore liquid chromatograph equipped with a Waters 510 pump, Ultrastyragel columns of pore sizes 1×10^4, 2×500, and 100 Å, and a Waters 410 differential refractometer. Polystyrene standards were used for calibration, and tetrahydrofuran was used as the mobile phase with a flow rate of 0.8 mL/min. Data were collected and processed using Millenium 2.12 software. Percent conversions were determined using thermogravimetric analysis (TGA).[10] NMR spectra of polymer samples dissolved in $CDCl_3$ with TMS as an internal reference (^1H NMR, ca. 50 mg/mL; ^{13}C NMR, ca. 150 mg/mL) were recorded at 25 °C on a Bruker AMX 400 spectrometer operating at a frequency of 400.13 MHz for ^1H and 100.63 MHz for ^{13}C NMR. Carbon spectra were acquired with a standard JMOD pulse sequence.[11]

ESR spectra were measured on a Bruker ESP300 spectrometer at room temperature. The samples were taken from the reaction mixture and weighed into an ESR sample tube (200 mg). The derivative spectra were integrated and the relative spin concentrations calculated from the area. The measured spin concentrations were corrected for small variations in the transfer weight to the ESR tube and were shown to be reproducible to ±5%. Spin concentrations were normalized to the initial nitroxide concentrations.

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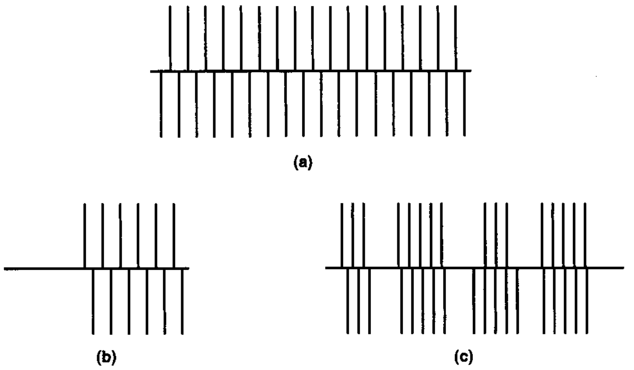


Figure 1. Influence of polymer backbone on the design of arborescent polymers: (a) conventional random, (b) block, and (c) segmental.

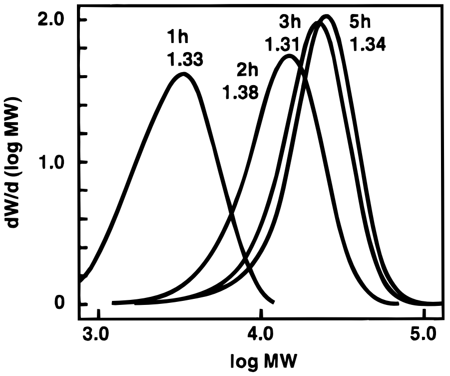
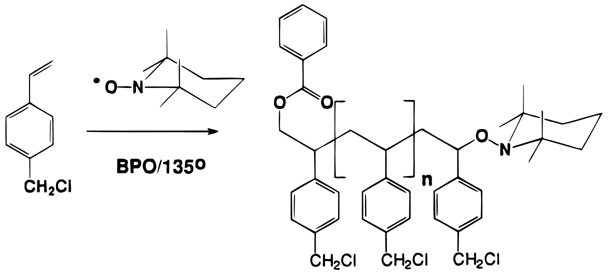


Figure 2. Successive determinations of poly[3/4-(chloromethyl)styrene] molecular weight distributions measured as a function of time. Reaction time and polydispersities are shown for each peak.

Scheme 2



Results and Discussion

Bulk 3/4-(chloromethyl)styrene, BPO, and TEMPO gave a very rapid reaction as indicated by an increase in viscosity. The molecular weight of the polymer increased monotonically over time (Figure 2), typical of a "living" reaction. Over the course of 5 h, the molecular weight (M_n) increases to 20 200 Da with a polydispersity of 1.34. The ^{13}C NMR spectrum of a sample of this polymer (M_n = 20 000) is shown in Figure 3. The chloromethylated aromatic carbons show well-resolved resonances at 137.0 ppm (*meta*) and 134.8 ppm (*para*); the relative intensity of these two peaks (ca. 2:1) is consistent with the *meta*/*para* ratio of the feed monomer. Figure 4 compares the ^{1}H NMR of poly[(3/4-(chloromethyl)styrene] (M_n = 20 000) with the ^{1}H NMR spectrum of polystyrene (M_n = 1550) synthesized under similar conditions (i.e., BPO initiated, TEMPO terminated). Both show a series of peaks (see inset) between 0.1 and 1.1 ppm which have previously been assigned to the methyl resonances of the chain-capping TEMPO moiety.[4] This complex pattern, which arises from a combination of polymer microstructure and TEMPO conformational effects,[4] is diagnostic for TEMPO-capped polystyrenes and is clear evidence that the poly[3/4-(chloromethyl)styrene] was obtained by the nitroxide-mediated stable free radical mechanism.[10,12,13] Further confirmation is provided by the presence of a benzoyloxy initiating moiety (7.3−7.9 ppm) in the approximate ratio of 1:1.

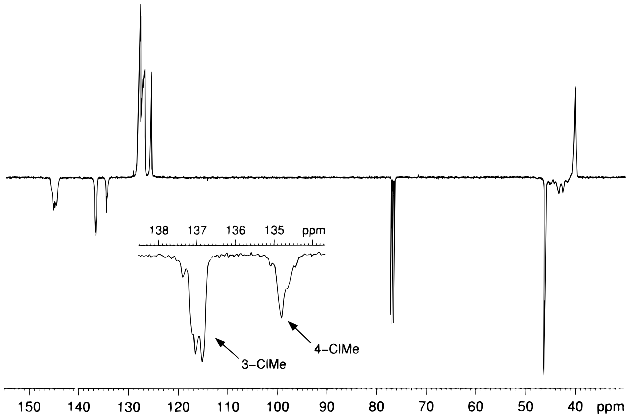


Figure 3. ^{13}C JMOD NMR spectrum 100.63 MHz of poly[3,4-(chloromethyl)styrene] (150 mg/mL, $CDCl_3$). CH_3 and CH peaks are plotted with positive intensity and CH_2 and C with negative intensity. The inset shows the 3-ClMe (δ 137.0) and 4-ClMe (δ 134.8) styrene *ipso* carbon resonances with approximate intensities of 2:1.

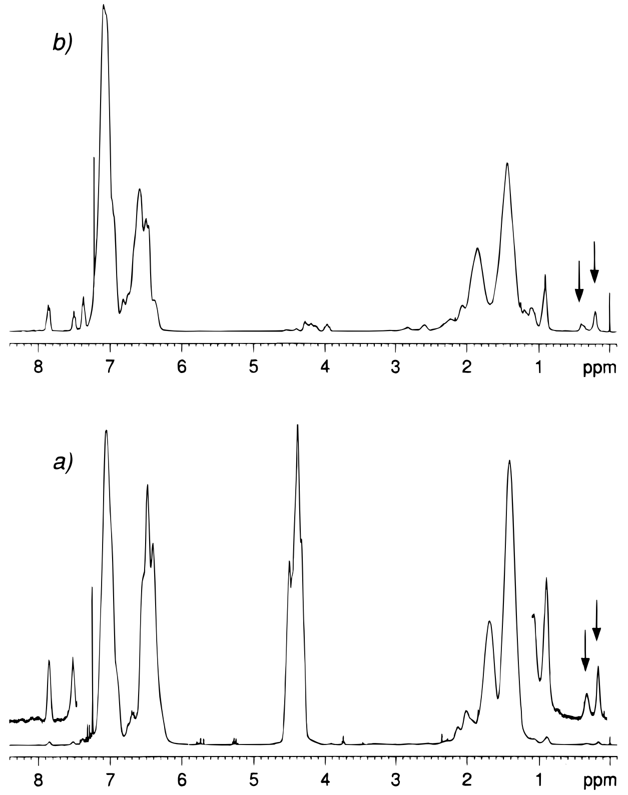


Figure 4. ^{1}H NMR spectrum (400.13 MHz) of (a) poly[3/4-(chloromethyl)styrene] (M_n = 20 000) and (b) polystyrene (M_n ca. 1550), both initiated with BPO and terminated with TEMPO. Insets show the benzoyloxy (δ 7.3−7.9) and tetramethylpiperidinyl (δ 0.1−1.1) resonances characteristic of stable free radical polymerized polystyrenes.

For comparison, control experiments were run under three sets of conditions. Thermal polymerization of CMS in the absence of BPO and TEMPO at 130 °C gave a 38% conversion to polymer (M_n = 103 000, PD = 1.88) within 2 h. It is significant that very early in the reaction (0.5 h), high molecular weight polymer is

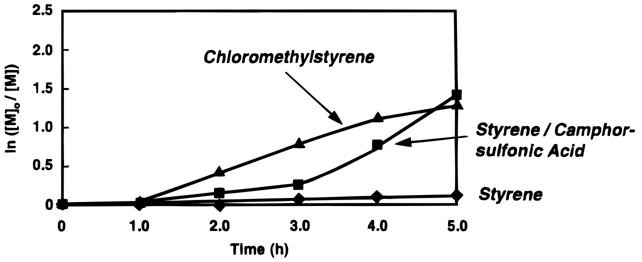


Figure 5. Rate profiles comparing conversions for styrene (◆) and CMS (△). Styrene accelerated with camphorsulfonic acid (□) is also shown.

Table 1. Preparation of Random Copolymers of CMS and Styrene under Stable Free Radical Conditions Using TEMPO and BPO

feed ratio[a] (%)	$M_n \times 10^3$	PD	% conversion
100	23.9	1.33	80.4
50	20.5	1.36	75.9
10	24.4	1.17	71.8
0[b]	19.8	1.18	76.0

[a] Feed ratio is defined as [CMS]/[styrene]. [b] Camphosulfonic acid was added to this reaction to increase the reaction rate.

obtained, a signature for a conventional mechanism. In the presence of TEMPO (no BPO), at 130 °C a conversion of 9% is achieved after 3 h, but the molecular weights are very low ($M_n = 1900$, PD 1.2). If benzoic acid (BA) is added (TEMPO:BA ratio of 1.3), again a conversion of about 10% is obtained in 3 h ($M_n = 4500$, PD = 1.21). Thus the thermal initiation rate appears to be higher for CMS than for the corresponding styrene system, and benzoic acid appears to inhibit thermal polymerization of CMS (same conversion but higher M_n implies that fewer chains were initiated in the same time period) in agreement with the observations for the styrene system.[14]

Two unusual features of the 3/4-(chloromethyl)styrene reaction are the observations that (a) the polymerization with this monomer proceeds at a much faster rate than the corresponding styrene congener and (b) the plot of $\ln(M_0/M_t)$ versus time shows substantial curvature. Figure 5 shows a comparative plot of $\ln(M_0/M_t)$ as a function of time. In this case, M_0 and M_t are the concentrations of the monomer at time $t = 0$ and time t, respectively. Without rate accelerants, using identical reaction conditions, the 3/4-(chloromethyl)styrene reaches conversions of 70% while styrene after 5 h reaches only 10% conversion. If a *rate accelerant* such as camphorsulfonic acid (CSA) is added to the styrene reaction, then over 5 h, conversions comparable to the *unaccelerated* 3/4−(chloromethyl)styrene (no CSA) are attained. Adding accelerant to the CMS system provides a further acceleration so that the reaction reaches 85% conversion in about 1.5 h.

For the preparation of conventional arborescent polymers, where the polymer branches are equally spaced along the main chain, it is necessary to control the number of (chloromethyl)styryl groups which reside on the main chain in order to control the density of branches inherent in any given structure. This is easily done by the preparation of random copolymers of styrene and CMS. Table 1 characterizes the product polymer obtained by the copolymerization of styrene and CMS at various feed ratios. Proton NMR of the random copolymer mixture confirms that the monomer incorporation into the polymer is the same as the feed ratio at the conversions shown in Table 1.

Novel arborescent block copolymers of styrene and CMS are also accessible via the nitroxide-mediated "living" reaction. Initial demonstration of this was accomplished by a simple chain extention of poly(CMS). Thus poly[3/4-(chloromethyl)styrene] was isolated by precipitation into methanol and then resubjected to the standard reaction conditions with more CMS. After the second reaction, an increase in molecular weight was obtained from $M_n = 32\,800$ (PD 1.39) to $M_n = 63\,400$ (PD = 1.67) over the course of 3 h. AB block copolymers were prepared starting either with polystyrene terminated with TEMPO for block A or with poly(CMS) terminated with TEMPO. In both cases, approximately 20 000 Da of block B polymer was added to the chain end, and a modest increase in polydispersity was observed. Block copolymer formation was confirmed by proton NMR in $CDCl_3$, since the two highest field methyl resonances of the TEMPO moiety (see arrows in Figure 4) consistently show 0.04 and 0.07 ppm upfield shifts for attachment to the CMS moiety, respectively, when compared to attachment to the styryl moiety. This consistent difference in the chemical shifts was observed for the homopolymers as well as AB diblocks (B = styryl and B = CMS). Furthermore, the increase in polydispersity observed on block copolymer formation (PD increases from 1.39 to 1.67) is consistent with some chain termination by chain transfer or due to some homopolymer formation.

Finally, it is important to return to the initial observation that the comparative plot of $\ln(M_0/M_t)$ as a function of time (Figure 6a) shows substantial curvature. The origin of the curvature can be understood qualitatively in the following way. It has been noted previously that the concentration of the nitroxide free radical is crucial to the rate of these reactions.[10] At $t <$ 1 h, when the TEMPO concentration is high, there is an induction period when the propagating carbon radical concentration is very low. Initiation by BPO and some thermal initiation (which is most significant in the early stages of the reaction) reduce the TEMPO concentration to a relatively constant value of 0.25% of the inital concentration. This relatively constant TEMPO concentration gives rise to the linear portion of the conversion−time plot. Later in the reaction, as the TEMPO concentration climbs due to a small amount of termination, the rate falls again as shown by a negative deviation from linearity after 3 h. This observation of some chain termination is not unexpected. The presence of chloromethyl groups, both on the monomer and on the polymer, suggests that chain transfer to monomer and polymer becomes significant as the propagation rate decreases at high conversions (the polymerization rate is proportional to monomer concentration). Figure 6b shows the concentration of TEMPO as a function of time for this reaction. As expected, early in the reaction, the TEMPO concentration is high and the reaction is slow. After this initial induction period, the TEMPO concentration levels off ($t = 1$ h to $t = 3$ h) and then rises again. The implications of this change in TEMPO concentration for the overall reaction are clear. For the nitroxide-mediated "living" reaction, the overall reaction rate (determined by k_{obs}) depends not only on the propagation rate constant k_p but also on the pre-equilibrium between TEMPO-terminated and carbon free radical intermediates as shown in Scheme 3. Thus k_{obs} is described by eq 1, where k_L and k_{-L} describe the rate constants governing carbon radical capture and homolytic bond dissociation of the TEMPO-terminated

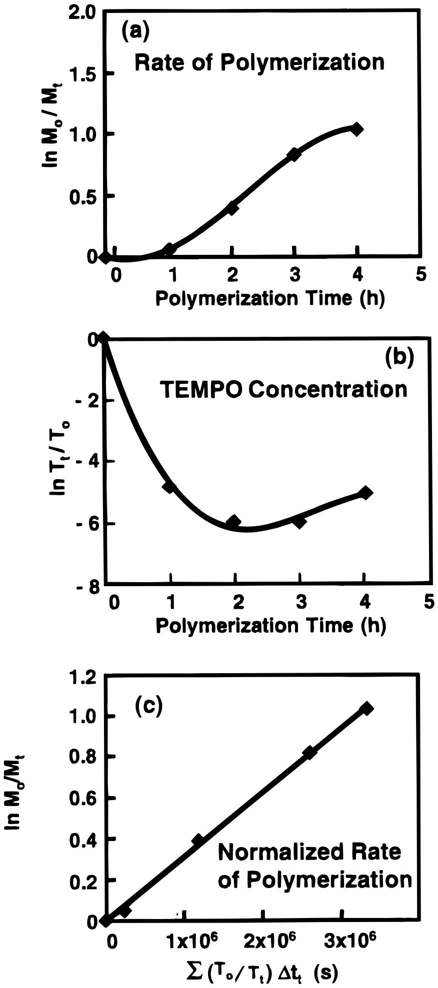
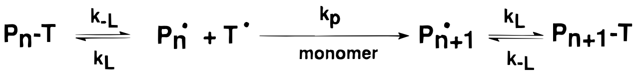


Figure 6. ln(M_0/M_t) versus time plot can be linearized if one corrects for changing TEMPO concentration during the course of the reaction: (a) raw data with no correction for TEMPO concentration, (b) TEMPO concentration as a function of time in the reaction mixture, and (c) data in plot a corrected for TEMPO concentration.

Scheme 3



$$P_n\text{-}T \underset{k_L}{\overset{k_{-L}}{\rightleftharpoons}} P_n^{\bullet} + T^{\bullet} \xrightarrow[\text{monomer}]{k_p} P_{n+1}^{\bullet} \underset{k_{-L}}{\overset{k_L}{\rightleftharpoons}} P_{n+1}\text{-}T$$

polymer chain, respectively.

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{p}}}{K_{\mathrm{L}}} = \frac{k_{\mathrm{p}} \times k_{-\mathrm{L}}}{k_{\mathrm{L}}} \qquad (1)$$

The rate expression for this reaction is given in eq 2. One cannot integrate this equation directly since the curvature in the ln(M_0/M_t) versus time plot clearly shows that T_t has a time dependence. This problem has been examined in detail previously[10] and can be treated by approximating the integral with a summation as shown in eq 3, where Δt_t is the time difference between successive data points. Since L, the number of capped chains, is approximately equal to the initial TEMPO concentration, T_0, one can correct for the rate dependence on the time dependent TEMPO concentration by replacing the time axis by a new abscissa $\Sigma(T_0/T_t)\Delta t_t$, where T_0 is the concentration of TEMPO at time $t = 0$, while T_t is the concentration of TEMPO at time t, and Δt_t is the time interval between successive data points. The result of this transformation is shown in Figure 6c. It is apparent from the linearity of this plot that the time variation of the TEMPO concentration determines the curvature in Figure 6a.[10]

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = -\frac{k_{\mathrm{p}}\,L}{K_{\mathrm{L}}T_t}[M] \qquad (2)$$

$$\ln\frac{[M]_t}{[M]_0} \approx -\mathrm{L}\frac{k_{\mathrm{p}}}{K_{\mathrm{L}}}\sum\nolimits_t \left(\frac{\Delta f_t}{T_t}\right) \qquad (3)$$

The value of the slope for the normalized rate of polymerization in Figure 6 is given by k_p/K_L. For CMS the slope is approximately 2.5-fold higher than for styrene, indicating a substantial substituent effect on these rate constants. Note that due to the complications of chain transfer for CMS, the magnitude of the substituent effect should be taken as an estimate only.

In summary, nitroxide-mediated “living” polymerization can be used to provide linear polymers of CMS. In contrast to copper-mediated “living” reactions[15] in which each chloromethyl moiety initiates a new polymer chain to produce dendritic structures, the nitroxide-mediated reaction leaves the chloromethyl groups intact and permits exceptional flexibility in further elaboration of the central polymer chain.

The rate of polymerization of CMS under “living” free radical conditions is substantially faster than styrene itself for comparable nitroxide concentrations. Substituent effects clearly play a major role in this process. The detailed role of substituents on this reaction, as well as the significance of substituents on solvation and bond dissociation of the nitroxide-capped species, will be presented elsewhere.

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