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Copolymerization of Styrene and α-Methylstyrene in the Presence of a Catalytic Chain Transfer Agent

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ABSTRACT: Copolymerizations of styrene (STY) and α-methylstyrene (AMS) have been performed at different monomer feed compositions and temperatures (40−70 °C) in the presence of the catalytic chain transfer agent bis(boron difluorodimethylglyoximate)cobaltate(II) (COBF). The average chain transfer constant, $\langle C_S \rangle$, was found to increase approximately 3 orders of magnitude upon going from pure STY to pure AMS. The addition of only 10% AMS increased the $\langle C_S \rangle$ by 1 order of magnitude. This behavior can be predicted from the relative fractions of growing radical end groups, which results in the majority of polymer chains being formed with an unsaturated AMS end group. No significant penultimate unit effects in the chain transfer reaction were observed. The addition of 10−20% AMS results in the majority of the growing radicals having AMS end groups, and hence AMS dominates the catalytic chain transfer reaction. The $\langle C_S \rangle$ values continue to increase as the AMS content is increased beyond 20%; however, this can be mostly attributed to a decrease in $\langle k_p \rangle$ rather than an increase in $\langle k_{tr} \rangle$. The expected end groups in the homopolymerization of AMS in the presence of COBF were confirmed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS).

Introduction

The use of cobalt(II) catalytic chain transfer agents is a highly effective way of controlling molecular weight in free-radical polymerization and has been recently reviewed.[1,2] The chain transfer constants of these catalysts are typically on the order of 10^3−10^4 as compared to 0.1−10 for typical chain transfer agents such as mercaptans,[3] and as a result, only ppm quantities are required to significantly reduce the molecular weight. To date, the usefulness of catalytic chain transfer polymerization has been demonstrated in solution/bulk polymerizations,[4−9] emulsion polymerization,[10−12] and miniemulsion polymerization.[13]

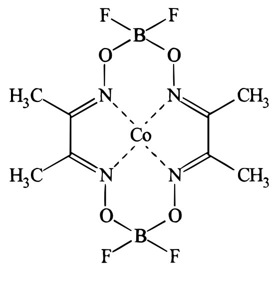
In catalytic chain transfer polymerization, initiation, propagation, and termination are thought to occur by a free-radical process. The chain transfer reaction[4,7] is thought to involve a growing polymer chain, $R_n^\bullet$, encountering a Co(II) complex, resulting in hydrogen abstraction, producing a dead polymer chain, P_n (with an unsaturated end group), and a Co(III)−H species. Monomer can then react with Co(III)−H to produce a monomeric radical, $R_1^\bullet$ (which then propagates to form another chain) and the original Co(II) catalyst. This mechanism is illustrated in Scheme 1.

In a recent publication,[14] we have reported the copolymerization of styrene (STY) and methyl methacrylate (MMA) in the presence of a catalytic chain transfer agent and shown that the behavior of the system could be described by a relatively simple copolymerization model. The present work continues this theme by investigating the copolymerization of styrene with α-methylstyrene (AMS) with the catalytic chain transfer agent bis(boron difluorodimethylglyoximate)cobaltate(II) (COBF).

Scheme 1

$$R_n^\bullet + \mathrm{Co(II)} \xrightarrow{k_{tr}} P_n + \mathrm{Co(III){-}H}$$

$$\mathrm{Co(III){-}H} + \mathrm{M} \longrightarrow R_1^\bullet + \mathrm{Co(II)}$$



COBF

Previously, it has been shown that COBF has a chain transfer constant with STY over 1 order of magnitude lower than that with MMA and this is attributed to the relative ease of abstracting a hydrogen atom from an α-methyl group of a propagating poly(MMA) radical over a β-hydrogen in the backbone of a poly(STY) radical.[6,9] Leading from this, a logical progression is to measure the chain transfer constant of styrene with an α-methyl group, i.e., α-methylstyrene, with COBF and see how it compares with the other two systems. It is expected that the chain transfer reaction of AMS with COBF is analogous to that of MMA[9] (see Scheme 2) and as such has a high chain transfer constant. In this work we measure the chain transfer constant of COBF in an AMS homopolymerization and copolymerization for a

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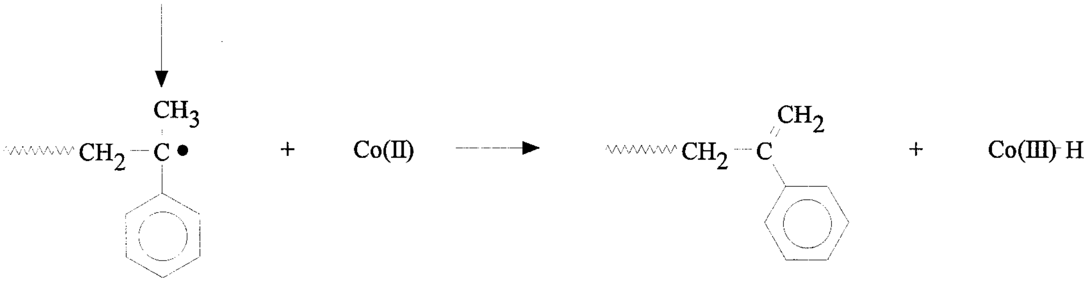
Scheme 2



series of STY/AMS compositions. The results are compared to predictions from a model that describes chain transfer in copolymerization systems.

Measuring the Chain Transfer Constant. The chain transfer constants were measured using the chain length distribution (CLD) method from the number molecular weight distribution.[15−20] For a polymerization completely governed by chain transfer, the molecular weight distribution can be expressed as the following exponential:[21]

$$P(M) \propto \exp\left(-C_S\frac{[S]}{[M]}\frac{M}{m_0}\right) \qquad (1)$$

where C_S is the chain transfer constant, [S] and [M] are the chain transfer agent and monomer concentrations, respectively, m_0 is the molecular weight of monomer, and $P(M)$ is the number of chains of molecular weight M. The number distribution, $P(M)$, is obtained from the calibrated size exclusion chromatography (SEC) distribution, $W(\log M)$, as follows:

$$P(M) = W(\log M)\frac{\log e}{M^2} \qquad (2)$$

The procedure for obtaining the transformed SEC distribution, $W(\log M)$, from the raw SEC chromatogram is described elsewhere.[19,22] By plotting the molecular weight distribution as ln $P(M)$ against M, a straight line should be obtained for the chain transfer controlled region of the distribution, which corresponds to $\Lambda = -C_S[S]/([M]m_0)$. Often there is some curvature present in the distribution, making it difficult to assign a unique slope, Λ, to the plot. Our experience shows that in these systems the best place to measure Λ is immediately to the right of M_w, as is discussed further elsewhere.[9,14] The chain transfer constant, C_S, is determined by plotting the Λ for a series of experiments with different catalyst concentrations, against [S]/[M] yielding a slope equal to $-C_S/m_0$.

Experimental Section

Synthesis of the Catalytic Chain Transfer Agent. Bis(boron difluorodimethylglyoximate) cobaltate(II) (COBF) was synthesized according to a modification of the method described by Bakac and Espenson.[6,7,23,24]

Materials. The monomers styrene (STY) and α-methylstyrene (AMS) (Aldrich, 99%) were purified by passing through a column of activated basic alumina to remove inhibitor and then vacuum distilled. The purified monomers were deoxygenated by purging with nitrogen for 1 h before use. AIBN (DuPont) was purified by recrystallization from methanol.

Polymerizations. All reactions were performed using standard Schlenk apparatus and syringe techniques under oxygen free conditions.[25] The reaction mixtures were prepared from stock solutions of AIBN/monomer and COBF/monomer. A stock solution of COBF, **1**, was prepared by dissolving COBF (3 mg, 7.8×10^{-6} mol) in the appropriate STY/AMS monomer mixture (30 mL). A second stock solution, **2**, was prepared by dissolving AIBN in the appropriate monomer mixture (~30 mmol·L^{-1}). Five reaction mixtures (4.4 mL) were prepared in sealable ampules: aliquots of **2** (4 mL) and **1** (0, 0.1, 0.2, 0.3 or 0.4 mL) were mixed and the solutions made up to volume (4.4 mL) by addition of the appropriate monomer mixture. The solutions were degassed by a freeze−pump−thaw procedure. The polymerizations were performed in a thermostated water bath, and reaction was stopped by cooling the solutions in an ice bath followed by the addition of hydroquinone. The polymer was isolated by evaporating off the residual monomer, initially in a fume cupboard to remove the bulk of the liquid and then in a vacuum oven at 70 °C (hydroquinone sublimes away completely under these conditions). Final conversions were measured by gravimetry.

Analyses. The molecular weight distributions were measured by size exclusion chromatography (SEC) on a modular system, comprising an autoinjector, guard column, two mixed bed columns (60 cm mixed C, and 30 cm mixed E, Polymer Laboratories), and a differential refractive index detector. The eluent was tetrahydrofuran at 1 mL·min^{-1}, and the system was calibrated with poly(STY) standards (MW 2.89×10^6, 2.10×10^6, 9.80×10^5, 7.06×10^5, 4.65×10^5, 1.70×10^5, 6.80×10^4, 3.45×10^4, 1.81×10^4, 9.20×10^3, 3.25×10^3, 1.25×10^3, 5.80×10^2 and styrene (MW 104)) and poly(AMS) standards (MW 1.25×10^6, 6.70×10^5, 4.20×10^5, 3.02×10^5, 1.35×10^5, 1.95×10^4, 1.05×10^4, 6.70×10^3, 4.70×10^3, 3.50×10^3 and AMS (MW 118)) from Polymer Laboratories.

An important factor in the accuracy of C_S obtained from these experiments is largely governed by the calibration of the SEC system. This can become a major problem, especially for copolymer samples. In a previous publication,[26] the calibration curves for poly(AMS) and poly(STY) were shown to overlay and therefore the molecular weight distributions of the copolymers were all analyzed using a poly(STY) calibration. This approach needs to be used with caution since it has been shown that in some instances, e.g., the copolymerization of methyl methacrylate/*n*-butyl acrylate,[27] even if the intrinsic viscosities of the homopolymers are similar, the intrinsic viscosities of the copolymers can be significantly different. For the copolymerization of AMS and STY, however, it has been shown that intrinsic viscosity of the copolymers are very close to that of both the homopolymers,[28] and so analyzing all of the molecular weight distributions against a poly(STY) calibration is justified.

MALDI Analysis. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectrum of poly(AMS) was obtained on a Voyager-DERP from PerSeptive Biosystems. The machine was operated in reflector mode, with a delayed extraction of 100 ns, and low mass gate set at 600 Da. The mass scale was calibrated using bovine insulin. The matrix solution (0.5 mL mixture of 9-nitroanthracene and silver trifluoroacetate in tetrahydrofuran) was deposited on the sample slide and allowed to dry. Subsequently, the polymer was deposited on the surface of the matrix (0.5 mL of polymer solution 4 mg·mL^{-1} in tetrahydrofuran) and allowed to dry.

Table 1. C_S and k_{tr} of COBF with AMS for Various Temperatures Measured Using the CLD Method

T/°C	C_S	$k_{tr}{}^a$/dm^3·mol^{-1}·s^{-1}
40	8.15×10^5	9.11×10^5
50	8.93×10^5	1.54×10^6

[a] k_p at 40 °C = 1.12 dm^3·mol^{-1}·s^{-1} and at 50 °C = 1.73 dm^3·mol^{-1}·s^{-1}.[26]

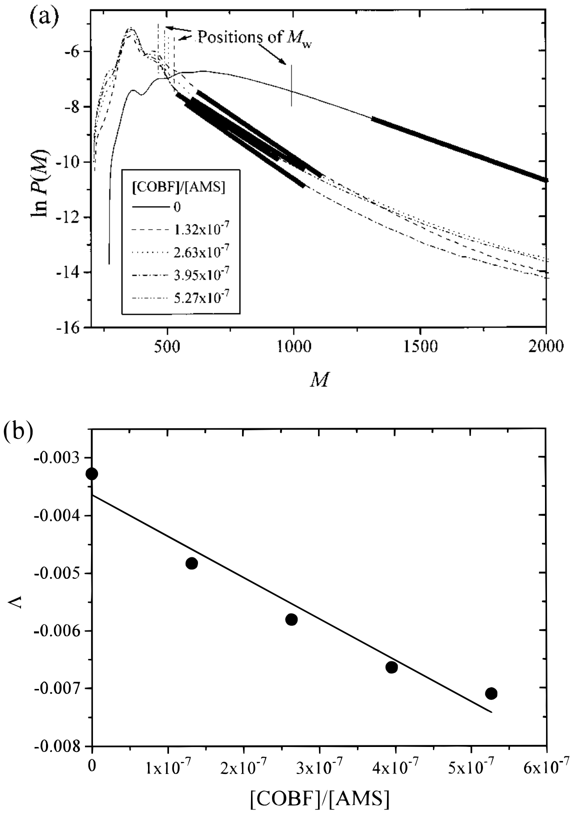


Figure 1. Determination of C_S using the CLD method for COBF with AMS at 50 °C. (a) log number distributions, ln $P(M)$, for various COBF concentrations. The heavy lines indicate the region were the slope, Λ, was measured. The position of M_w is indicated for reference. (b) Λ vs [COBF]/[AMS] used to determine C_S.

Results and Discussion

Homopolymerization of α-Methylstyrene with COBF. The chain transfer constants, C_S, for COBF with AMS were measured at 40 and 50 °C and are listed in Table 1, along with the chain transfer rate coefficients, k_{tr}. Temperatures above 50 °C were not investigated since AMS has a ceiling temperature of 61 °C.[29,30] The values of C_S (~8×10^5) are approximately 20 times higher than those measured previously for MMA[9] (~3×10^4) and approximately 1000 times greater than that for STY[9] (~10^3). Although the C_S is very high, the value for k_{tr} (~10^6) is intermediate between MMA[9] (~10^7) and STY[9] (~10^5). The reason C_S for AMS with COBF is so high is that k_p for AMS is very low, see Figure 7 ($k_p{}^{AMS}$ = 1.73 dm^3·mol^{-1}·L^{-1} [26] as compared to $k_p{}^{STY}$ = 240 dm^3·mol^{-1}·L^{-1} [31]). Since the sites of hydrogen abstraction in MMA and AMS are similar, the lower value of k_{tr} suggests that the phenyl substituent may have a negative effect on k_{tr}.

The molecular weight distributions plotted as ln $P(M)$ vs M for different concentrations of COBF at 50 °C are shown in Figure 1a. The distributions show some curvature and so it is only possible to estimate the true value of C_S. To obtain the chain transfer constant, the slope of the ln $P(M)$ distribution, Λ, for a series of different COBF concentrations, is plotted against [COBF]/[M] giving another slope equal to $-C_S/m_0$, as shown in Figure 1b.

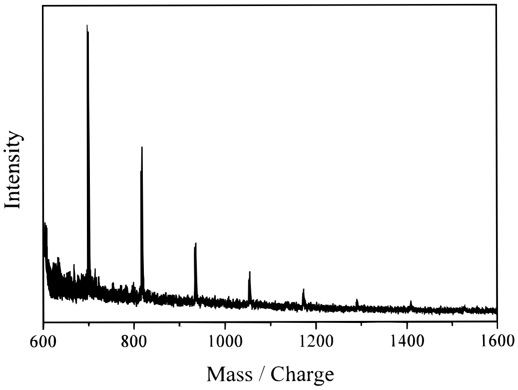


Figure 2. MALDI-MS spectrum of poly(AMS) prepared in the presence of COBF and initiated with AIBN at 50 °C. [COBF]/[AMS] = 5.27×10^{-7}, [AIBN] = 30.4 mmol·L^{-1}, M_n = 460, PDI = 1.69.

The curvature in Figure 1a may be due to several reasons: (i) there may be errors in the SEC analysis originating from too few low molecular weight calibration standards and the differential refractive index detector response is chain length dependent for low molecular weight chains[32] (so it is difficult to ascertain whether the curvature is real or an artifact of the analysis); (ii) it has been shown previously that C_S is chain length dependent for short chains[7,33] (i.e., the region of interest in this case), which can introduce curvature in the ln $P(M)$ vs M plots;[33-35] (iii) as previously mentioned, eq 1 gives approximate character in the case of short chains.[21]

The Mayo[30,36] method was not suitable for measuring the C_S of COBF with AMS since the molecular weights produced were very low, causing difficulty in determining accurate values of the number average molecular weight, M_n.[33,34] In the absence of COBF, the M_n of AMS produced was quite low, in the order of 10^3, and in the presence of COBF the molecular weights produced were even lower. It is difficult to obtain reliable estimates for M_n from very low molecular weight samples since the molecular weight distribution cannot be resolved adequately from the solvent peak in SEC. Another consequence of producing low molecular weight polymer with catalytic chain transfer is that monomer is regenerated as a product of the reaction (i.e., polymer of degree of polymerization = 1). This will cause an overestimation in the value of M_n, as it is not possible to distinguish between unreacted monomer and monomer regenerated as part of the chain transfer reaction.

End Group Analysis by MALDI MS. The MALDI-TOF-MS[37-41] spectrum of an AMS polymer produced at 50 °C is shown in Figure 2. The main feature of this spectrum is a single series of peaks regularly spaced by 118.2 Da, i.e., the molecular weight of the AMS repeat unit. This indicates that all the polymer chains contain the same end groups. The mass of each peak is described by the general relationship $m = \mathrm{DP_n}118.2 + 107.9$, where DP$_n$ is the degree of polymerization of the chain, and 107.9 is the mass of the silver counterion. The molecular weight of the AIBN initiating group is 68.1. A polymer chain resulting from initiation with AIBN and terminated by chain transfer or disproportionation would have a mass of $m = \mathrm{DP_n}118.2 + 68.1 + 107.9$, and a chain initiated by AIBN and terminated by combination with another AIBN-initiated chain would have a mass of $m = \mathrm{DP_n}118.2 + 2(68.1) + 107.9$. No peaks corresponding to these two latter relationships are observed, indicating that the majority of chains are stopped by reaction with Co(II) and are initiated by $\mathrm{Co^{III}{-}H}$ in the catalytic chain transfer mechanism.

Chain Transfer in Copolymerization. In the copolymerization of STY and AMS in the presence of COBF there are two possible chain transfer reactions that can occur, each with its own rate coefficient, depending on the active end group of the growing polymer chain:

$$\sim\mathrm{STY}^{\bullet} + \mathrm{Co(II)} \xrightarrow{k_{\mathrm{tr}}{}^{\mathrm{STY}}} \sim\mathrm{STY} + \mathrm{Co^{III}{-}H} \tag{3}$$

$$\sim\mathrm{AMS}^{\bullet} + \mathrm{Co(II)} \xrightarrow{k_{\mathrm{tr}}{}^{\mathrm{AMS}}} \sim\mathrm{AMS} + \mathrm{Co^{III}{-}H} \tag{4}$$

When measuring the experimentally observable chain transfer constant, one obtains an average chain transfer constant, $\langle C_{\mathrm{S}}\rangle$, that results from a combination of both of the above reactions. The average chain transfer constant is related to the average chain transfer and propagation rate coefficients, $\langle k_{\mathrm{tr}}\rangle$ and $\langle k_{\mathrm{p}}\rangle$, by the following expression:

$$\langle C_{\mathrm{S}}\rangle = \langle k_{\mathrm{tr}}\rangle / \langle k_{\mathrm{p}}\rangle \tag{5}$$

The average chain transfer rate coefficient, $\langle k_{\mathrm{tr}}\rangle$, is related to the rate of chain transfer for the two chain transfer reactions in eqs 3 and 4 by the following expression:

$$\langle k_{\mathrm{tr}}\rangle[\mathrm{COBF}]([\sim\mathrm{AMS}^{\bullet}] + [\sim\mathrm{STY}^{\bullet}]) = k_{\mathrm{tr}}{}^{\mathrm{AMS}}[\mathrm{COBF}][\sim\mathrm{AMS}^{\bullet}] + k_{\mathrm{tr}}{}^{\mathrm{STY}}[\mathrm{COBF}][\sim\mathrm{STY}^{\bullet}] \tag{6}$$

which can be expressed as:

$$\langle k_{\mathrm{tr}}\rangle = k_{\mathrm{tr}}{}^{\mathrm{AMS}} \frac{[\sim\mathrm{AMS}^{\bullet}]}{[\sim\mathrm{AMS}^{\bullet}] + [\sim\mathrm{STY}^{\bullet}]} + k_{\mathrm{tr}}{}^{\mathrm{STY}} \frac{[\sim\mathrm{STY}^{\bullet}]}{[\sim\mathrm{AMS}^{\bullet}] + [\sim\mathrm{STY}^{\bullet}]} \tag{7}$$

$$\langle k_{\mathrm{tr}}\rangle = \phi_{\mathrm{AMS}} k_{\mathrm{tr}}{}^{\mathrm{AMS}} + \phi_{\mathrm{STY}} k_{\mathrm{tr}}{}^{\mathrm{STY}} \tag{8}$$

where ϕ_{AMS} is the fraction of growing chains that have an AMS radical as the propagating end group, and ϕ_{STY} ($=1 - \phi_{\mathrm{AMS}}$) is the fraction of STY radical end groups. The fraction of radical end groups can be calculated by considering the steady-state concentrations of the two radicals in the reaction[30]

$$k_{\mathrm{p}}{}^{\mathrm{AMS-STY}}[\sim\mathrm{AMS}^{\bullet}][\mathrm{STY}] = k_{\mathrm{p}}{}^{\mathrm{STY-AMS}}[\sim\mathrm{STY}^{\bullet}][\mathrm{AMS}] \tag{9}$$

which can be rearranged to obtain[42]

$$A_{\mathrm{AMS-STY}} = \frac{[\sim\mathrm{AMS}^{\bullet}]}{[\sim\mathrm{STY}^{\bullet}]} = \frac{k_{\mathrm{p}}{}^{\mathrm{STY}} r_{\mathrm{AMS}} f_{\mathrm{AMS}}}{k_{\mathrm{p}}{}^{\mathrm{AMS}} r_{\mathrm{STY}} f_{\mathrm{STY}}} \tag{10}$$

and from this, the fraction of AMS radical end groups can be calculated:

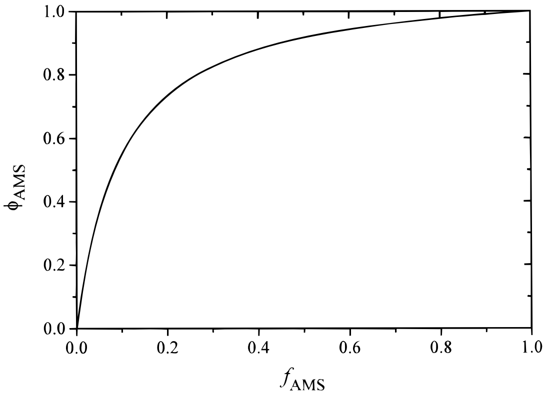


Figure 3. Predicted fraction of AMS radical end groups, ϕ_{AMS}, as a function of the fraction of AMS monomer in the reaction, f_{AMS}, using eqs 10 and 11. The parameters used were data at 40 °C from Table 3.

Table 2. Values of $\langle C_{\mathrm{S}}\rangle$ and $\langle k_{\mathrm{tr}}\rangle$ for the Copolymerization of AMS and Styrene at Various Temperatures[a]

T/°C	f_{AMS}	$\langle C_{\mathrm{S}}\rangle$	$\langle k_{\mathrm{tr}}\rangle^{b}$/dm^3·mol^{-1}·s^{-1}
40	0	9.60×10^{2}	1.55×10^{5}
40	0	1.07×10^{3}	1.72×10^{5}
40	0	1.05×10^{3}	1.69×10^{5}
40	0.0892	6.48×10^{3}	4.71×10^{5}
40	0.0896	1.53×10^{4}	1.11×10^{6}
40	0.181	1.66×10^{4}	7.63×10^{5}
40	0.370	2.98×10^{4}	7.15×10^{5}
40	0.370	4.95×10^{4}	1.19×10^{6}
50	0	7.42×10^{2}	1.76×10^{5}
50	0	3.56×10^{2}	8.44×10^{4}
50	0	5.00×10^{2}	1.19×10^{5}
50	0.0892	6.08×10^{3}	6.55×10^{5}
50	0.0896	8.48×10^{3}	9.11×10^{5}
50	0.181	1.12×10^{4}	7.23×10^{5}
50	0.370	2.81×10^{4}	9.09×10^{5}
50	0.370	7.53×10^{3}	2.43×10^{5}
60	0	3.45×10^{2}	1.35×10^{5}
60	0	9.75×10^{2}	3.82×10^{5}
60	0.0896	5.21×10^{3}	1.49×10^{6}
60	0.181	4.26×10^{3}	7.01×10^{5}
60	0.370	4.87×10^{4}	3.23×10^{6}
60	0.370	3.10×10^{4}	2.05×10^{6}
70	0	2.89×10^{2}	1.60×10^{5}
70	0	2.41×10^{2}	1.34×10^{5}
70	0.0896	3.56×10^{3}	1.29×10^{6}
70	0.181	5.34×10^{3}	1.24×10^{6}
70	0.370	1.02×10^{4}	9.58×10^{5}
70	0.370	4.17×10^{3}	3.93×10^{5}

[a] Values for $f_{\mathrm{AMS}} = 0$ taken from elsewhere.[9] [b] Calculated using the terminal model fit for $\langle k_{\mathrm{p}}\rangle$[26] using the parameters in Table 3.

$$\phi_{\mathrm{AMS}} = \frac{A_{\mathrm{AMS-STY}}}{1 + A_{\mathrm{AMS-STY}}} \tag{11}$$

Figure 3 shows the predicted fraction of AMS radical end groups, ϕ_{AMS}, as a function of the fraction of AMS in the monomer feed, f_{AMS}. What is apparent is that AMS is the dominant radical end group even at fractions of AMS in the monomer feed as low as 0.1. From this, it is predicted that a small addition of AMS to a styrene reaction should significantly increase the $\langle C_{\mathrm{S}}\rangle$. Once the fraction of AMS monomer reaches 0.2, approximately 75% of the radical end groups are AMS, and so the reaction shown in eq 4 should be the dominant chain transfer reaction.

Copolymerization of Styrene and α-Methylstyrene with COBF. The average chain transfer constants, $\langle C_{\mathrm{S}}\rangle$, measured in the copolymerization of styrene and AMS are listed in Table 2, along with those

Table 3. Parameters Used in Model Predictions

T/°C	$k_p^{\mathrm{AMS}\,a}$	$k_p^{\mathrm{STY}\,b}$	r_{AMS}^{c}	r_{STY}^{c}	$k_{tr}^{\mathrm{STY}\,d}$	$k_{tr}^{\mathrm{AMS}\,e}$
40	1.12	161	0.0969	0.954	1.65×10^5	9.11×10^5
50	1.73	237	0.124	0.982	1.26×10^5	1.54×10^5
60	2.61	341	0.157	1.01	2.59×10^5	$2.40 \times 10^{6\,f}$
70	3.84	480	0.196	1.03	1.47×10^5	$1.18 \times 10^{6\,f}$

[a] $\mathrm{dm^3{\cdot}mol^{-1}{\cdot}s^{-1}}$; calculated using $k_p^{\mathrm{AMS}} = 10^{6.17}\exp(-(36.7\ \mathrm{kJ{\cdot}mol^{-1}})/(RT))$.[26] [b] $\mathrm{dm^3{\cdot}mol^{-1}{\cdot}s^{-1}}$; calculated using $k_p^{\mathrm{STY}} = 10^{7.630}\exp(-(32.51\ \mathrm{kJ{\cdot}mol^{-1}})/(RT))$.[31] [c] From ref 46: $\log r_{\mathrm{AMS}} = 2.48 - 1094/T$ and $\log r_{\mathrm{STY}} = 0.378 - 125/T$. [d] $\mathrm{dm^3{\cdot}mol^{-1}{\cdot}s^{-1}}$; average of $f_{\mathrm{AMS}} = 0$ values in Table 2. [e] $\mathrm{dm^3{\cdot}mol^{-1}{\cdot}s^{-1}}$. [f] Calculated to give best model fit.

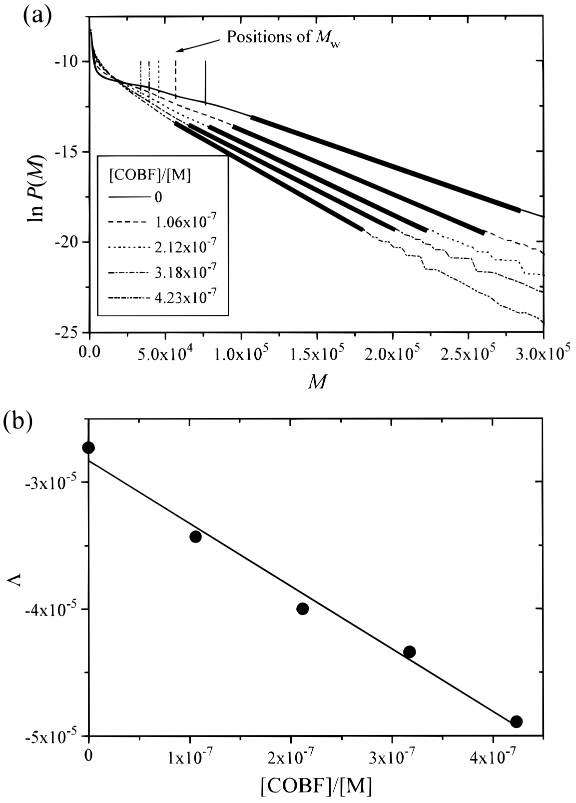


Figure 4. Determination of C_S using the CLD method for COBF in the copolymerization of STY/AMS ($f_{\mathrm{AMS}} = 0.0896$) at 60 °C. (a) log number molecular weight distributions, ln $P(M)$, for various COBF concentrations. The heavy lines indicate the region where Λ was measured. M_w is indicated for reference. (b) Λ vs [COBF]/[AMS] used to determine $\langle C_S\rangle = 5.21 \times 10^3$.

previously obtained for the homopolymerization of styrene.[9] Figures 4 and 5 show typical molecular weight distributions and C_S determination plots for $f_{\mathrm{AMS}} = 0.0896$ and 0.370, respectively.

Figure 6 shows the dependence of $\langle C_S\rangle$ on the fraction of AMS in the reaction for the data at 40 °C. The line is the model fit using eqs 5 and 8 and the ϕ_{AMS} relationship shown in Figure 3. As expected, there is a significant increase in $\langle C_S\rangle$ even for the addition of a small amount of AMS, going from $\sim 10^3$ for pure styrene to $\sim 10^4$ for $f_{\mathrm{AMS}} = 0.1$. As the fraction of AMS is increased, $\langle C_S\rangle$ continues to increase up to the value for pure AMS ($\sim 10^6$). What, at first inspection, is unexpected is that $\langle C_S\rangle$ continues to increase over the whole composition range, even though AMS dominates the radical end groups, and hence the chain transfer reaction, once $f_{\mathrm{AMS}} = 0.2$. This is highlighted in the insert in Figure 6, which shows, on a linear scale, how much greater the C_S of pure AMS is compared to that at $f_{\mathrm{AMS}} = 0.370$. To explain this, it needs to be considered that $\langle C_S\rangle$ is equal to $\langle k_{tr}\rangle/\langle k_p\rangle$ and so changes in both $\langle k_{tr}\rangle$ and $\langle k_p\rangle$ affect $\langle C_S\rangle$.

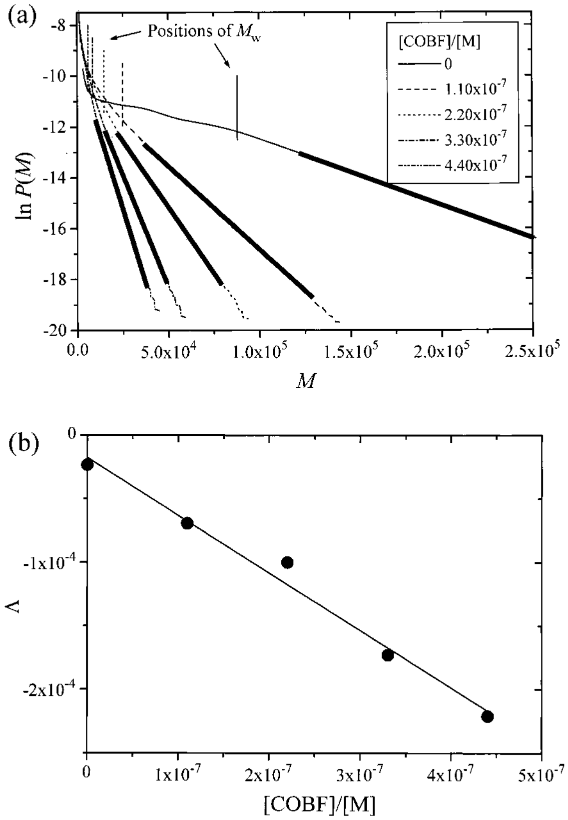


Figure 5. Determination of C_S using the CLD method for COBF in the copolymerization of STY/AMS ($f_{\mathrm{AMS}} = 0.370$) at 40 °C. (a) log number molecular weight distributions, ln $P(M)$, for various COBF concentrations. The heavy lines indicate the region where Λ was measured. M_w is indicated for reference. (b) Λ vs [COBF]/[AMS] used to determine $\langle C_S\rangle = 4.95 \times 10^4$.

From eq 8 it can be seen that the behavior of $\langle k_{tr}\rangle$ directly reflects the behavior of ϕ_{AMS} and hence the continual increase in $\langle C_S\rangle$ must be due to a continual reduction in $\langle k_p\rangle$. This is indeed the case, as can be seen in Figure 7, which shows that $\langle k_p\rangle$ decreases by 2 orders of magnitude in going from pure STY to pure AMS.[26] Parts a–c of Figure 8 show the $\langle C_S\rangle$ vs f_{AMS} plots for the data at 50, 60, and 70 °C, respectively.

Overall, the model provides a good description of how $\langle C_S\rangle$ depends on f_{AMS}, suggesting that the dominant kinetic processes are being adequately described. It should be noted that there are no adjustable parameters in the model. What is very interesting is that penultimate unit effects in chain transfer do not appear to play an important part in the copolymerization of styrene and AMS. Previously, we have shown that the terminal model gives a good description of $\langle k_p\rangle$ with respect to composition,[26] and since the model for chain transfer, also based on terminal kinetics, gives a good description of the data, it suggests that penultimate unit effects[43] are of minor importance in this system.

Penultimate unit effects in chain transfer may, however, be present, even though they do not play an important role in the overall kinetics of reaction. By considering the two chain transfer reactions for styrene and AMS, eqs 3 and 4 respectively, it would be expected that any penultimate unit effects in eq 4 would be small; however, they may be significant in eq 3. The sites of

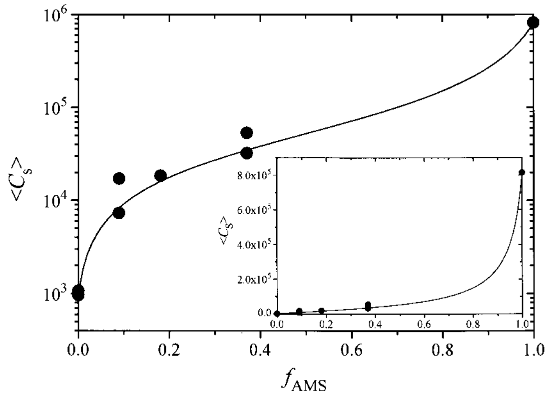


Figure 6. Dependence of the average chain transfer constant, $\langle C_S \rangle$, on the fraction of AMS, f_{AMS}, in the copolymerization of styrene and AMS with COBF at 40 °C. The points are experimental data, and the line is the prediction using eqs 5, 8, and 11 and the parameters in Table 3. The insert shows, on a linear scale, how much greater the C_S of pure AMS is compared to that at $f_{AMS} = 0.370$.

hydrogen abstraction for both reactions are shown in Charts 1 and 2 for AMS and styrene, with different penultimate groups, respectively. In chain transfer with AMS, hydrogen abstraction occurs from the α-methyl group, which is three carbons away from the penultimate group, and so the nature of the penultimate group is expected to have a minor effect on the reactivity. In chain transfer with styrene, however, hydrogen abstraction occurs from the backbone,[5,6] which is only one carbon away from the penultimate group. It can be expected that the chain transfer reaction will be more difficult, due to steric hindrance, if the penultimate group is AMS instead of styrene. The reason that penultimate unit effects may not be seen in this system is that AMS radical end groups are dominating, even if the monomer is present in relatively small quantities (see ϕ_{AMS} vs f_{AMS} in Figure 3). Since penultimate unit effects are likely to be small with AMS, no significant effects are seen in the overall copolymerization behavior.

Prediction of End Groups. It is of interest to be able to predict the end groups formed in the copolymerization of styrene and α-methylstyrene with catalytic chain transfer agents, as the double bond formed can be used in subsequent reactions. The unsaturated end group in AMS is external on the end of the chain and so is likely to be more reactive than the unsaturated end group of styrene, which is located in the backbone, and hence more sterically hindered, see Chart 3.

The fraction of unsaturated AMS end groups produced by catalytic chain transfer, Φ_{AMS}, can be calculated from the probability that a growing AMS radical will react with COBF, $P(\sim\text{AMS}\cdot \mid \text{COBF})$:[44,45]

$$\Phi_{AMS} = \frac{\phi_{AMS}P(\sim\text{AMS}^{\bullet}|\text{COBF})}{\phi_{AMS}P(\sim\text{AMS}^{\bullet}|\text{COBF}) + \phi_{Sty}P(\sim\text{STY}^{\bullet}|\text{COBF})} \quad (12)$$

This assumes that chain transfer to cobalt is the dominant chain-stopping mechanism; i.e., chain-stopping by radical−radical termination is not significant.

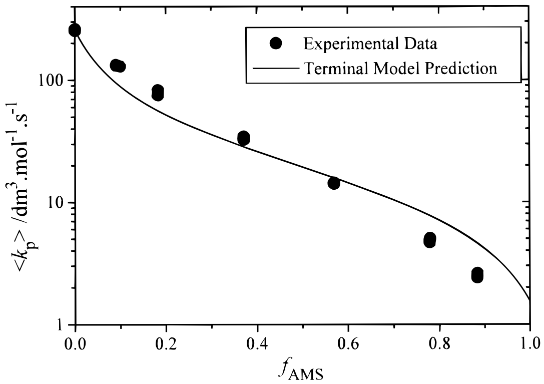


Figure 7. Dependence of the average propagation rate coefficient, $\langle k_p \rangle$, in the copolymerization of STY and AMS on the fraction of AMS, f_{AMS}, at 47.4 °C measured by pulsed laser polymerization.[26] $\langle k_p \rangle$ decreases by 2 orders of magnitude over the range (note the log $\langle k_p \rangle$ scale).

The probability of an AMS radical reacting with COBF is calculated from the ratio of the rate of chain transfer to the sum of the rates of all possible fates for the AMS radical (i.e., propagation with AMS, propagation with STY, and chain transfer to COBF):

$$P(\sim\text{AMS}^{\bullet}|\text{COBF}) = k_{tr}^{\text{AMS}}[\sim\text{AMS}^{\bullet}][\text{COBF}]/ (k_p^{\text{AMS}}[\sim\text{AMS}^{\bullet}][\text{AMS}] + k_p^{\text{AMS-STY}}[\sim\text{AMS}^{\bullet}][\text{STY}] + k_{tr}^{\text{AMS}}[\sim\text{AMS}^{\bullet}][\text{COBF}]) \quad (13)$$

by dividing by k_p^{AMS} $[\sim\text{AMS}^{\bullet}]$ one obtains

$$P(\sim\text{AMS}^{\bullet}|\text{COBF}) = \frac{C_S^{\text{AMS}}[\text{COBF}]}{[\text{AMS}] + \frac{[\text{STY}]}{r_{\text{AMS}}} + C_S^{\text{AMS}}[\text{COBF}]} \quad (14)$$

similarly

$$P(\sim\text{STY}^{\bullet}|\text{COBF}) = \frac{C_S^{\text{STY}}[\text{COBF}]}{[\text{STY}] + \frac{[\text{AMS}]}{r_{\text{STY}}} + C_S^{\text{STY}}[\text{COBF}]} \quad (15)$$

The fraction of unsaturated AMS end groups as a function of f_{AMS} is shown in Figure 9. It is obvious that AMS dominates the end groups over the whole range, as even the addition of only 1% AMS ($f_{AMS} = 0.01$) results in 89% of the end groups being AMS. Therefore, the addition of a very small quantity of AMS (ca. 1−5%) in a STY polymerization will provide the less hindered (and more reactive) AMS unsaturated end groups on virtually all the chains.

Rate of Reaction. A disadvantage of the use of α-methylstyrene as a comonomer in a styrene polymerization is that the rate of reaction is significantly reduced, as expected from the low propagation rate coefficient of AMS (Figure 7). Figure 10 shows the rate of reaction for the copolymerization of STY and AMS as a function of the fraction of AMS monomer content in the reaction at 50 °C. The rate of reaction decreases significantly as the AMS content is increased. This decrease in reaction rate needs to be considered in optimizing the reaction conditions if AMS is to be used as a comonomer to increase the chain transfer rate in a catalytic chain transfer reaction with styrene. However, from these results, and the results shown in Figures 8 and 9, it is clear that oligomeric products virtually consisting of only a poly(STY) backbone and an AMS end group (see Scheme 5) can be obtained very ef-

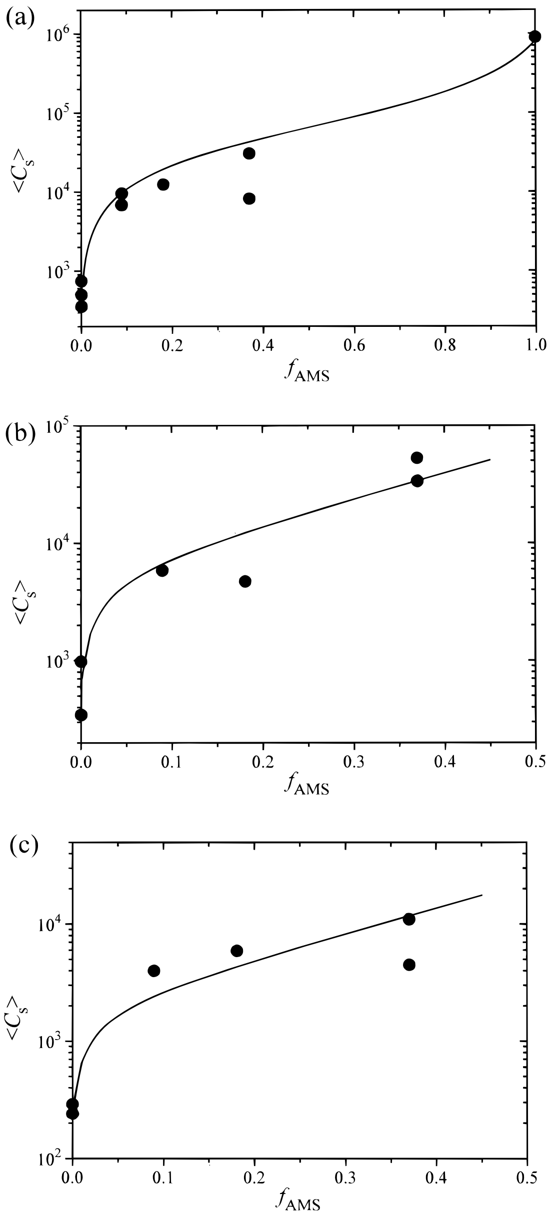
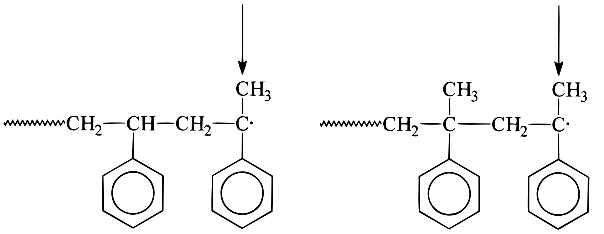


Figure 8. Dependence of the average chain transfer constant, $\langle C_S \rangle$, on the fraction of AMS, f_{AMS}, in the copolymerization of styrene and AMS with COBF at (a) 50 °C, (b) 60 °C, and (c) 70 °C. The points are experimental data, and the line is the model prediction.

Chart 1



fectively by the addition of about 5% AMS ($\langle C_S \rangle$ increased by about 1 order of magnitude) at the cost of less than 50% of the rate!

Conclusions

The copolymerization of styrene and α-methylstyrene in the presence of the catalytic chain transfer agent COBF has been investigated. The average chain transfer constant, $\langle C_S \rangle$, was found to increase approximately 3 orders of magnitude upon going from pure STY to pure AMS. The addition of only 10% AMS increased the $\langle C_S \rangle$ by 1 order of magnitude. This behavior is predicted excellently from the relative fractions of growing radical end groups, which also predicts that the majority of polymer chains contain an unsaturated AMS end group. Penultimate unit effects in the chain transfer reaction did not need to be included for an adequate prediction by the model. The addition of 10−20% AMS results in the majority of the growing radicals having AMS end

Chart 2

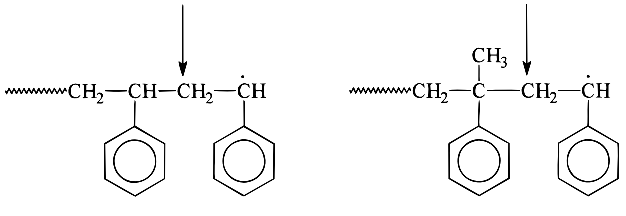
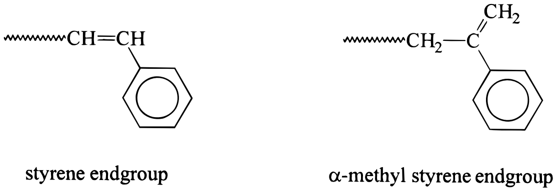


Chart 3



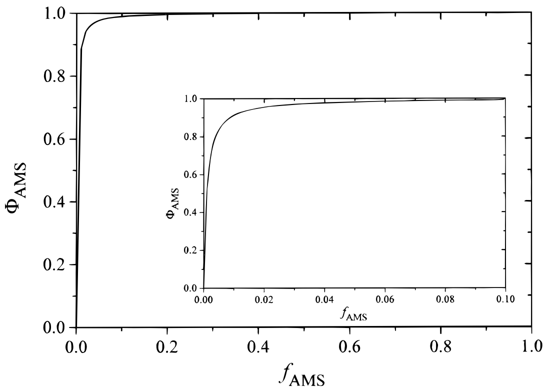


Figure 9. Predicted fraction of unsaturated AMS end groups produced by catalytic chain transfer, Φ_{AMS}, as a function of the fraction of AMS monomer in the reaction, f_{AMS}, using eqs 12, 14, and 15. The parameters used were data at 40 °C from Table 3, ϕ_{AMS} from Figure 3, $C_S^{STY} = 1.03 \times 10^3$, $C_S^{AMS} = 8.15 \times 10^5$, and [COBF] = 10^{-5} mol·L^{-1}. The insert shows a zoom of the region $f_{AMS} = 0-0.1$.

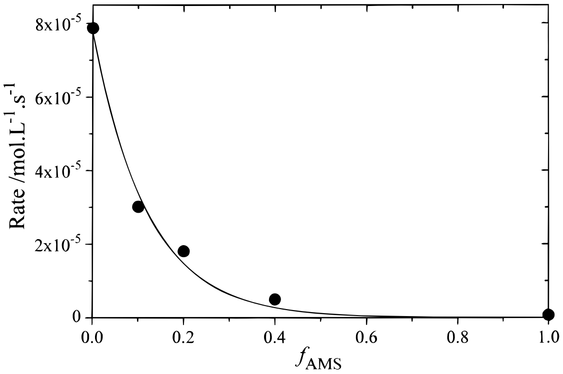


Figure 10. Dependence of the rate of reaction on f_{AMS} in the copolymerization of STY and AMS at 50 °C, [COBF] = 0. The line is an exponential decay fit to the data.

groups, and hence AMS dominates the catalytic chain transfer reaction. The $\langle C_S \rangle$ continues to increase as the AMS content is increased; however, this is primarily attributed to a decrease in $\langle k_p \rangle$ rather than an increase in $\langle k_{tr} \rangle$. The expected end group in the homopolymerization of AMS in the presence of COBF was confirmed by MALDI mass spectrometry.

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References and Notes

(1) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365.

(2) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243.

(3) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.

(4) Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 879.

(5) Haddleton, D. M.; Maloney, D. R.; Suddaby, K. G.; Muir, A. V. G.; Richards, S. N. *Macromol. Symp.* **1996**, *111*, 37.

(6) Suddaby, K. G.; Maloney, D. R.; Haddleton, D. M. *Macromolecules* **1997**, *30*, 702.

(7) Sanayei, R. A.; O'Driscoll, K. F. *J. Macromol. Sci., Chem* **1989**, *A26*, 1137.

(8) Burczyk, A. F.; O'Driscoll, K. F.; Rempel, G. L. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3255.

(9) Kukulj, D.; Davis, T. P. *Macromol. Chem. Phys.*, in press.

(10) Kukulj, D.; Davis, T. P.; Suddaby, K. G.; Haddleton, D. M.; Gilbert, R. G. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 859.

(11) Suddaby, K. G.; Haddleton, D. M.; Hastings, J. J.; Richards, S. N.; O'Donnell, J. P. *Macromolecules* **1996**, *29*, 8083.

(12) Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M. *Macromol. Symp.* **1996**, *111*, 13.

(13) Kukulj, D.; Davis, T. P.; Gilbert, R. G. *Macromolecules* **1997**, *30*, 7661.

(14) Heuts, J. P. A.; Kukulj, D.; Forster, D. J.; Davis, T. P. *Macromolecules* **1998**, *31*, 2894.

(15) Gilbert, R. G. *Trends Polym. Sci.* **1995**, *3*, 222.

(16) See, for example: Gilbert, R. G. *Emulsion Polymerization, A Mechanistic Approach*; Academic Press: London, 1995.

(17) (a) Christie, D. I.; Gilbert, R. G. *Macromol. Chem. Phys.* **1996**, *197*, 403. (b) Errata. *Macromol. Chem. Phys.* **1997**, *198*, 663.

(18) Hutchinson, R. A.; Paquet, D. A.; McMinn, J. H. *Macromolecules* **1995**, *28*, 5655.

(19) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552.

(20) Whang, B. C. Y.; Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *Aust. J. Chem.* **1991**, *44*, 1133.

(21) It should be stressed here that eq 1 is, in principle, a limit for the high molecular weight region of the molecular weight distribution, since the low molecular weight region may be affected by curvature arising from chain length dependent termination.[19] However, in the case of chain length independent termination or *all* chain stopping occurring by chain transfer, the proportionality of eq 1 is valid over the entire range of molecular weights. Since the chain transfer reaction is the dominating chain stopping event in these systems, eq 1 is expected to provide sufficiently accurate values for the chain transfer constant.

(22) Shortt, D. W. *J. Liq. Chromatogr.* **1993**, *16*, 3371.

(23) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197.

(24) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108.

(25) See, for example: Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(26) Kukulj, D.; Davis, T. P. *Macromolecules* **1998**, *31*, 5668.

(27) Hutchinson, R. A.; McMinn, J. H.; Paquet, D. A.; Beuermann, S.; Jackson, C. *Ind. Eng. Chem. Res.* **1997**, *36*, 1103.

(28) Kang, B. K.; O'Driscoll, K. F. *Macromolecules* **1974**, *7*, 886.

(29) McCormick, H. W. *J. Polym. Sci.* **1957**, *25*, 488.

(30) See, for example: Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991.

(31) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.

(32) Gridnev, A. A.; Ittel, S. D.; Fryd, M. *J. Polym. Sci., A: Polym. Chem.* **1995**, *33*, 1185.

(33) Smirnov, B. R.; Marchenko, A. P.; Plotnikov, V. D.; Kuzayev, A. I.; Yenikolopyan, N. S. *Polym. Sci. U.S.S.R. (Engl. Transl.)* **1981**, *23*, 1169.

(34) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864.

(35) Smirnov, B. R.; Marchenko, A. P.; Korolev, G. V.; Belgovshii, I. M.; Yenikolopyan, N. S. *Polym. Sci. U.S.S.R. (Engl. Transl.)* **1981**, *23*, 1158.

(36) Mayo, F. R. *J. Am. Chem. Soc.* **1943**, *65*, 2324.

(37) Maloney, D. R.; Hunt, K. H.; Lloyd, P. M.; Muir, A. V. G.; Richards, S. N.; Derrick, P. J.; Haddleton, D. M. *J. Chem. Soc., Chem. Commun.* **1995**, 561.

(38) Lloyd, P. M.; Suddaby, K. G.; Varney, J. E.; Scrivener, E.; Derrick, P. J.; Haddleton, D. M. *Eur. Mass Spectrom.* **1995**, *1*, 293.

(39) Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F.; Giessman, U. *Anal. Chem.* **1992**, *64*, 2866.

(40) Castro, J. A.; Koester, C.; Wilkins, C. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 239.

(41) Danis, P. O.; Karr, D. E.; Simonsick, W. J.; Wu, D. T. *Macromolecules* **1995**, *28*, 1229.

(42) Schoonbrood, H. A. S.; Pierik, S. C. J.; van den Reijen, B.; Heuts, J. P. A.; German, A. L. *Macromolecules* **1996**, *29*, 6717.

(43) Fukuda, T.; Ma, Y.-D.; Inagaki, H. *Macromolecules* **1985**, *18*, 17.

(44) Heuts, J. P. A.; Coote, M. L.; Davis, T. P.; Johnston, L. P. M. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1997; Vol. 685, p 120.

(45) Galbraith, M. N.; Moad, G.; Solomon, D. H.; Spurling, T. H. *Macromolecules* **1987**, *20*, 675.

(46) Fischer, J. P. *Makromol. Chem.* **1972**, *155*, 211.

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