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Copolymerization of Styrene and Methyl Methacrylate in the Presence of a Catalytic Chain Transfer Agent

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ABSTRACT: Copolymerizations of styrene and methyl methacrylate have been performed using different monomer feed compositions in the presence of a catalytic chain transfer agent at 40 °C. Average chain transfer constants as a function of monomer feed composition were determined with the conventional Mayo procedure using both number (M_n) and weight (M_w) average molecular weights, and with the chain length distribution procedure using both high (Λ_H) and peak (Λ_P) molecular weight slopes. It is found that the average chain transfer constants determined from M_w and Λ_P are generally very similar, with those obtained from M_n and Λ_H being larger and smaller, respectively. The average chain transfer constants obtained from M_w and Λ_P are compared with model predictions based upon both the terminal and penultimate unit models of free-radical copolymerization and are in satisfactory agreement. These two models are used to predict the fraction of propagating radicals with a terminal styrene unit, and it is found, similar to earlier studies reported in the literature, that this parameter is very sensitive to the penultimate model s values (in contrast to the average propagation rate coefficient), and a satisfactory agreement between model and experiment is obtained for $s_M = 2$. This finding possibly suggests a complimentary route to measuring average propagation rate coefficients, for the determination of penultimate model s values.

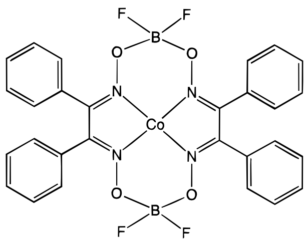
Introduction

The properties of a polymer product depend on both molecular weight distribution and structure, and in many applications relatively low molecular weight polymers bearing different functional groups are required. A decreased molecular weight is generally obtained by the addition of very large amounts of initiator (which increases the bimolecular termination reaction) or the addition of chain transfer agents (which causes the chain stopping of a growing polymer chain and initiation of a new chain).[1] The introduction of several different functional groups can be accomplished by copolymerization of different monomers.[1−3] Use of both procedures provides a potentially powerful tool to create a wide range of different polymers with different properties but yields a relatively complex system for kinetic modeling[4−7] and hence for product and process control.

To cause a large molecular weight reduction with conventional chain transfer agents such as mercaptans and carbon halides, undesirably large quantities of these species are required, and an attractive alternative has appeared over the past decade in the form of catalytic chain transfer agents. It was found that certain low-spin Co(II) complexes catalyze the chain transfer to monomer reaction in a wide range of monomers.[8] Furthermore, these Co(II) complexes possess very high chain transfer constants, and hence only small amounts (i.e., parts per million quantities) of the catalyst are required for a very significant molecular weight reduction.[9]

Considering the relatively large interest in catalytic chain transfer agents and creating low-molecular weight copolymers, it is surprising that to date only a limited number of studies[10] have been published on the use of catalytic chain transfer agents in free-radical copolymerization. Greuel and Harwood[10a] studied the copolymerization of styrene and methyl methacrylate at 70 °C in the presence of cobaloxime/pyridine and found that the fraction of styrene end-groups originating from the catalytic chain transfer reaction was proportional to the fraction of styrene in the monomer feed. However, this paper contained only limited results, and the system requires a better characterization for obtaining conclusive mechanistic information.

The aim of the present work is to investigate the kinetics of free-radical copolymerization in the presence of a catalytic chain transfer agent, and in order to do so, we chose a very well characterized and documented system, i.e., the copolymerization of styrene and methyl methacrylate at 40 °C.[11−13] We will focus on both the kinetics of the catalytic chain transfer reaction with bis[(difluoroboryl)diphenylglyoximato]cobalt(II) (abbreviated as COPhBF in the remainder of this paper), **1**, and some outstanding problems in conventional free-radical copolymerization.



COPhBF, **1**

Theoretical Background

Catalytic Chain Transfer. Low molecular weight polymers are commonly prepared by the (deliberate)

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addition of a chain transfer agent, X, to which the “radical activity” of the growing polymer chain is transferred, resulting in a dead polymer chain and a small radical (often) capable of reinitiation (eq 1).[2]

$$R_n^\bullet + X \xrightarrow{k_{\mathrm{tr,X}}} P_n + X^\bullet \tag{1}$$

Here, $R_n^\bullet$ is the polymeric radical containing n monomer units, X is the chain transfer agent, and P_n is the dead polymer chain containing n monomer units. The transfer of “radical activity” occurs generally via the transfer of an atom, such as a hydrogen atom (e.g., thiols) or a halogen atom (e.g., CCl_4 and CBr_4), between the chain transfer agent and the growing radical chain.[2] The efficiency of a chain transfer agent X is expressed in the chain transfer constant, C_X, which is the ratio of the rate coefficient of the chain transfer reaction, $k_{\mathrm{tr,X}}$, and the propagation rate coefficient, k_p:[1]

$$C_X = \frac{k_{\mathrm{tr,X}}}{k_p} \tag{2}$$

Chain transfer constants for conventional chain transfer agents[14] such as thiols and carbon halides typically lie in the range 10^{-2}–10, which means that relatively large amounts of these chain transfer agents are required for a significant reduction in molecular weight.

As stated before, an attractive alternative to using conventional chain transfer agents for the production of low-molecular weight polymers is the use of catalytic chain transfer agents, such as certain low-spin Co(II) complexes.[9] These species catalyze the chain transfer to monomer reaction and hence reduce the average molecular weight of the produced polymer. Cobalt(II) porphyrins and their derivatives have received much attention over the past decade, and many kinetic and mechanistic studies have been reported.[8,15–22] Currently, the most widely accepted mechanism of the chain transfer to monomer reaction catalyzed by low-spin Co(II) complexes is[8,9,15,16,18,20,21]

$$R_n^\bullet + \mathrm{Co(II)} \rightarrow P_n + \mathrm{Co(III)}{-}\mathrm{H} \tag{3a}$$

$$\mathrm{Co(III)}{-}\mathrm{H} + \mathrm{Mon} \rightarrow R_1^\bullet + \mathrm{Co(II)} \tag{3b}$$

where Co(II) is a low-spin Co(II) complex, Co(III)–H is its derived hydride, P_n is a dead polymer chain containing n monomer units and a terminal double bond, and Mon is a monomer molecule. Since the reaction is truly catalytic, the chain transfer agent is not consumed by the chain transfer reaction and is not incorporated in the polymer chain. The former fact, in combination with chain transfer constants in the order of 10^3–10^4 makes it possible to produce very low-molecular weight polymers with only ppm quantities of the chain transfer agent.

Free-Radical Copolymerization. Copolymerizations obey normal free-radical polymerization kinetics, with the difference that more reactions are possible, because of the presence of, in principle, two types of radicals and monomers. In the case of the propagation reaction in a binary copolymerization of styrene (S) and methyl methacrylate (MMA), there are four distinctly different propagation reactions to consider:[3]

$$\sim S^\bullet + S \xrightarrow{k_{SS}} \sim SS^\bullet \tag{4a}$$

$$\sim S^\bullet + \mathrm{MMA} \xrightarrow{k_{SM}} \sim \mathrm{SMMA}^\bullet \tag{4b}$$

$$\sim \mathrm{MMA}^\bullet + S \xrightarrow{k_{MS}} \sim \mathrm{MMAS}^\bullet \tag{4c}$$

$$\sim \mathrm{MMA}^\bullet + \mathrm{MMA} \xrightarrow{k_{MM}} \sim \mathrm{MMAMMA}^\bullet \tag{4d}$$

This model for copolymerization is called the terminal or Mayo–Lewis model[3] and forms the basis for more elaborate and detailed models proposed in more recent years.[3,11]

Within the terminal model, the mole fraction of monomer i in the instantaneously formed copolymer, F_i, can be expressed as a function of the mole fraction of monomer i in the feed, f_i[3]

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2 f_i f_j + r_j f_j^2} \quad (i, j = S \text{ or } M, i \neq j) \tag{5}$$

where r_i and r_j are the monomer reactivity ratios given by

$$r_i = \frac{k_{ii}}{k_{ij}} \quad (i, j = S \text{ or } M, i \neq j) \tag{6}$$

In general, the terminal model is found to adequately describe the copolymer composition (eq 5), but it fails to describe the average propagation rate coefficient, $\langle k_p \rangle$, simultaneously.[3,11,23] Several different models have been proposed to account for the discrepancy between the terminal model predictions and the experimentally found average propagation rate coefficients,[3,11] and their (apparent) success lies in the fact that they introduce more fit parameters in the expression for the average propagation rate coefficient.[3,11] Since several studies have indicated that the penultimate (i.e., the second last) unit in the growing radical chain is likely to affect the reactivity of the radical,[24–28] we will adopt the penultimate unit model, as strongly promoted by Fukuda et al.,[3,23–25] as a physically realistic model for the description of the average propagation rate coefficient in the copolymerization of styrene and methyl methacrylate. In the case where no penultimate unit effects are observed in the copolymer composition (as in the case of styrene and methyl methacrylate),[11,23] the average propagation rate coefficient is given by the expression

$$\langle k_p \rangle = \frac{r_S f_S^2 + 2 f_S f_M + r_M f_M^2}{\dfrac{r_S f_S}{\bar{k}_{SS}} + \dfrac{r_M f_M}{\bar{k}_{MM}}} \tag{7}$$

where the average homopropagation rate coefficient, $\bar{k}_{ii}$, is given by

$$\bar{k}_{ii} = \frac{k_{iii}(r_i f_i + f_j)}{r_i f_i + \dfrac{f_j}{s_i}} \quad (i, j = S \text{ or } M, i \neq j) \tag{8}$$

In this equation, the penultimate unit effect is introduced via the radical reactivity ratio, which is given by

$$s_{\mathrm{i}} = \frac{k_{\mathrm{jii}}}{k_{\mathrm{iii}}} \quad (\mathrm{i, j} = \mathrm{S\ or\ M,\ i} \neq \mathrm{j}) \tag{9}$$

In eqs 4−9, $k_{(\mathrm{x})\mathrm{yz}}$ denotes the rate coefficient for the addition of a monomer z to a propagating radical with terminal unit y and penultimate unit x.

In the presence of a catalytic chain transfer agent, two more reactions are important, i.e., the transfer reactions of the two different propagating radicals:

$$\sim\mathrm{S}^{\bullet} + \mathrm{Co(II)} \xrightarrow{k_{\mathrm{tr,CoS}}} \sim \mathrm{S} + \mathrm{Co(III)}{-}\mathrm{H} \tag{10a}$$

$$\sim\mathrm{MMA}^{\bullet} + \mathrm{Co(II)} \xrightarrow{k_{\mathrm{tr,CoM}}} \sim \mathrm{MMA} + \mathrm{Co(III)}{-}\mathrm{H} \tag{10b}$$

If penultimate unit effects in these two transfer reactions are negligible, then the chain transfer constants for the two reactions can be given by

$$\bar{C}_{\mathrm{Co,i}} = \frac{k_{\mathrm{tr,Coi}}}{\bar{k}_{\mathrm{ii}}} \quad (\mathrm{i} = \mathrm{S\ or\ M}) \tag{11}$$

It should be noted here, that even if we neglect penultimate unit effects in chain transfer, they are still operative in the propagation step, and hence the average chain transfer constant for the two propagating radicals contains the average homopropagation rate coefficient, $\bar{k}_{\mathrm{ii}}$. This means that the chain transfer constants for both radicals will vary with monomer feed composition. The experimentally accessible average chain transfer constant will then be composed of $\bar{C}_{\mathrm{Co,M}}$ and $\bar{C}_{\mathrm{Co,S}}$, and will also vary with monomer feed composition, decreasing from $C_{\mathrm{Co,M}}$ to $C_{\mathrm{Co,S}}$.

Measurement of Chain Transfer Constants. Chain transfer constants are commonly measured via the so-called Mayo method[1,29] and the more recently developed chain length distribution (CLD) method.[30−34] The Mayo method depends on measuring the number average degree of polymerization, $\mathrm{DP_n}$, as a function of the ratio of the chain transfer agent and monomer concentrations. As can be seen from eq 12, a plot of

$$\frac{1}{\mathrm{DP}_n} = \frac{(2 - F_{\mathrm{c}})\langle k_{\mathrm{t}}\rangle[\mathrm{R}^{\bullet}]}{k_{\mathrm{p}}[\mathrm{Mon}]} + C_{\mathrm{M}} + C_{\mathrm{X}}\frac{[\mathrm{X}]}{[\mathrm{Mon}]} \tag{12}$$

$\mathrm{DP_n}^{-1}$ vs [X]/[Mon], should give a straight line with a slope equal to the chain transfer constant C_{X} and an intercept equal to the inverse of the degree of polymerization in the absence of chain transfer agent. In eq 12, F_{c} is the fraction of termination by combination, $\langle k_{\mathrm{t}}\rangle$ is the average termination rate coefficient, $[\mathrm{R}^{\bullet}]$ the total radical concentration, and C_{M} the chain transfer constant for chain transfer to monomer. This method is straightfowardly applicable if the changes in the first term of eq 12 upon changing [X]/[Mon] are neglible. In an elaborate comparison of several different modifications of eq 12, recently reported by Suddaby et al.,[22] it was shown that this is indeed the case in catalytic chain transfer polymerization.

Instead of the number average degree of polymerization, the weight average degree of polymerization, $\mathrm{DP_w}$, can be used in the expression of eq 12, taking into account that $\mathrm{DP_w/DP_n} = 2$ in a chain-transfer dominated system.[35] Since the values of M_{n} and M_{w} are relatively sensitive and insensitive, respectively, to baseline deviations, the use of $\mathrm{DP_w}/2$ is often preferred in chain-transer dominated systems.[36,37] Here, we will investigate the use of both $\mathrm{DP_n}$ and $\mathrm{DP_w}/2$.

In the more recently developed chain length distribution method,[30−34] a general expression is derived for the number molecular weight distribution, $P(M)$, which for large degrees of polymerization is given by the proportionality of eq 13, where M and m_0 are the mass of the

$$\lim_{M\to\infty} P(M) \propto \exp\left\{-\left(\frac{\langle k_{\mathrm{t}}\rangle[\mathrm{R}^{\bullet}]}{k_{\mathrm{p}}[\mathrm{Mon}]} + C_{\mathrm{M}} + C_{\mathrm{X}}\frac{[\mathrm{X}]}{[\mathrm{Mon}]}\right)\frac{M}{m_0}\right\} \tag{13}$$

dead polymer and monomer, respectively.[38] It is then easily seen that the high molecular weight slope, Λ_{H}, of a plot of $\ln(P(M))$ vs M is given by

$$\lim_{M\to\infty} \frac{\mathrm{d}(\ln P(M))}{\mathrm{d}M} = -\left(\frac{\langle k_{\mathrm{t}}\rangle[\mathrm{R}^{\bullet}]}{k_{\mathrm{p}}[\mathrm{Mon}]} + C_{\mathrm{M}} + C_{\mathrm{X}}\frac{[\mathrm{X}]}{[\mathrm{Mon}]}\right){m_0}^{-1} = \Lambda_{\mathrm{H}} \tag{14}$$

Measuring this slope, Λ_{H}, for varying chain transfer agent to monomer concentration ratios, and plotting Λ_{H} vs [X]/[Mon] should then give a straight line with slope equal to $-C_{\mathrm{X}}/m_0$.

In a recent comparison[39] of the two procedures in the case that chain stoppage is predominantly by chain transfer, it was shown that both methods are in principle identical (i.e., $\mathrm{DP_n} = -(m_0\Lambda_{\mathrm{H}})^{-1}$). To reduce baseline correction errors, it was recommended to use the slope in the peak (Λ_{P}) and not the high (Λ_{H}) molecular weight region of the molecular weight distribution, and for similar reasons, the chain length distribution procedure is preferred over the Mayo procedure. In the present investigations, we will use both the Mayo (using $\mathrm{DP_n}$ and $\mathrm{DP_w}$) and chain length distribution (using Λ_{H} and Λ_{P}) procedures and compare their results.

Experimental Procedures

Materials. The bis(methanol) complex of COPhBF (**1**), was prepared according to the method described by Bakač et al.[40] replacing dimethyl glyoxime in the described procedure by diphenyl glyoxime in the present preparation. Since purification and characterization of this catalyst is extremely difficult, one single batch of COPhBF was used throughout this work. Styrene (Aldrich, 99%) and methyl methacrylate (Aldrich, 99%) were passed through a column of activated basic alumina (ACROS, 50−200 μm) and purged with high purity nitrogen (BOC) for 1.5 h prior to use. AIBN (DuPont) was recrystallized twice from methanol and used as initiator.

General Polymerization Procedure. Polymerizations were carried out as described by Suddaby et al.[22] Two stock solutions were prepared: (i) a catalyst stock solution and (ii) an initiator stock solution. (i) The catalyst stock solution was prepared by dissolution of approximately 3 mg of catalyst into 10 mL of monomer and a subsequent 10-fold dillution with monomer. (ii) The initiator solution was prepared by dissolution of approximately 220 mg of AIBN in 45 mL of monomer. Five reaction mixtures were then prepared, each containing 4.0 mL of initiator solution and 0.50 mL of a mixture of catalyst stock solution and monomer. The amounts of catalyst solution used were 0.0, 0.10, 0.20, 0.30, and 0.40 mL for the five runs. The reaction ampules, specially modified for use with standard Schlenck equipment, were deoxygenated by two freeze−pump−thaw cycles and subsequently placed in a water bath (thermostated at 40 °C), for 45 min (100% MMA) to 3 h (100% styrene), ensuring final conversions were maintained below 3%.

Polymer Analysis. Molecular weight distributions were determined by size exclusion chromatography using a GBC Instruments LC1120 HPLC pump, a GBC LC1650 Autoinjector, a column set consisting of a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm) followed by two linear PL columns (10^3 and 10^5) and one PL mixed bed column (300 × 7.5 mm, mixed E), and a differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as eluent at 1 mL/min. Calibration of the SEC equipment was performed with narrow polystyrene (Polymer Laboratories; molecular weight range 580 to 3.0×10^6) and poly(methyl methacrylate) (Polymer Laboratories; molecular weight range 200 to 1.6×10^6) standards. Average copolymer compositions were determined by ^{1}H NMR analysis with a 300 MHz (Bruker ACF 300) spectrometer using CCl_4 (Aldrich, 99.9+%, HPLC grade) as a solvent. The fraction of styrene in the copolymer, F_S, was determined using the expression

$$F_S = \frac{3A_{\text{phenyl}}}{3A_{\text{phenyl}} + 5A_{\text{methoxy}}} \qquad (15)$$

where A_{phenyl} is the peak area of the phenyl protons of styrene ($\delta = 7.5-6.5$ ppm) and A_{methoxy} is the peak area of the methoxy protons of methyl methacrylate ($\delta = 3.5-2.2$ ppm).[12]

Results and Discussion

Copolymer Composition. As can be seen from eq 5, the instantaneous copolymer composition is largely governed by the monomer reactivity ratios r_S and r_M. These two reactivity ratios govern the relative fractions of propagating radicals, which govern the observed average chain transfer constant in a copolymerization (vide infra). Since it is known from the literature that the apparent monomer reactivity ratios may be chain length dependent,[7,27,41,42] it is important to establish whether the long-chain values are still valid for the current studies in which we produce shorter chain lengths. To do so, we compared the copolymer composition predicted by the long chain monomer reactivity ratios[11,12] with the copolymer compositions of two polymers produced in the same set of experiments to determine an average chain transfer constant, i.e., the one produced without COPhBF (longest chain) and the one produced with the highest COPhBF concentration (shortest chain). The experimental results are compared with the long-chain theoretical predictions in Figure 1. It can be seen that the low and high molecular weight polymers have the same composition within experimental error and that the long-chain monomer reactivity ratios provide a sufficiently accurate description for the systems in the present investigations.

Molecular Weight Distributions from Size Exclusion Chromatography. As outlined above, the measurement of chain transfer constants relies upon the measurement of the molecular weight distribution; in the case of the Mayo method, M_n or M_w are required, and in the chain length distribution method, Λ_H and Λ_P are required. In the present investigations, all these properties are obtained from molecular weight distributions measured by size exclusion chromatography. Here, we will discuss the obtained results and, more importantly, the procedures used for determining these data.

(i) Baseline and Peak Selection. Everyone familiar with the analysis of size exclusion chromatograms knows that the first step in such analysis involves the selection of a baseline and the peak to be analyzed. This seemingly trivial exercise, however, can significantly affect the final results when the obtained molecular weight distribution is to be used for the determination of rate coefficients, as in the present investigations. In Figure 2, two typical chromatograms are shown, and it is immediately clear from this figure that there is no significant baseline drift during the chromatographic analyses. Upon closer examination of the chromatograms in the region of the polymer peak (see insets), it can be noted that the peaks do not seem to return completely to the baselines labeled 1 in the insets. This may indicate that there is a slight baseline drift, but it is more likely that some very low-molecular weight polymer has been formed, especially in the case of chromatogram B. It is therefore difficult to decide exactly where to locate the peak and how to identify the baseline. To investigate the effect of this selection procedure, we determined M_n, M_w, Λ_H, and Λ_P for two different selections of baseline and peak in chromatogram A (i.e., most frequently observed chromatogram in the present study) and three different selections in chromatogram B (i.e., a less frequently observed chromatogram). Baseline selections 1 and 2 correspond to a baseline taken from the stable baseline regions before and after the signal of the polymer sample and from the onset of the peak to the first minimum behind the peak, respectively. In chromatogram A, the selection of the peak was the same for the two baselines, and in chromatogram B, the same was done, but now also including one low molecular weight "hump" in the peak selection. The results are compared in Table 1, and it can be seen from this table that M_n is very sensitive, M_w is less sensitive, and Λ_P and Λ_H are relatively insensitive to the procedure of baseline and peak selection. For consistency reasons, all chromatograms were analyzed using a {baseline, peak} selection corresponding to the combination {1, a} in Figure 2.

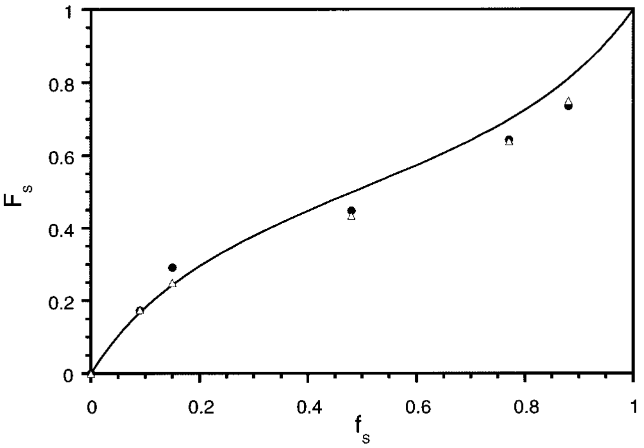

Figure 1. Fraction of styrene in copolymer (F_S) as a function of the fraction of styrene in the monomer feed (f_S): (—) terminal model prediction using the parameters listed in Table 5; (●) copolymer prepared with [Co]/[Mon] = 0.00; (△) copolymer prepared with [Co]/[monomer] = 4.89×10^{-7}.

Finally, it can be seen that only slight changes in the baseline can significantly affect the polydispersity index. However, upon examination of these results, it can be concluded that the true polydispersity index is close to a value of 2, and hence the use of $DP_w/2$ in the Mayo procedure is justified.

(ii) Determination of M_n and M_w for Copolymers. To obtain accurate results from size exclusion chroma-

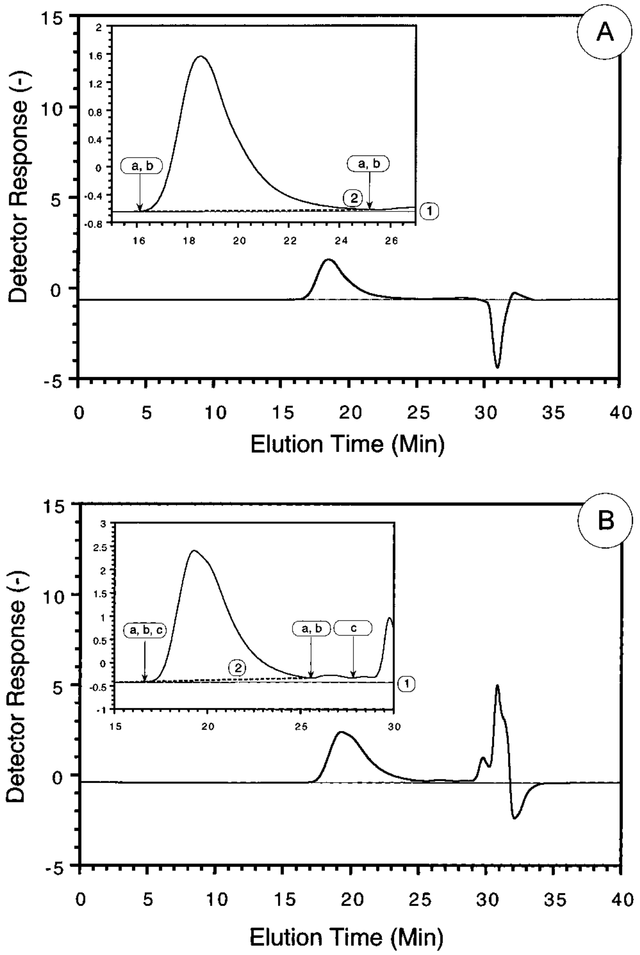

Figure 2. Size exclusion chromatograms of two different polymers prepared with COPhBF at 40 °C. Chromatogram A is of a copolymer ($f_S = 0.15$) and B is of poly(methyl methacrylate). The insets show an enlargement of the polymer peak region, where the labels 1 and 2 indicate the baselines and a, b, and c the peak markers used in the analysis of the chromatograms.

Table 1. Effect of Baseline and Peak Selection on the Number and Weight Average Molecular Weights and the High and Peak Molecular Weight Slopes

chromato-gram[a]	base-line[a]	peak[a]	M_n	M_w	PDI[b]	$\Lambda_H/10^{-5}$ [c]	$\Lambda_P/10^{-5}$ [d]
A	1	a	32 556	72 629	2.231	−1.97	−2.48
A	2	b	36 870	74 076	2.009	−1.99	−2.48
B	1	a	20 647	42 078	2.038	−3.64	−4.34
B	2	b	23 583	43 374	1.839	−3.68	−4.27
B	1	c	14 377	40 847	2.841	−3.64	−4.28

[a] Defined in Figure 2. [b] Polydispersity index = M_w/M_n. [c] Slope of an ln($P(M)$) vs M plot in the high molecular weight region. [d] Slope of an ln($P(M)$) vs M plot in the peak molecular weight region.

Table 2. Dependence of the Weight Average Molecular Weight[a] on the Monomer Feed Composition and Used Reference Polymer

fraction of styrene	$M_{w,MMA}$[b]	$M_{w,S}$[c]	$M_{w,copol}$[d]
0.0	*e*	*e*	*e*
0.0	703 570		703 570
0.09	399 610	290 456	381 764
0.10	477 502	352 874	456 794
0.15	235 101	176 347	221 555
0.48	258 862	195 014	226 939
0.48	338 446	252 704	295 527
0.77	249 158	187 931	205 582
0.77	254 928	192 033	210 359
0.78	250 072	188 585	206 276
0.88	252 291	190 312	201 337
0.88	229 108	173 446	183 348
0.88	282 204	211 589	224 151
1.0		297 792	297 792
1.0		309 450	309 450

[a] Values listed correspond to the polymers obtained in the absence of COPhBF. [b] Weight average molecular weight obtained by assuming the analyte polymer is poly(methyl methacrylate). [c] Weight average molecular weight obtained by assuming the analyte polymer is polystyrene. [d] $M_{w,copol} = F_S M_{w,S} + (1 - F_S) M_{w,MMA}$. [e] This sample could not be analyzed.

tography, it is necessary to use a detector which is either sensitive to absolute molecular weights or which has been calibrated with standards of the analyte polymer.[43] Since the differential refractive index detector in the present investigations is not sensitive to absolute molecular weights, we need an appropriate calibration. However, even though standards are readily available for many different homopolymers, this is not the case for copolymers, and an approximate treatment is required. Since the solution behavior of styrene and methyl methacrylate homopolymers in tetrahydrofuran is very similar (as evidenced by their respective Mark–Houwink constants), we make the following approximation for their copolymers:

$$M_{\text{copol}} \approx F_S M_S + (1 - F_S) M_{\text{MMA}} \tag{16}$$

M_{copol} is the molecular weight of the copolymer which contains a mole fraction F_S of styrene monomer units and a mole fraction of $(1 - F_S)$ of methyl methacrylate monomer units. M_S and M_{MMA} are the molecular weights obtained for the copolymer when analyzing it as if it where polystyrene or poly(methyl methacrylate), respectively. Although this treatment does not have a rigorous theoretical basis, this assumption has been justified in a careful experimental study.[13] In Table 2, the values obtained for the weight average molecular weights of the (co)polymers produced in the absence of COPhBF are listed. The averaged values were used as an estimate for the true molecular weights in all our further analyses.

(iii) Determination of Λ_H and Λ_P for Copolymers. The chain length distribution approach to the calculation of chain transfer constants requires the determination of the high and peak molecular weight slopes of the ln($P(M)$) distributions. In Figure 3 a typical molecular weight distribution obtained in the presence of COPhBF is shown as $w(\log(M))$ vs $\log(M)$ (Figure 3a) and ln($P(M)$) vs M (Figure 3b). The positions of the relevant molecular weight averages are also indicated in both plots. Upon examination of Figure 3b, it can be seen that there is a slight curvature over the complete range of molecular weights—this is observed in all our samples. This result, which was previously reported by Suddaby et al.[22] for the catalytic chain transfer polymerizations of styrene and methyl methacrylate at 60 °C, is rather remarkable. The observed curvature places us in the dilemma of choosing a region for the determination of a slope. It is still possible to identify regions which can be fitted by a straight line with a good regression coefficient (R^2 values of 0.998 are a rule), especially in the high molecular weight region (between the markers A and B, see Figure 3), and in the peak molecular weight region (starting between M_n and M_w and ending between M_z and M_{z+1}). An argument for selecting the high molecular slope

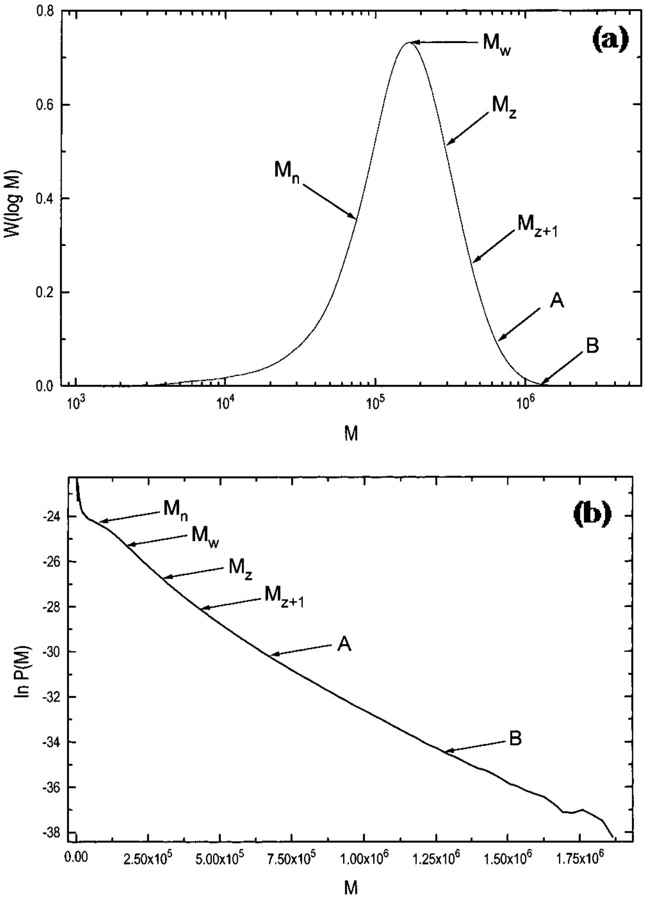

Figure 3. Molecular weight distribution of a copolymer of styrene and methyl methacrylate (f_S = 0.88, [Co]/[Mon] = 1.22 × 10^{-7}, 40 °C) analyzed using a polystryrene calibration curve, plotted as (a) $w(\log(M))$ vs $\log(M)$, and (b) $\ln(P(M))$ vs M. The positions of the most important molecular weight averages, and the position where Λ_H is determined (A→B) are indicated.

arises from the original derivation[30] of eq 13 where the high molecular weight limit ensures that any possible effects of chain-length-dependent termination are negligible. The choice of the peak molecular weight slope is justified by recent results obtained by Moad and Moad,[39] who argue that the high molecular weight slope may be affected by deviations in the baseline. However, as was shown in Table 1, this effect seems to be insignificant in the present investigations. Since, at this point, there seems to be no convincing argument for an a priori choice of a particular slope, we will investigate both slopes (all consistently taken over the molecular weight ranges as indicated above) and will return to this discussion in a later section.

We furthermore need to establish an appropriate method for averaging the slopes obtained using polystyrene and poly(methyl methacrylate) calibration curves. Similar to the situation of the average molecular weights, we will weight the respective contributions of the homopolymers according to the copolymer composition. Since $-(m_0\Lambda)^{-1} \approx \mathrm{DP_n}$ (see above), we will average Λ^{-1}, for consistency reasons, as

$$\Lambda_{\mathrm{copol}}^{-1} \approx F_S \Lambda_S^{-1} + (1 - F_S)\Lambda_{\mathrm{MMA}}^{-1} \tag{17}$$

where Λ_{copol} is the slope for the copolymer, and Λ_S and Λ_{MMA} are the slopes of an $\ln(P(M))$ plot considering the analyte polymer to be polystyrene and poly(methyl methacrylate), respectively. In Table 3 the averaged values of the peak molecular weight slopes are compared with those obtained treating the copolymers as either polystyrene or poly(methyl methacrylate). The averaged slopes are used in all our further analyses.

Table 3. Dependence of Peak Molecular Weight Slopes of ln(*P*(*M*)) Plots[a] on Monomer Feed Composition

fraction of styrene	$\Lambda_{\mathrm{MMA}}/10^{-6}$ [b]	$\Lambda_S/10^{-6}$ [c]	$\Lambda_{\mathrm{copol}}/10^{-6}$ [d]
0.0	*e*	*e*	*e*
0.0	−3.51		−3.51
0.09	−5.61	−6.28	−5.71
0.10	−4.43	−6.05	−4.64
0.15	−5.68	−6.80	−5.90
0.48	−7.79	−10.4	−8.90
0.48	−6.02	−8.07	−6.90
0.77	−7.58	−10.8	−9.62
0.77	−8.05	−11.4	−10.2
0.78	−8.17	−11.2	−10.1
0.88	−8.22	−10.8	−10.2
0.88	−9.39	−12.6	−11.9
0.88	−7.50	−10.1	−9.48
1.0		−8.78	−8.78
1.0		*f*	*f*

[a] Values listed correspond to the polymers obtained in the absence of COPhBF. [b] Peak molecular weight slope of ln(*P*(*M*)) plot obtained by assuming the analyte polymer is poly(methyl methacrylate). [c] Peak molecular weight slope of ln(*P*(*M*)) plot obtained by assuming the analyte polymer is polystyrene. [d] $\Lambda_{\mathrm{copol}}^{-1} = F_S\Lambda_S^{-1} + (1 - F_S)\Lambda_{\mathrm{MMA}}^{-1}$. [e] This sample could not be analyzed. [f] Not determined.

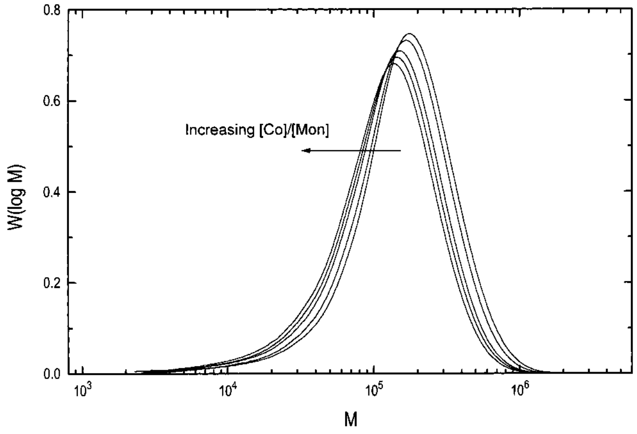

Figure 4. Molecular weight distributions (plotted as *w*(log *M*) vs log *M*) for a copolymerization of styrene and methyl methacrylate (f_S = 0.88) at 40 °C for the following [Co]/[monomer] ratios: 0.00, 1.22 × 10^{-7}, 2.45 × 10^{-7}, 3.67 × 10^{-7}, and 4.89 × 10^{-7}. In the molecular weight analysis, the analyte copolymer was treated as polystyrene.

(iv) General Observations. In Figure 4, an example is given of the molecular weight distributions obtained from a typical experiment for determining chain transfer constants. The effect of increasing the chain transfer agent concentration is immediately seen from the shift of the entire molecular weight distribution to lower molecular weights, as expected. Comparing the results obtained with high styrene fractions in the monomer feed with those obtained with high methyl methacrylate fractions in the monomer feed shows that the decrease in molecular weight is more dramatic for the latter systems, as expected from the differences in the catalytic chain transfer constants for the two homopolymerizations (ca. 700 for styrene and 17 × 10^3 for methyl methacrylate at 60 °C).[19e]

Average Chain Transfer Constants. As described above, average chain transfer constants were determined from the following four properties of a molecular

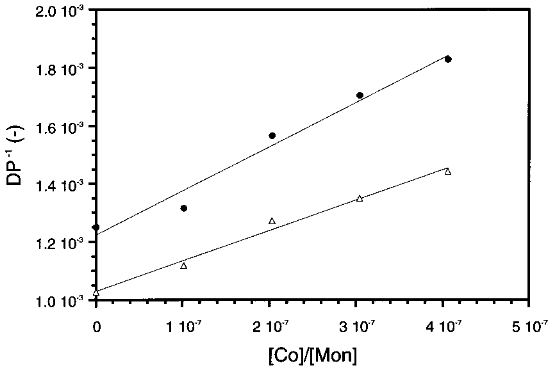

Figure 5. Mayo plots of a copolymerization of styrene and methyl methacrylate ($f_s = 0.88$) with COPhBF at 40 °C: (●) DP = DP_n, $\langle C_{Co} \rangle = 1.5 \times 10^3$; (△) DP = $DP_w/2$, $\langle C_{Co} \rangle = 1.1 \times 10^3$.

Table 4. Average Chain Transfer Constants[a] for the Free-Radical Copolymerization of Styrene and Methyl Methacrylate at 40 °C in the Presence of COPhBF

	Mayo		chain length distribution	
f_S	DP_n	$DP_w/2$	Λ_H	Λ_P
0.0	15	19	14	19
0.0	23	18	12	17
0.09	12	12	4.0	10
0.10	13	12	4.5	8.5
0.15	7.1	6.4	3.9	6.2
0.48	2.7	2.4	1.6	2.0
0.48	3.3	2.9	2.5	2.6
0.77	2.3	1.7	0.96	1.7
0.77	1.9	0.99	0.75	0.88
0.78	1.5	1.1	0.59	0.94
0.88	1.5	1.1	0.47	0.95
0.88	0.81	0.56	0.34	0.38
0.88	1.0	0.94	0.79	0.90
1.0	0.13	0.40	0.20	0.41
1.0	0.57	0.38	*b*	*b*

[a] The values listed here were obtained using the averages defined by eqs 16 and 17 and should be multiplied by 10^3. [b] Not determined.

weight distribution: M_n, M_w, Λ_H, and Λ_P. It was shown in Table 1 that M_n seems to be affected most by possible errors in baseline and peak selection (which is also claimed for Λ_H, but this seems to be insignificant in the present investigations),[22,39] and therefore the use of M_w may be preferred. In Figure 5, a plot is shown of DP_n^{-1} and $2DP_w^{-1}$ vs [Co]/[Mon] (we will refer to these plots as "Mayo plots") for the same polymer samples. It can be seen that the use of both DP_n^{-1} and $2DP_w^{-1}$ give straight line plots here, but that the average chain transfer constants are significantly different: 1.5×10^3 and 1.1×10^3 for DP_n^{-1} and $2DP_w^{-1}$, respectively. We find a similar situation for several other series of chain transfer constant experiments, but in general, the Mayo plots involving $2DP_w^{-1}$, are straighter than those involving DP_n^{-1} (in contrast to the situation shown in Figure 5). Furthermore, the chain transfer constants obtained from Mayo plots involving DP_n^{-1} are generally higher than those from Mayo plots involving $2DP_w^{-1}$ (see Table 4).

At this stage, it is still unclear whether Λ_H or Λ_P should be used for the determination of the chain transfer constant (we use the term "CLD plot" for a plot of Λ vs [Co]/[Mon]), and here we investigate the use of both. In Figure 6, a CLD plot is shown using both Λ_H and Λ_P of the same polymer samples, and it can be seen again that data from both regions result in straight line plots, but with significantly different average chain transfer constants: 0.47×10^3 and 0.95×10^3 for Λ_H and Λ_P, respectively. Generally, we find very similar situations for all our experiments, i.e., the chain transfer constant obtained from Λ_H being smaller than the one obtained from Λ_P (see Table 4), and both CLD plots having similarly straight slopes.

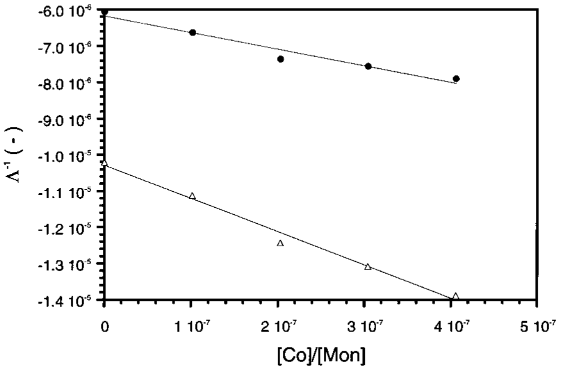

Figure 6. CLD plots of a copolymerization of styrene and methyl methacrylate ($f_s = 0.88$) with COPhBF at 40 °C: (●) $\Lambda = \Lambda_H$, $\langle C_{Co} \rangle = 0.47 \times 10^3$; (△) $\Lambda = \Lambda_P$, $\langle C_{Co} \rangle = 0.95 \times 10^3$.

In Table 4, the results obtained with both the Mayo (based upon M_n and M_w) and chain length distribution (based upon Λ_H and Λ_P) procedures are compiled, and it can be seen that the results obtained from M_w and Λ_P are generally very similar, with those obtained from M_n being larger and those obtained from Λ_H being smaller. Furthermore, it is immediately clear that the results based upon M_w and Λ_P show the best reproducibility from experiment to experiment.

Although one may be tempted to conclude immediately from these results that M_w and Λ_P are indeed the most suitable properties of a molecular weight distribution to be used for the determination of chain transfer constants, one should first consider the following important points carefully:

(1) Except for possible baseline artifacts,[39] there is no obvious preference of the chain length distribution over the Mayo procedure, as it was shown by Olaj and coworkers that the effect of chain-length-dependent termination on a chain-transfer dominated system is negligible.[37]

(2) M_w is preferred over M_n as the latter is more prone to baseline selection errors.

(3) It has been pointed out[39] that Λ_H may suffer from baseline artifacts and that therefore Λ_P is preferred. Furthermore, the peak molecular weight region contains more polymer than the high molecular weight region.

(4) Not disputing the general applicability of point 3, this point seems to be relatively insignificant in the present study (see Table 1).

(5) Although the peak molecular weight region contains more polymer than the high molecular weight region, we consistently choose a region which contains a significant amount of polymer (see Figure 3, region A−B).

(6) The generally straight CLD plots using Λ_H suggest that whatever is causing a different slope is systematic in nature.

(7) The high molecular weight region in a $\ln(P(M))$ plot is obtained from the corresponding region in a $w(\log(M))$ plot, by making the following transformation: $P(M) \sim w(\log(M))/M^2$. This means that an already small signal in the $w(\log(M))$ plot will be divided by very

large numbers, possibly causing a very large propagation of errors.

Consideration of points 1 and 2 leads to the conclusion that the chain transfer constants obtained from M_w are relatively reliable and probably close to the true values. Points 4 and 5 strongly suggest that point 3 may not be the appropriate justification for taking Λ_P instead of Λ_H in our particular experiments, and it is more likely that point 7 plays a more important role. The seemingly constant effect (within a series of experiments to determine one chain transfer constant) causing the discrepancy between Λ_P and Λ_H, as mentioned in point 6, is of obvious concern, as it suggests that this effect may not be an experimental artifact, but the manifestation of a truly mechanistic event.

From the consideration of these points, together with the consistently good agreement between the results obtained from M_w and Λ_P, we draw the conclusion that Λ_P is indeed the region in which to select the slope of a $\ln(P(M))$ plot, which is similar to the conclusion reached previously by Suddaby et al.[22] However, we wish to stress here that *our choice is mainly determined by the good agreement between the* Λ_P *and* M_w results, and not by any a priori theoretical justification.

Having established which data sets are most reliable, we will now discuss the chemical aspects of the results. It can be seen from the results listed in Table 4 that upon increasing the fraction of styrene in the monomer feed, the average chain transfer constant decreases, as expected. In what follows, these results will be rationalized by a kinetic model which is based upon the restricted penultimate model for propagation[23,25,44] and the terminal model for chain transfer.[3,44]

Kinetic Modeling. The results in Table 4 show that the decrease in average chain transfer constant is not linear with the monomer feed composition, which can be explained by the fact that the fraction of radicals with a styrene terminal unit ($\sim$S$^\bullet$), ϕ_S, is always larger than the fraction of styrene in the monomer feed, f_S, in the copolymerization of styrene and methyl methacrylate.[44] An expression for the fraction of propagating $\sim$S$^\bullet$ radicals is given by eq 18. The ratio of the concentrations of $\sim$S$^\bullet$ and $\sim$M$^\bullet$ radicals, A_{SM}, can be derived straightforwardly from the steady-state assumption in the radical concentrations and is given by

$$\phi_S = \frac{A_{SM}}{1 + A_{SM}} \tag{18}$$

$$A_{SM} = \frac{[\sim S^\bullet]}{[\sim M^\bullet]} = \frac{\bar{k}_{MM} r_S f_S}{\bar{k}_{SS} r_M f_M} \tag{19}$$

The value of A_{SM} depends on the average homopropagation rate coefficients $\bar{k}_{SS}$ and $\bar{k}_{MM}$, and hence upon the values of the radical reactivity ratios s_S and s_M (see eq 8).[44-46] In previous studies,[44-46] especially in the case of the copolymerization of styrene with methyl acrylate,[45] it was shown that the effect of using (incorrect) s values can be quite dramatic. Large uncertainties are associated with the determination of the s values, and in general, many sets of radical reactivity ratios will provide an adequate fit to the average propagation rate coefficient data.[13,46] However, these different sets of radical reactivity ratios predict very different behavior of A_{ij} and associated parameters.[46] In Figure 7, the fraction of $\sim$S$^\bullet$ radicals is plotted as a function of the fraction of styrene in the monomer feed for both the terminal and penultimate models, using the kinetic parameters listed in Table 5. It is clear from Figure 7 (and from previous studies)[44,45] that the fraction of $\sim$S$^\bullet$ radicals is always larger than the fraction of styrene in the monomer feed, which qualitatively explains the results listed in Table 4.

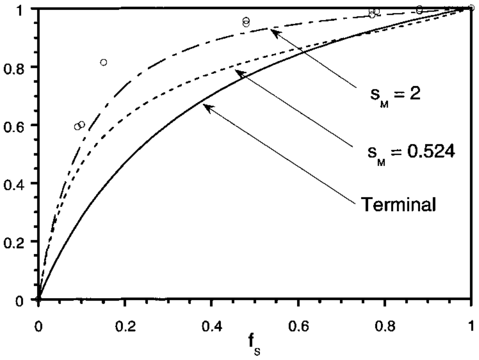

Figure 7. Dependence of the fraction of $\sim$S$^\bullet$ radicals (ϕ_S) on the fraction of styrene in the monomer feed (ϕ_S) of a copolymerization of styrene and methyl methacrylate at 40 °C. Parameter values of model predictions are listed in Table 5: (—) terminal model prediction; (- - -) penultimate model prediction with $s_M = 0.524$; (-•-) Penultimate model prediction with $s_M = 2$; (○) experimental values listed in Table 6.

Table 5. Summary of Parameters Used for Kinetic Modeling[a]

parameter	styrene	ref	methyl methacrylate	ref
k_p (dm^3 mol^{-1} s^{-1})	160	52	496	52
r	0.48	11	0.42	11
s	0.367[b]	13	0.524,[b] 2[c]	13
C_{Co}	400	this work	18 500	this work

[a] In the calculations a constant [Co] of 10^{-5} M was used. [b] Point estimate for radical reactivity ratios obtained from fitting average propagation rate coefficients at 37.5 °C,[13] using the monomer reactivity ratios shown in this table. [c] Estimate for s_M, ceteris paribus, which still gives a satisfactory agreement between the penultimate model and experimental values of the average propagation rate coefficients at 37.5 °C.[46]

In an attempt to quantify the observed behavior, we define the average chain transfer constant, $\langle C_{Co}\rangle$, as the ratio of the average chain transfer rate coefficient, $\langle k_{tr,Co}\rangle$, and the average propagation rate coefficient, $\langle k_p\rangle$:

$$\langle C_{Co}\rangle = \frac{\langle k_{tr,Co}\rangle}{\langle k_p\rangle} \tag{20}$$

The measurement of the average chain transfer constant as outlined in this paper, and the measurement of the average propagation rate coefficient using, e.g., pulsed laser polymerization,[13,47] will then enable the determination of the average chain transfer rate coefficient, which is given as the weighted average of the two homopolymerization chain transfer rate coefficients:

$$\langle k_{tr,Co}\rangle = \phi_S k_{tr,CoS} + (1 - \phi_S) k_{tr,CoM} \tag{21}$$

In eq 21 it is assumed that penultimate unit effects are negligible for the chain transfer reaction. This assumption is not readily tested, and it is very difficult to make an a priori guess of the magnitude of possible penultimate unit effects, as the mechanism of the hydrogen abstraction step is still not fully understood. Since the abstraction of a hydrogen in the case of a $\sim$S$^\bullet$ radical

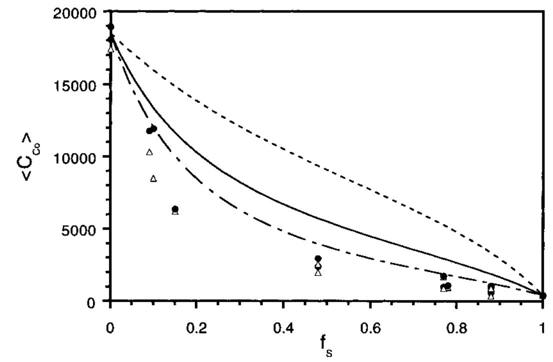

Figure 8. Dependence of the experimental and calculated average chain transfer constants ($\langle C_{Co}\rangle$) on the fraction of styrene in the monomer feed (f_S) of a copolymerization of styrene and methyl methacrylate in the presence of COPhBF at 40 °C. Parameter values are listed in Table 5: (●) experimental values obtained with the Mayo method (M_w); (Δ) experimental values obtained with the CLD method (Λ_P); (—) terminal model prediction; (- - -) penultimate model prediction with $s_M = 0.524$; (—•—) Penultimate model prediction with $s_M = 2$.

Table 6. Comparison of Experimental and Calculated Fractions of Styrene Radicals for Different Monomer Feed Compositions

f_S	experimental ϕ_S[a]	calculated ϕ_S[b]
0.00	0.000	0.000
0.00	0.000	0.000
0.09	0.595	0.506
0.10	0.602	0.537
0.15	0.816	0.655
0.48	0.958	0.916
0.48	0.947	0.916
0.77	0.977	0.973
0.77	0.990	0.973
0.78	0.989	0.974
0.88	0.989	0.986
0.88	0.998	0.986
0.88	0.991	0.986
1.00	1.000	1.000
1.00	1.000	1.000

[a] Obtained from eqs 20 and 21 using experimental values for $\langle C_{Co}\rangle$ (from this work) and $\langle k_p\rangle$ (calculated from eq 7 and the parameters listed in Table 5—this corresponds to *experimental* values). [b] Calculated from eqs 8 and 19 using the parameters listed in Table 5 and $s_{MMA} = 2$.

occurs from the polymer backbone[16] and in the case of a ~M• radical from the α-methyl group,[15] it is conceivable that penultimate unit effects in the latter case may be small. From the data in Table 4 it is clear that $k_{tr,CoM} \approx 50k_{tr,CoS}$ which indicates that up to a fraction of ~S• radicals of about 75%, $\langle k_{tr,Co}\rangle$ will be governed by more than 95% by the ~M• radicals (see eq 21). Hence, possible penultimate unit effects are expected to be negligible for f_S smaller than about 0.3 (see Figure 7).

We now use our model to predict $\langle C_{Co}\rangle$ as a function of the fraction of styrene in the monomer feed. In Figure 8, the theoretical predictions of the terminal and the penultimate models (using the kinetic parameters listed in Table 5) are compared with the experimental results, and it can be seen that both models predict the correct trend but that the quantitative agreement is poor for the terminal model and the penultimate model using $s_M = 0.524$. It is even more surprising that the terminal model prediction seems to be better than the penultimate model prediction, considering the poor performance of the former model in the description of average propagation rate coefficients. However, it was stated before that a large uncertainty is associated with the radical reactivity ratios, and hence, these parameters may need some adjusting.

As was shown in a previous publication,[46] changing the value for s_M from 0.524 to 2 only slightly affects the penultimate model prediction for the average propagation rate coefficient. However, using $s_M = 2$[48] greatly affects the behavior of the calculated $\langle C_{Co}\rangle$ and it can be seen from Figure 8 that using $s_M = 2$ leads to a satisfactory agreement between experimental and calculated values of $\langle C_{Co}\rangle$.

Implications. Comparison of the experimental and modeling data suggests that the model encompasses the most important physical processes governing free-radical copolymerization in the presence of a catalytic chain transfer agent, and good agreement is obtained by sensibly adjusting the value of the radical reactivity ratio of methyl methacrylate.[48] This suggests, as outlined in a previous publication,[46] that measurements of the average chain transfer constants may provide a valuable set of data, complimentary to average propagation rate coefficient measurements, for obtaining radical reactivity ratios. Furthermore, provided that eq 21 is correct, measurements of the average chain transfer constants will directly provide a means of determining the fractions of the different propagating radicals. Since these fractions determine many aspects of the overall kinetics[44,45] and polymer properties (especially the end groups),[10a,46] direct measurement of their values may lead to a better process and product design.

In Table 6 we compare the calculated and experimentally deduced ratios of the propagating radical concentrations. The calculated results are directly obtained from eq 18 using the parameters listed in Table 5 and $s_M = 2$, whereas the experimentally deduced values are obtained from eqs 20 and 21 using experimental values for $\langle k_p\rangle$ and $\langle C_{Co}\rangle$. It can be seen that in general there is a reasonable agreement, except at $f_S = 0.15$ (see also Figure 7). This discrepancy may be a reflection of any shortcomings of our model. The predictions of the terminal model and the penultimate model (using the point estimate of 0.524 for s_M) are generally poor (see Figure 7).

At this point it needs to be stressed, however, that *the above is only valid if the model is correct*, and even though the model seems to provide an adequate description of the process, this is not sufficient proof that it is completely correct. Some of the uncertainties in the assumptions underlying the model we have adopted are discussed in the following section.

Uncertainties. In the previous section it was pointed out that the presented model may be a valuable tool for predicting copolymer properties and obtaining extra data for extracting radical reactivity ratios, provided that the assumptions made to derive the presented equations are correct. Here, we discuss some of the assumptions we made and how they may affect our results:

(i) The Mechanism of the Chain Transfer Reaction. Our model assumes that Co(III)−H is an intermediate of the chain transfer process, an assumption which seems to be generally accepted.[8,9,15,16,18,20,21] However, it is well-documented that certain organometallic reactions proceed directly at the metal center, i.e., a direct reaction of one of the ligands with a second reactant.[49] If a similar process takes place here, then not just two chain transfer reactions need to be taken into account, but four (i.e., two different radicals can react with two

different monomers at the catalytic site), and cross-chain transfer can occur.[44−46] In that case, our model would be significantly incomplete.

(ii) Solvent Effects. In our model we ignore solvent effects, which are known to affect the chain transfer constant, C_{Co}.[9,16,19,22] These may be operative in two distinctly different ways: through competition with the reactants for the occupation of catalytically active sites or through occupying the base ligand position of COPhBF. In particular, the latter effect could be important, because this means that the catalyst itself may change with monomer feed composition; i.e., a mixture of COPhBF·MMA and COPhBF·STY may be present. Our model does not take into account such possibilities and considers the catalyst that reacts with either of the radical species to be the same as in their respective homopolymerizations.

(iii) Penultimate Unit Effects on the Chain Transfer Reaction. In conventional free-radical copolymerization, several studies have been reported which strongly suggest that penultimate unit effects may be operative in the chain transfer reaction,[25−27] and may be of the same magnitude for propagation and chain transfer.[25,27] However, there is no evidence that the transition states of the hydrogen abstraction by the present chain transfer agents resemble those of "conventional" hydrogen-transfer reactions,[27] and hence it is not possible to make any sensible estimates for the magnitude of possible penultimate unit effects. It is conceivable though, as outlined above, that penultimate unit effects may be negligible if the terminal unit is methyl methacrylate, as the penultimate unit substituent is three carbon atoms removed from the reaction site, which is one carbon atom further away than in conventional free-radical copolymerization.[28] Hence, neglecting penultimate unit effects in methyl methacrylate-rich systems is expected to cause smaller errors than in styrene-rich systems. Considering the fact that a reasonable agreement between theory and experiment is obtained over the whole range of monomer feed compositions with a single set of parameters, penultimate unit effects may also be negligible for radicals with a terminal styrene unit.

(iv) Effect on the Propagation Rate. In our model, we assume that the propagation rate coefficients are not affected by the presence of COPhBF, although it has been well documented in the literature that the addition of catalytic chain transfer agents causes a decrease in the rate of polymerization.[16,18,22] This can explained by two possible mechanisms, which are likely to be operative simultaneously. The first one is that the creation of more small radicals will increase the average termination rate coefficient,[18,22] as termination rate coefficients are chain length dependent.[50] The second one is that cobalt−carbon bonds are formed during the polymerization, a phenomenon that is well documented in the organometallic literature[51] and directly shown by Gridnev et al.[17] for the free-radical homopolymerizations of styrene and methyl methacrylate in the presence of cobaloximes. However, we do not believe that such a process will affect our current results, as the formation of cobalt−carbon bonds will decrease the overall radical concentration, and this is a parameter which cancels when we compare the rates of chain transfer ($=k_{tr}[R^•]\cdot[Co]$) and propagation ($=k_p[R^•][Mon]$).

Summary. Here, we have highlighted some of the uncertainties about the mechanism and the kinetics which may affect the modeling results to an unknown extent. It is important to highlight such uncertainties, because the model can then be adjusted sensibly when possible shortcomings become apparent and more information about the mechanism becomes available. These uncertainties could have been allowed for in the model by introducing more specific rate coefficients, which is mathematically and physically possible but which in practice would only result in the introduction of more fit parameters. Since it is not the aim of the present work to get a perfect fit to our data but to try gaining physical insight into the polymerization process, we decided to omit all these extra parameters. Furthermore, the satisfactory agreement between theory and experiment, using sensible kinetic parameters, suggests that it may not be necessary to account for the phenomena mentioned above. This agreement, however, does not rule out a fortuitous cancellation of errors.

Conclusions

In this paper we described copolymerization studies of styrene and methyl methacrylate at 40 °C in the presence of the catalytic chain transfer agent COPhBF. Average chain transfer constants were determined with the conventional Mayo procedure using both number (M_n) and weight (M_w) average molecular weights and with the chain length distribution procedure using both high (Λ_H) and peak (Λ_P) molecular weight slopes. A comparison of these results showed that the results obtained when using M_w or Λ_P are in good agreement with a reasonable reproducibility of the results. Chain transfer constants obtained when using M_n and Λ_H are respectively higher and lower than those obtained when using the other two parameters, and their reproducibility is worse. The sensitivity of M_n to baseline errors leads to the conclusion that M_w is a more reliable molecular weight average to use for determining chain transfer constants. The situation is not as clear-cut in the situation of Λ_H and Λ_P, where we conclude, after consideration of several observations reported in the literature and in the present work, that Λ_P is the preferred choice for CLD plots, but that this choice is only dictated by the good agreement of the chain transfer constants obtained from M_w and Λ_P. We therefore recommend the use of M_w and Λ_P for the determination of chain transfer constants but recommend that the results may be checked against those obtained using Λ_H.

The experimental average chain transfer constants are in good agreement with the predictions made by a model which consists of the restricted penultimate model for propagation and the terminal model for chain transfer. Although some assumptions we made in our model may not be completely justified, a close examination of the assumptions leads to the conclusion that probably the most important physical processes in the system are adequately described. From the experimental data, assuming that the chain transfer reaction is not subject to significant penultimate unit effects, the fraction of propagating styrene radicals was determined, and it was shown that there is a large disagreement between these results and the a priori predictions of this parameter by the terminal model and the penultimate model using the point estimates of the radical reactivity ratios (s values). However, a sensible adjustment of only one of the parameters, i.e., s_M, yielded a satisfactory agreement between model and experiment. This leads to the conclusion that the type of experiments described in this paper may be a valuable complimentary tool to the measurement of propagation rate coefficients for the determination of physically realistic radical reactivity ratios in free-radical copolymerization.

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