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Reversible Cobalt−Carbon Bond Formation in Catalytic Chain Transfer Polymerization

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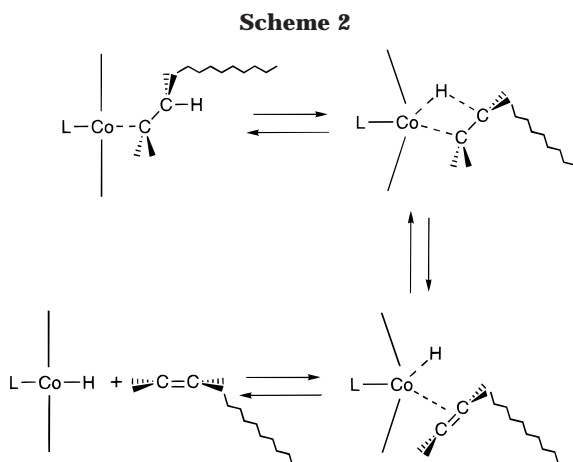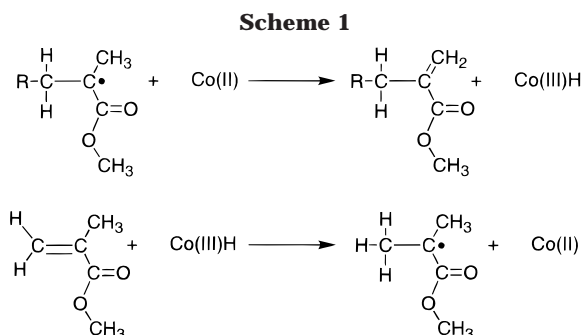
ABSTRACT: The reversible bond formation between cobalt(II) catalytic chain transfer agents and propagating radicals was studied using electron paramagnetic resonance and conventional kinetic measurements. It was found that this reversible cobalt−carbon bond formation has no significant effect on the catalytic chain transfer polymerization of methyl methacrylate but does affect the polymerization behavior of styrene. In both systems significant induction periods are observed which seem to disappear in the methyl methacrylate system but persist in the styrene system upon decreasing the initial concentration of the cobalt(II) complex. The overall rates of polymerizations are found to be readily described by "classical" free-radical polymerization kinetics, including a chain-length-dependent average termination rate coefficient. Furthermore, in contrast to the situation observed in methyl methacrylate polymerization where constant molecular weights are produced over the entire conversion range, it was found that the molecular weight in styrene increases with conversion until a constant molecular weight is obtained which is given by the Mayo equation. The kinetic behavior and the molecular weight evolution could simply be modeled by a reaction scheme providing a constant radical concentration and the presence of a chain transfer agent.

Introduction

Catalytic chain transfer polymerization is a very efficient technique for the production of low molecular weight polymers by free-radical polymerization and involves the use of certain low-spin Co(II) complexes such as cobalt porphyrins and cobaloximes in only ppm quantities.[1−3] These complexes, which typically have chain transfer constants on the order of $10^2−10^4$ in styrene and methacrylate polymerizations, were shown to catalyze the chain transfer to monomer reaction, yielding a dead polymer chain with a terminal double bond and a monomeric radical.[4−6] Although no conclusive evidence exists regarding the actual mechanism by which this process takes place, it is generally believed that it involves a two-step process consisting of a hydrogen abstraction by the cobalt(II) complex and a subsequent reinitiation reaction between a monomer molecule and the formed cobalt(III) hydride complex (see Scheme 1 for this process in methyl methacrylate polymerization).[7−13]

Although the general consensus seems to be that the two steps in Scheme 1 are conventional hydrogen-transfer reactions, a possible β-elimination of a hydrogen atom from a coordinated radical cannot be ruled out at present (see Scheme 2).[14]

These β-elimination reactions are well documented in the organometallic literature,[15] and they often occur

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Scheme 1

Scheme 2

after the formation of a bond between an organic radical and a transition metal complex. It is well-known that such organocobalt complexes can be formed by the radical−radical recombination of a Co(II) complex and an organic radical, and many such organocobalt com-
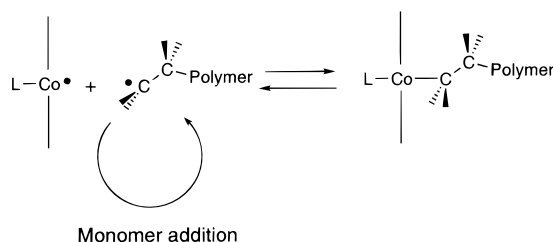
Scheme 3

Monomer addition

pounds have been observed.[9,16] The formation of the Co—C bonds in these compounds is reversible, and in some cases, such as in the case of the free-radical polymerization of acrylates in the presence of Co(II) complexes, this process leads to "living" polymerization characteristics (see Scheme 3).[17-20]

The above clearly indicates that reversible Co—C bond formation is directly affecting the polymerization behavior in catalytic chain transfer, either through a possible role in the chain transfer mechanism or through regulating the concentrations of free Co(II) complexes and propagating radicals. It is therefore important to study the role of this process, and in this paper we will attempt to further elucidate the role of reversible Co—C bond formation in the catalytic chain transfer homopolymerizations of styrene and methyl methacrylate. We will build upon early electron paramagnetic resonance (EPR) studies reported by Gridnev et al.[21] and extend these studies with more elaborate kinetic and molecular weight data. Finally we will discuss the implications of our findings with reference to previously published measurements.

Experimental Procedures

Materials. The bis(methanol) complex of bis[(difluoroboryl)-diphenylglyoximato]cobalt(II) (COPhBF, **1**), was prepared

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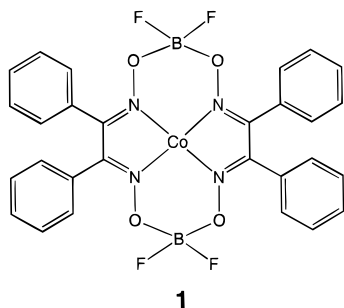
according to the method described by Bakaet al.,[22] replacing dimethylglyoxime in the described procedure by diphenylglyoxime. Since purification and characterization of the catalyst is extremely difficult, one single batch of COPhBF was used throughout this work. Styrene (Chameleon Chemicals, >99%; Aldrich, 99%) and methyl methacrylate (Chameleon Chemicals, >99%; 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. MAIB (WAKO Chemicals) and AIBN (DuPont) were recrystallized twice from hexane and methanol, respectively, and used as initiatior. Toluene (Ajax, analytical reagent) was purged with high-purity nitrogen for 1.5 h prior to use, without any further purification.

EPR Experiments. *Sample Preparation.* First, a catalyst stock solution (10^{-3} mol of catalyst per dm^3 of monomer) was prepared by dissolution of the required amount of COPhBF in 15 mL of monomer. From this solution, a small sample (∼0.7 mL) was used in the EPR measurements, and 10 mL was used to prepare an initiator solution (10^{-2} M) by dissolution of

approximately 23 mg of MAIB. Approximately 0.7 mL of this solution was then transferred into an EPR tube and subsequently polymerized at 60 °C in a water bath for 1 h, after which it was quenched in liquid nitrogen prior to the EPR measurement. At all times, great care was taken to exclude oxygen from the reagents, and after transfer of the solutions into the EPR tubes, these were further degassed by four freeze−pump−thaw cycles, after which the tubes were sealed under vacuum.

Measurements. Electron paramagnetic spectra were recorded using a Bruker ESP 300 spectrometer, equipped with a Bruker ER 4111 VT variable temperature unit and an Advantest R5372 microwave counter. During the measurements, the temperature in the probe cavity was maintained at 128 ± 2 K, provided by cold nitrogen gas.

General Polymerization Procedures. *Time-Dependent Experiments.* A round-bottom flask was charged with the required amount of COPhBF (∼1−30 mg), AIBN (0.5 or 1.0 g; 2×10^{-2} M), and a magnetic stirrer bar and subsequently sealed with a rubber septum. After (three times) evacuating and subsequent purging with nitrogen, the purged monomer and toluene were charged into the round-bottom flask using a cannula, maintaining an oxygen-free system. Polymerizations were carried out for ∼48 h in a water bath thermostated at 60 ± 1 °C. At regular intervals, samples were taken using standard syringe techniques, always ensuring to keep oxygen from the reaction mixture. Polymerization of the samples was stopped by exposure to air and addition of hydroquinone. The samples were initially left to dry overnight in a fume hood after which they were dried in a vacuum oven at 60 °C. Conversions were measured by gravimetry.

Chain Transfer Constant Measurements. Chain transfer constants were determined for 2:1 (v/v) toluene:monomer mixtures at 60 °C using the procedures described previously.[13,23−25]

Molecular Weight Analysis. Molecular weight distributions were determined by size exclusion chromatography using a GBC Instruments LC1120 HPLC pump, a Shimadzu SIL-10A autoinjector, a column set consisting of a Polymer Laboratories 3.0 μm bead-size guard column (50 × 7.5 mm) followed by four linear PL columns (10^6, 10^5, 10^4, and 10^3), and a VISCOTEK Dual Detector model 250 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 580−3.0 × 10^6) and poly(methyl methacrylate) (Polymer Laboratories, molecular weight range 200−1.6 × 10^6) standards.

Results and Discussion

Chain Transfer Constants. Chain transfer constants of COPhBF were measured for styrene and methyl methacrylate in toluene at 60 °C. As discussed in great detail in a previous paper,[23] two procedures can be used, i.e., the Mayo[26] and the chain length distribution procedures.[27] The former procedure requires the measurement of the average degree of polymerization, DP_n, as a function of the amount of chain transfer agent. By plotting these results according to the Mayo equation (eq 1), i.e., as DP_n^{-1} vs the ratio of chain transfer agent (i.e., the COPhBF catalyst) and monomer concentrations (i.e., [Co(II)]/[M]), a straight line should be observed, with a slope equal to the chain transfer constant, C_s:

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_s \frac{[Co(II)]}{[M]} \qquad (1)$$

In this equation, $DP_{n,0}$ is the average degree of polymerization that is obtained in the absence of added chain transfer agent (assuming that the rate of bimolecular termination does not change with changing chain length; this term is of minor importance when the
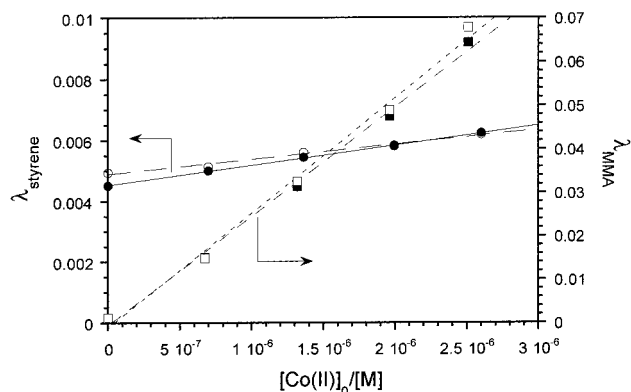
Figure 1. Mayo (closed symbols) and CLD (open symbols) plots for the determination of the chain transfer constant of COPhBF for styrene (circles) and methyl methacrylate (squares) polymerizations in toluene (solvent:monomer = 2:1 v/v) at 60 °C. $\lambda = 2m_0/M_w$ (Mayo plots) or $\lambda = -\Lambda_{peak}m_0$ (CLD plots).

Table 1. Chain Transfer Constants for COPhBF in Solution Polymerizations of Styrene and Methyl Methacrylate at 60 °C

	Mayo procedure[a]		CLD procedure[b]	
	M_n	$M_w/2$	Λ_{high}	Λ_{peak}
methyl methacrylate 1	19.5×10^3	24.2×10^3	20.7×10^3	25.8×10^3
methyl methacrylate 2	20.1×10^3	25.3×10^3	24.4×10^3	26.7×10^3
styrene 1	1.2×10^3	775	758	718
styrene 2	1.4×10^3	657	552	478

[a] Listed chain transfer constants were measured using eq 1, by using either M_n or $M_w/2$. [b] Listed chain transfer constants were measured using eq 2, by using either the high molecular weight slope (Λ_{high}) or the peak molecular weight slope (Λ_{peak}).

system is chain transfer dominated). The average degree of polymerization can be determined readily from the molecular weight distribution obtained by size exclusion chromatography and is defined as $DP_n = M_n/m_0$, where M_n is the number-average molecular weight and m_0 is the monomer mass. However, the determination of M_n from a molecular weight distribution can be subject to a large uncertainty due to baseline subtraction errors,[23,28] and therefore the use of half the weight-average degree of polymerization, DP_w, is often the preferred choice in systems that are governed by chain transfer.[29] The number-average degree of polymerization is then given by $DP_n = DP_w/2 = M_w/(2m_0)$, where M_w is the weight-average molecular weight.

The chain length distribution involves plotting of the molecular weight distribution as the natural logarithm of the number distribution, $P(M)$, as a function of the molecular weight, M, and then determining the high molecular weight slope of this plot, Λ (eq 2).[27]

$$\lim_{M \to \infty} \frac{d\ln(P(M))}{dM} = \Lambda = -C_s \frac{[Co(II)]}{[M]} \frac{1}{m_0} \qquad (2)$$

A plot of $-\Lambda m_0$ vs $[Co(II)]/[M]$, which we will call a CLD plot in this paper, should then yield a straight line with a slope equal to C_s. Recently a discussion has started in the literature about the molecular weight region in which Λ should be determined,[13,23,28,30] i.e., whether the slope should be determined in the high molecular weight region (Λ_{high}), which is the correct theoretical limit,[27] or in the region of the peak molecular weight (Λ_{peak}), which suffers less from experimental uncertainties.[28] In a previous study, we found that Λ_{peak} results compare most favorably with the $M_w/2$ results and therefore concluded that this should be the preferred option.[23]

Since there is no a priori theoretical justification for the preferred use of any of the four above-mentioned parameters (i.e., M_n, $M_w/2$, Λ_{high}, and Λ_{peak}), we continue to determine the chain transfer constants using all four of them. In Figure 1, Mayo and CLD plots are shown for styrene and methyl methacrylate. The chain transfer constants, which were determined from these plots, are given in Table 1. From this table it is clear that, similar to what we found in our previous studies, there is good agreement between the chain transfer constants obtained from Mayo plots using $M_w/2$ and CLD plots using Λ_{peak}. Using these values as estimates for the true chain transfer constants, we obtain values of $(6.6 \pm 1.1) \times 10^2$

and $(25.3 \pm 0.9) \times 10^3$ for styrene and methyl methacrylate, respectively.

EPR Experiments. Since low-spin Co(II) complexes are radicals, and their corresponding radical adducts are nonradical Co(III) species, the process of cobalt−carbon bond formation should be readily accessible with EPR spectroscopy. As mentioned in the Introduction, Gridnev et al.[21] in the mid-1980s measured the EPR spectra of cobaloximes in monomer solutions in the absence and presence of radical initiators. To confirm these results, we repeated these experiments for COPhBF in styrene and methyl methacrylate. Due to the very fast relaxation times of transition metal complexes, spectra have to be recorded at cryogenic temperatures, which necessarily implies that spectra cannot be recorded under polymerization conditions.[31] The spectra of COPhBF in monomer solutions were straightforwardly recorded by freezing the solution in the EPR cavity, which was thermostated at 128 K, and are given in Figures 2a and 3a for methyl methacrylate and styrene, respectively, and show the characteristic features of low-spin Co(II) macrocycles, which have been investigated and described in great detail in the past.[22,32−37] A second series of experiments were performed in which initiator was added to the COPhBF in monomer solutions, after which these solutions were heated at 60 °C for 1 h and subsequently frozen in liquid nitrogen. The obtained spectra are shown in Figures 2b and 3b for methyl methacrylate and styrene, respectively. It is immediately clear that the spectrum for COPhBF in the methyl methacrylate solution has not changed dramatically, whereas the spectrum in the styrene solution has nearly completely disappeared; the signal intensity has decreased by at least an order of magnitude. A similar observation regarding the disappearance of the Co(II) signal in styrene polymerization was made by Gridnev et al.,[21] and together with corresponding observations in the UV−vis spectra, they concluded that this decrease in Co(II) signal was due to the formation of a bond between the organic styryl radical and the Co(II) complex, forming an organocobalt-(III) complex:

$$R^\bullet + Co(II) \rightleftarrows R_n{-}Co(III) \qquad (3)$$
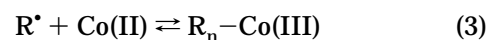
The fact that this reaction seems to be significant in styrene polymerization and not in methyl methacrylate polymerization is straightforwardly explained by noting that in the former case secondary and in the latter case tertiary radicals are present. Firstly tertiary radicals are more stable than secondary radicals, and secondly the formation of a bond between Co(II) and a tertiary radical has greater steric requirements.
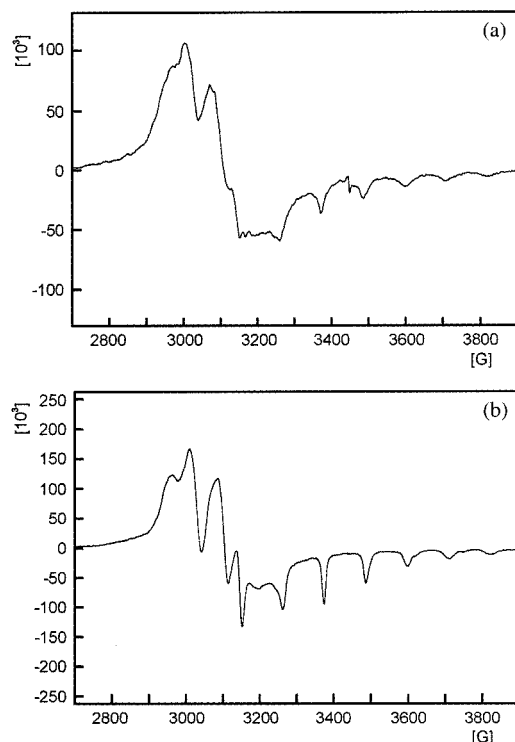
Figure 2. Electron paramagnetic resonance spectrum of COPhBF in methyl methacrylate measured at 128 K: (a) in bulk and (b) in bulk after heating at 60 °C in the presence of an initiator.
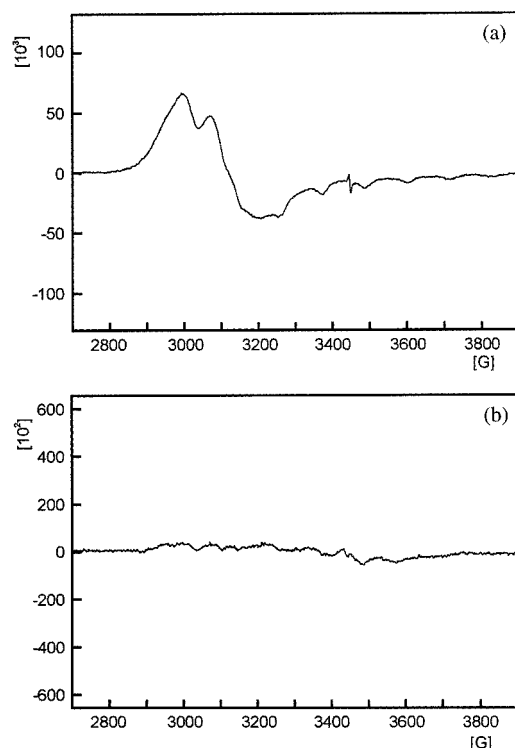

Figure 3. Electron paramagnetic resonance spectrum of COPhBF in styrene measured at 128 K: (a) in bulk and (b) in bulk after heating at 60 °C in the presence of an initiator.

What does this formation of cobalt−carbon bonds mean for catalytic chain transfer polymerization? The effect seems to be twofold: it reduces the concentrations of both the propagating radicals and the Co(II) complex, which acts as a chain transfer agent. The former effect is only of importance in the early stages of polymeriza-
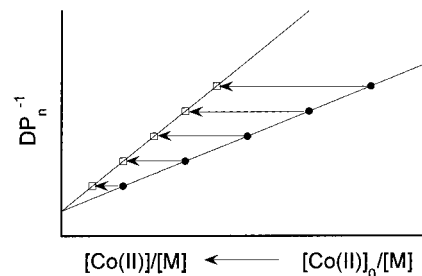

Figure 4. Effect of decreasing the effective initial COPhBF concentration from $[Co(II)]_0$ to $[Co(II)]$ on a Mayo plot. The measured points all shift horizontally to the left, resulting in a steeper line and hence a higher chain transfer constant.

tion, as the steady-state radical concentration is fully governed by the overall rates of initiation and bimolecular termination, and hence this effect should exhibit itself through an increasing induction period for increasing amounts of added Co(II). The second effect is more important, because the effective concentration of chain transfer agent is much lower than what one expects. This implies that the chain transfer constant measured from a Mayo plot based on the intially added $[Co(II)]$ (defined as $[Co(II)]_0$) is too low, an effect which was already briefly mentioned in a previous paper.[24] A simplified representation of this effect on the Mayo procedure is given in Figure 4.

The actual $[Co(II)]/[M]$ ratios are lower than the $[Co(II)]_0/[M]$, because of the Co(II)−R−Co(III) equilibrium. This means that the "true" $[Co(II)]/[M]$ values on the horizontal axis can be obtained by a horizontal shift of the points to lower values, yielding a steeper slope of the Mayo plot and hence a higher chain transfer constant. Since all measurements to date of the chain transfer constant in styrene polymerization (including the one in the present study) have been determined using $[Co(II)]_0/[M]$, it can be concluded that all of these values are only apparent values and do not reflect the true chemistry of the catalytic chain transfer reaction. This further implies that the chain transfer rate coefficients for methyl methacrylate and styrene are probably not as different as may seem at first from comparing the "apparent" chain transfer constants (which we will denote C_s' in the remainder of this discussion). The question remains now whether measuring an apparent chain transfer constant is useful. The short answer to that question is affirmative; since the average molecular weight is governed by the product of C_s and $[Co(II)]$, the effect of the cobalt−carbon bond formation cancels:

$$(C_s[Co(II)])_{true} = (C_s'[Co(II)]_0)_{observed}$$

At this point, it is important to note that this argument is only of importance if the chain transfer reaction is indeed an abstraction/transfer reaction and not a reaction involving a coordinated radical. In the latter case, the large reduction in $[Co(II)]$ would only reflect the fact that the chain transfer reaction in styrene polymerization is indeed much slower.

Kinetic Studies. As stated in the previous section, the cobalt−carbon bond formation decreases the concentration of free radicals and hence should affect the rate (at least in the initial stages) of polymerization. The result shown in Figure 3b is very interesting if one considers that, under ordinary free-radical polymerization conditions, the steady-state radical concentrations are of the order of $10^{-7}-10^{-8}$ M and that the $[Co(II)]$ is
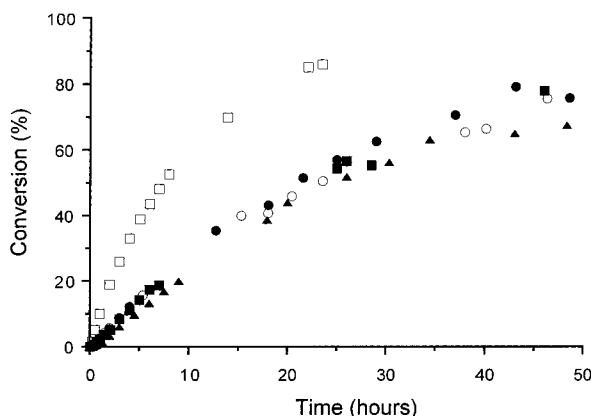
Figure 5. Conversion−time profiles for styrene and methyl methacrylate polymerizations in the presence of varying amounts of COPhBF. In all cases: $T = 60\,°C$, toluene:monomer = 2:1 (v/v), [AIBN] = 2×10^{-2} mol dm^{-3}; (▲) styrene, [Co(II)]$_0$ = 2.57×10^{-4} mol dm^{-3}; (●) styrene, [Co(II)]$_0$ = 6.22×10^{-5} mol dm^{-3}; (■) styrene, [Co(II)]$_0$ = 1.58×10^{-5} mol dm^{-3}; (○) methyl methacrylate, [Co(II)]$_0$ = 3.08×10^{-5} mol dm^{-3}; (□) methyl methacrylate, [Co(II)]$_0$ = 1.85×10^{-5} mol dm^{-3}.

several orders of magnitude higher. This means that the newly formed radicals from initiator decomposition must be consumed by Co(II) to form R−Co(III) and that polymerization does not start until the equilibrium between Co(II) and R−Co(III) has been established. Furthermore, the time required to establish equilibrium should depend on the initial concentration of the Co(II) complex. It is therefore interesting to investigate the conversion−time behavior for different initial concentrations of COPhBF. The results of solution polymerizations (toluene:monomer = 2:1 (v/v)) at 60 °C are shown in Figure 5, and several different kinetic parameters derived from these results are listed in Table 2.

It is clear from the results in Figure 5 that nearly all polymerizations proceed with a similar rate, except for the methyl methacrylate experiment with the lowest initial COPhBF concentration. This result is easily explained by the fact that methyl methacrylate has a higher propagation rate coefficient than styrene but that, in the case of the higher initial Co(II) concentration, this effect is compensated for by a much higher average termination rate coefficient (see Table 2).

In Table 2, we have listed the induction times observed in these experiments, which we estimated from a linear extrapolation from the conversion−time data in the initial 2 h of polymerization. It can be seen that for the experiments labeled styrene Ia and Ib (i.e., those with the highest [Co(II)]$_0$) the induction times are largest ($\sim$20 min) and that the induction times seem to become constant ($\sim$10 min) upon lowering the initial Co-(II) concentration. This result is consistent with the formation of R−Co(III) species between the Co(II) and styryl radicals. However, if we compare these results with the results obtained in methyl methacrylate polymerization, where, at first glance, we expected any induction periods to be absent, we still see a significant induction period ($\sim$9 min) for the highest initial Co(II) concentration, which disappears upon lowering the initial Co(II) concentration. Although the propagating methyl methacrylate radicals do not undergo cobalt−carbon bond formation, the primary radicals created by AIBN decomposition are known to undergo this reaction, and the presence of such organocobalt complexes has been shown by Gridnev et al. in previous studies.[9,16] It is therefore likely that the induction periods in both

monomer systems are primarily caused by the primary (methacrylonitrile) radicals formed by initiator decomposition but that a further decrease in the free Co(II) concentration (and the longer induction periods) in the styrene polymerizations is caused by the cobalt−carbon bond formation between the Co(II) complex and the propagating styryl radicals.

The finding that different initial Co(II) concentrations lead to different induction times prompts us to make a cautionary note about the validity of previously reported studies of the chain-length dependence of the average termination rate coefficients in catalytic chain transfer polymerization.[13,24] In those studies, the rate of polymerization was set equal to the final conversion divided by the time of reaction in the very early stages of polymerization. This procedure is only valid in cases where there is a negligible induction period. As shown here, the induction periods can be quite significant at higher [Co(II)]$_0$, and in those circumstances the approach taken in those previous studies is not valid anymore. Fortunately, the [Co(II)]$_0$ used in the mentioned studies was low enough for the results to be negligibly affected by possible induction periods.

A more reliable procedure to study the chain-length dependence of the average termination rate coefficient $\langle k_t \rangle$ would involve the measurement of the rate at an interval in which the steady state has already been established. In Table 2, we compare the values of the rate of polymerization in the first 2 h of polymerization. It can be seen that all styrene experiments have similar rates of polymerization, leading to very similar average termination rate coefficients, which decrease slightly with increasing average degree of polymerization (i.e., decreasing [Co(II)]$_0$). Although the experimental results are not accurate enough to establish the exponent in the power law relating the average termination rate coefficient to the average degree of polymerization (i.e., $\langle k_t \rangle \propto DP_n^{-a}$), it is clear that this exponent is likely to be closer to 0.18 (indicating segmental diffusion-controlled termination),[38] rather than 0.5 (indicating translational diffusion-controlled termination).[38] This situation is quite different for the methyl methacrylate polymerization, where there is a large decrease in $\langle k_t \rangle$ in going from an average degree of polymerization of about 4 to about 8. A detailed discussion of this result is beyond the scope of this paper and is the subject of further work.[39] However, we wish to point out that these results suggest that different mechanisms may control the termination rate in different molecular weight regimes.

Molecular Weight Evolution. Although the main usage of catalytic chain transfer polymerization is molecular weight control, hardly any data have been published on the time evolution of the molecular weight distributions. One striking feature of catalytic chain transfer polymerization is the (generally accepted) fact that one can produce a high-conversion polymer product with a desired average degree of polymerization and polydispersity index close to 2 in a batch procedure using conditions obtained from low-conversion experiments. This result, which is not anticipated as the Mayo equation (eq 1) predicts a decreasing average degree of polymerization in time due to an increasing [Co(II)]/[M] ratio, implies that uniform molecular weight distributions are produced during the entire course of polymerization. Uniform products during the course of polymerization have indeed been observed for methyl

Table 2. Dependence of Steady-State Rates of Polymerization[a] on the Initial COPhBF Concentration in the Free-Radical Polymerizations of Styrene and Methyl Methacrylate at 60 °C

	$[Co]_0{}^b$	$t_{ind}{}^c$	$R_p{}^d$	$k_{app}{}^e$	$[R^\bullet]^f$	$\langle k_t \rangle^g$
styrene Ia	2.70×10^{-4}	20	2.3×10^{-5}	7.9×10^{-6}	2.3×10^{-8}	1.9×10^8
styrene Ib	2.57×10^{-4}	20	1.8×10^{-5}	5.9×10^{-6}	1.7×10^{-8}	3.4×10^8
styrene IIa	6.30×10^{-5}	11	2.4×10^{-5}	8.5×10^{-6}	2.5×10^{-8}	1.7×10^8
styrene IIb	6.22×10^{-5}	9	2.4×10^{-5}	8.4×10^{-6}	2.4×10^{-8}	1.8×10^8
styrene IIIa	1.58×10^{-5}	12	2.3×10^{-5}	7.9×10^{-6}	2.3×10^{-8}	1.9×10^8
styrene IIIb	1.46×10^{-5}	9	2.5×10^{-5}	8.6×10^{-6}	2.5×10^{-8}	1.7×10^8
MMA Ia	3.02×10^{-5}	9	1.9×10^{-5}	6.1×10^{-6}	7.2×10^{-9}	2.0×10^9
MMA Ib	3.08×10^{-5}	9	2.6×10^{-5}	8.2×10^{-6}	9.8×10^{-9}	1.1×10^9
MMA IIa	1.85×10^{-5}	2	9.2×10^{-5}	3.0×10^{-5}	3.5×10^{-8}	8.6×10^7
MMA IIb	1.29×10^{-5}	0	8.7×10^{-5}	3.0×10^{-5}	3.4×10^{-8}	8.8×10^7

[a] Determined over the initial 2 h of polymerization. [b] Initial COPhBF concentration (mol dm^{-3}). [c] Induction period (min). [d] Rate of polymerization (mol dm^{-3} s^{-1}). [e] Slope of first-order kinetic plot (s^{-1}). [f] Overall radical concentration determined from R_p and k_{app} (mol dm^{-3}). [g] Average termination rate coefficient, determined from $[R^\bullet]$ and eq 15 assuming $f k_d = 0.5 \times 10^{-5}$ s^{-1} at 60 °C (dm^3 mol^{-1} s^{-1}).
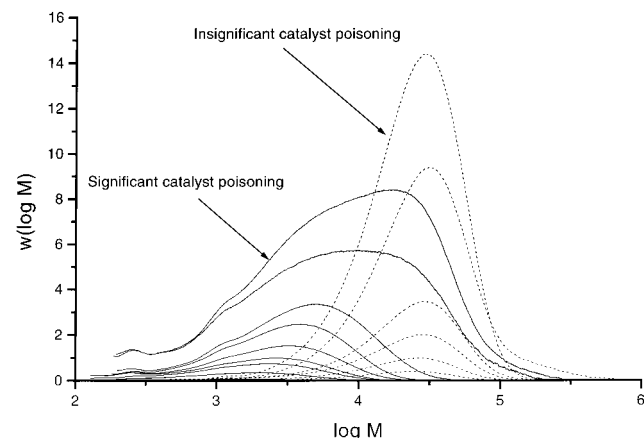

Figure 6. Evolution of cumulative molecular weight distributions observed in catalytic chain transfer polymerization. The solid and dashed lines represent the polymers formed in the experiments corresponding to (▲) and (■), respectively, in Figures 5 and 7. The broadening of the distributions with the solid lines is probably caused by catalyst poisoning.

Figure 7. Evolution of the cumulative weight-average molecular weight, M_w, for styrene and methyl methacrylate polymerizations in the presence of varying amounts of COPh-BF. In all cases: $T = 60$ °C, toluene:monomer = 2:1 (v/v), [AIBN] = 2×10^{-2} mol dm^{-3}; (▲) styrene, $[Co(II)]_0 = 2.57 \times 10^{-4}$ mol dm^{-3}; (●) styrene, $[Co(II)]_0 = 6.22 \times 10^{-5}$ mol dm^{-3}; (■) styrene, $[Co(II)]_0 = 1.58 \times 10^{-5}$ mol dm^{-3}; (○) methyl methacrylate, $[Co(II)]_0 = 3.08 \times 10^{-5}$ mol dm^{-3}; (□) methyl methacrylate, $[Co(II)]_0 = 1.85 \times 10^{-5}$ mol dm^{-3}.

methacrylate homopolymerization[24] and the terpolymerization of styrene, methyl methacrylate, and 2-hydroxyethyl methacrylate.[40] The reason for this observation is as yet unknown, but it has been speculated that this may be caused by catalyst poisoning, which is substantiated by a very early paper reporting changes in the UV spectrum of the catalyst during the course of polymerization.[4] In Figure 6, we have shown the evolutions of the molecular weight distributions in time for two different styrene experiments. In the case of the highest used initial COPhBF concentration in our present study (solid lines in Figure 6; see Table 1, styrene Ia and Ib), we observe a shift of the molecular weight distribution to higher molecular weights and a broadening in time, which we believe is due to significant poisoning of the catalyst. In all other investigated cases (for both styrene and methyl methacrylate), we observe a behavior similar to that represented by the dashed curves in Figure 6. The overall features, i.e., the average molecular weights and polydispersity indices, do not seem to change significantly in time and can be predicted from the Mayo equation. However, a closer examination of the evolution of the average molecular weights at very low conversion (see Figure 7) reveals a different picture for the styrene and methyl methacrylate polymerizations.[41] Whereas a constant (within experimental error) average degree of polymerization is observed from the very early stages in the methyl methacrylate experiments, the average degrees of polymerization in the styrene experiments seem to in-
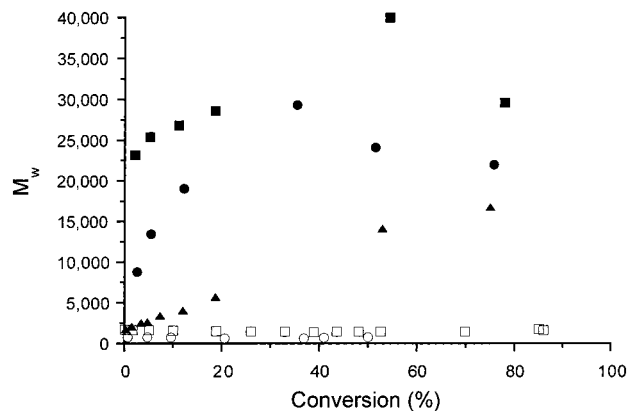
crease until they level off at a value that is predicted by eq 1.

It is clear that, at the very early stages of polymerization, the behavior of the styrene and methyl methacrylate systems is different, and a possible explanation for this fact may lie in the differences we observe in the extent of the cobalt–carbon bond formation in the two systems. In the styrene system the extent of cobalt–carbon bond formation is significant, and we know that in the case of the cobalt(II) porphyrin-mediated free-radical polymerization of the acrylates this cobalt–carbon bond formation is reversible and leads to "living" behavior.[17–20,24] The growth of molecular weight in time, observed in the styrene systems, is consistent with "living" radical polymerization,[42] but it is obvious that this cannot be the full explanation of our observations. Since, overall, our molecular weight distribution is governed by chain transfer, this process must dominate over a possible "living" behavior.[43] In the following section, we combine these thoughts of a "living" polymerization with those of a catalytic chain transfer polymerization, and the resulting kinetic model will be shown to adequately describe our experimental observations.

Kinetic Model. In the previous sections we investigated the kinetics and molecular weight evolutions as a function of time, and it is the aim of this section to arrive at a comprehensive model to describe these

features of the polymerization. As mentioned in the previous section, the Co(II)−R−Co(III) equilibrium causes a regulation of the growing radical concentration,[19] which in the case of acrylate polymerization leads to "living" radical behavior. There is no obvious reason to believe that this would be any different in styrene polymerization. However, the overall behavior is different, because in the case of the cobalt(II) porphyrin-mediated radical polymerization of acrylates,[17−20,24] negligible chain transfer occurs, whereas this does occur in the polymerization of styrene. Hence, it is conceivable that the present systems can be described by a model that describes an otherwise living polymerization in the presence of added initiator and chain transfer agent.[44,45]
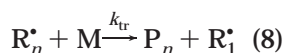
The reactions of importance are firstly the four common steps in free-radical polymerization:

(i) initiator decomposition: $I \xrightarrow{k_d} 2R_0^{\bullet}$ (4)

and addition to monomer: $R_0^{\bullet} + M \xrightarrow{k_i} R_0M^{\bullet}$ (5)

(ii) propagation: $R_n^{\bullet} + M \xrightarrow{k_p} R_{n+1}^{\bullet}$ (6)

(iii) bimolecular termination:

$$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{\langle k_t \rangle} \text{dead polymer}$$ (7)

(iv) chain transfer to monomer:

$$R_n^{\bullet} + M \xrightarrow{k_{tr}} P_n + R_1^{\bullet}$$ (8)

The first modification now is the description of the chain transfer to monomer reaction iv. This reaction is now catalyzed by the Co(II) complex and should be written in terms of the elementary reactions:

$$R_n^{\bullet} + Co(II) \xrightarrow{k_{Co}} P_n + Co(II)H$$ (9a)

$$Co(III)H + M \rightarrow R_1^{\bullet} + Co(II)$$ (9b)
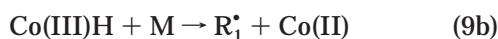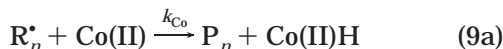
Assuming that the abstraction reaction is rate determining, the rate coefficient for chain transfer to monomer, k_{tr}, should be rewritten as follows:

$$k_{tr} = k_{Co} \frac{[Co(II)]}{[M]}$$ (10)

The second modification of the conventional polymerization scheme is made by including the reversible cobalt−carbon bond formation.

$$R_n^{\bullet} + Co(II) \underset{k_2}{\overset{k_1}{\rightleftarrows}} R_n{-}Co(III)$$ (11)
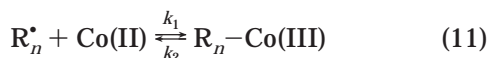
At this point, all the reactions have been defined and the appropriate differential equations need to be solved. We start with the expressions for the initiator decomposition and the radical concentrations.

$$\frac{d[I]}{dt} = -k_d[I] \Rightarrow [I] = [I]_0 \exp(-k_d t)$$ (12)

$$\frac{d[R^{\bullet}]}{dt} = 2fk_d[I] - 2\langle k_t \rangle[R^{\bullet}]^2 - k_1[R^{\bullet}][Co(II)] + k_2[R{-}Co(III)]$$ (13)

At the onset of polymerization, i.e., the equilibrium of eq 11 has been established, the last two terms of eq 13 are equal, and the expression reduces to the simple expression of conventional free-radical polymerization:[46]

$$\frac{d[R^{\bullet}]}{dt} = 2fk_d[I] - 2\langle k_t \rangle[R^{\bullet}]^2$$ (14)

The steady-state radical concentration is thus given by

$$[R^{\bullet}] = \sqrt{\frac{fk_d[I]}{\langle k_t \rangle}}$$ (15)

Furthermore, at equilibrium, the following relationship holds for the Co(II) and Co(III)−R concentrations:

$$[Co(II)] = \frac{k_2[R{-}Co(III)]}{k_1[R^{\bullet}]} = K^{-1}\frac{[R{-}Co(III)]}{[R^{\bullet}]}$$ (16)

With knowledge of the equilibrium constant K and the steady-state radical concentration, the relative fractions of Co(II) and R−Co(III) are readily determined.

The description of the monomer consumption (which allows one to determine the time dependence of conversion) is also given by a simple expression.

$$\frac{d[M]}{dt} = -(k_p[M] + k_{tr}[M])[R^{\bullet}] = -\left(k_p[M] + k_{Co}\frac{[Co(II)]}{[M]}[M]\right)[R^{\bullet}]$$

$$= -(k_p[M] + k_{Co}[Co(II)])[R^{\bullet}]$$ (17)

The expression of eq 17 could be solved exactly, but the resulting expression is unnecessarily complicated. It is simpler to assume that $[R^{\bullet}]$ is constant, which is conceivable because at our experimental conditions there is only a slow decrease in [I], which is counteracted by a slow decrease in $\langle k_t \rangle$ due to increasing viscosity. Integration of eq 17 then yields

$$[M] = [M]_0 \exp(-k_p[R^{\bullet}]t) + (\exp(-k_p[R^{\bullet}]t) - 1) \times \frac{k_{Co}}{k_p}[Co(II)]$$

$$= [M]_0 \exp(-k_p[R^{\bullet}]t) + (\exp(-k_p[R^{\bullet}]t) - 1)C_s[Co(II)]$$ (18)

In this equation, we have a factor $C_s[Co(II)]$, which refers to the true C_s value and the true [Co(II)]. It was discussed before that we do not know either of these quantities, which possibly limits the usefulness of the derived expression. However, since the average degree of polymerization is governed by $C_s[Co(II)]$, and not by the two individual factors, this product can be replaced by the product of the apparent measured chain transfer constant, C_s', and the initial COPhBF concentration, $[Co(II)]_0$:

$$[M] = [M]_0 \exp(-k_p[R^{\bullet}]t) + (\exp(-k_p[R^{\bullet}]t) - 1)C_s'[Co(II)]_0$$ (19)

Having derived an expression to describe the kinetics of the system, we now need an expression to describe

the evolution of the average degree of polymerization, which is defined as

$$DP_n = \frac{\text{no. of reacted monomer units}}{\text{no. of initiator fragments}} \quad (20)$$

This expression can be derived straightforwardly if one realizes that the initiation occurs via three different mechanisms: (a) via initiator-derived radicals, (b) via the dormant R−Co(III) "living" radical initiator, which is present at the onset of polymerization, and (c) via the chain transfer mechanism. The average degree of polymerization is thus given by

$$DP_n = \frac{[M]_0 - [M]}{2f([I]_0 - [I]) + [R-Co(III)] + \epsilon[Co(II)]} \quad (21)$$

where ϵ is the turnover number for the catalyst, which is defined as follows:[4]

$$\epsilon = ([M]_0 - [M])(DP_n^{-1} - DP_{n,0}^{-1})\frac{1}{[Co(II)]} \quad (22)$$

From the Mayo equation the following substitution can be made:

$$DP_n^{-1} - DP_{n,0}^{-1} = C_s\frac{[Co(II)]}{[M]} \quad (23)$$

Since the molecular weight distributions do not seem to change in time (i.e., high conversion polymers are produced with the same M_n as predicted using the chain transfer constant determined at low conversion), the following substitution is made:

$$C_s\frac{[Co(II)]}{[M]}\Big|_{\text{at any time } t} = C_s'\frac{[Co(II)]_0}{[M]_0} \quad (24)$$

This then leads to the following expression for the average degree of polymerization:

$$DP_n = \frac{[M]_0 - [M]}{2f([I]_0 - [I]) + [R-Co(III)] + XC_s'[Co(II)]_0} \quad (25)$$

where X is the fractional conversion.

In Figure 8, the results of the model are shown for systems similar to styrene and methyl methacrylate under current experimental conditions. It can be seen that in the styrene-like system (with 90% of its initial Co bound in R−Co(III)) an initial increase in molecular weight is observed which levels out at a value given by the Mayo equation, whereas this value is immediately reached for the methyl methacrylate-like system. In both cases, a linear first-order kinetic plot is predicted. Comparison of these model predictions with the experimental data presented in this paper shows that there is a good agreement, suggesting the derived model provides an adequate representation of the physical chemistry of a catalytic chain transfer polymerization.

It is now interesting to look at the effect of the degree of cobalt−carbon bond formation on the molecular weight evolution. In Figure 9 we compare the average degrees of polymerization during the first 6% conversion obtained when different amounts of the initial cobalt-(II) concentration are bound as R−Co(III). It can be seen that, especially for smaller values of $[Co(II)]/[Co(II)]_0$
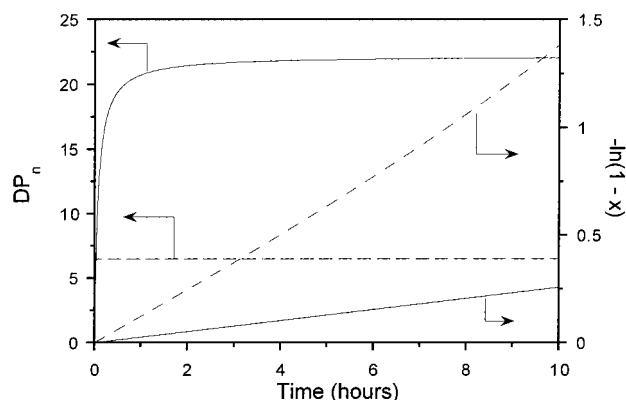

Figure 8. Model predictions for the cumulative number-average degree of polymerization (left axis) and $-\ln(1 - x)$ (right axis) as a function of time for systems similar to those in the present investigations. $[M]_0 = 3$ dm³ mol⁻¹, $[AIBN] = 2 \times 10^{-2}$ mol dm⁻³, (- - -) $C_s = 25 \times 10^3$, $[Co(II)]_0 = 1.85 \times 10^{-5}$ mol dm⁻³, $[Co(II)]/[Co(II)]_0 = 1$ or 0, $k_p = 831$ dm³ mol⁻¹ s⁻¹, and (−) $C_s = 500$, $[Co(II)]_0 = 2.57 \times 10^{-4}$ mol dm⁻³, $[Co(II)]/[Co(II)]_0 = 0.1$, $k_p = 340$ dm³ mol⁻¹ s⁻¹.
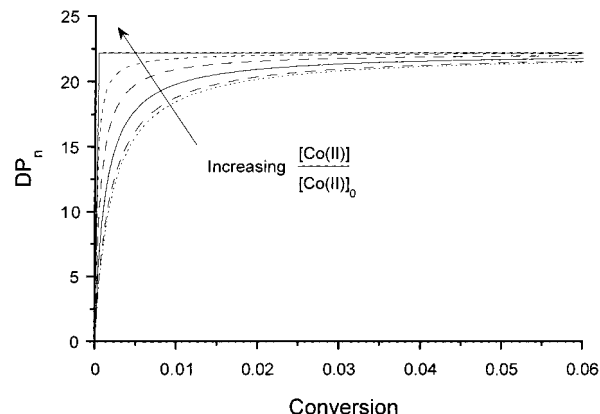

Figure 9. Model predictions of the effect of the amount of R−Co(III) formation on the molecular weight evolution in a catalytic chain transfer system, similar to styrene in the current experiments. Model parameters are the same as those for the solid line system in Figure 8, varying $[Co(II)]/[Co(II)]_0$ from 0 to 1.

(i.e., a large extent of R−Co(III) formation), only after several percent conversion is the final average degree of polymerization obtained. This result implies that measurements of chain transfer constants in catalytic chain transfer polymerization are most reliably performed when final conversions are about 5%, which is in contrast to the general rule for conventional chain transfer where conversions should be as low as possible. Thus, the use of very low-conversion polymers in catalytic chain transfer measurements may lead to erroneous results depending on the extent of R−Co(III) formation.

Conclusions

The work described in this paper confirms earlier findings that there is significant Co−C bond formation in the COPhBF-mediated catalytic chain transfer polymerization of styrene, whereas this seems to be absent in the case of methyl methacrylate. Considering the fact that the Co−C bond formation leads to a decrease in the concentration of free catalyst implies that the chain transfer constants for styrene determined so far are only apparent values; it can be concluded that the true values are probably much closer to the chain transfer constants

observed in methyl methacrylate than has been assumed previously. Furthermore, it is found that this formation of R−Co(III) in the early stages of the polymerization causes an induction period, which can be ascribed to a reaction of the Co(II) complex with the initiator-derived primary radicals in both methyl methacrylate and styrene polymerizations and a further reaction with propagating styryl radicals in styrene polymerization. Rates of polymerization can straightforwardly be described by the "classical" kinetic scheme for free-radical polymerization, including a chain-length-dependent average termination rate coefficient. Monitoring the average molecular weight in time shows that in the case of methyl methacrylate a uniform molecular weight distribution is formed in time, whereas in the case of styrene the molecular weight increases in time until, after a few percent conversion, it reaches a steady value which is determined by the chain transfer constant. This result can be explained by a model that describes an otherwise "living" radical polymerization after the addition of a chain transfer agent.

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(41) We used weight-average molecular weights in Figure 7, because these are more reliably obtained from gel permeation chromatograms than number-average molecular weights; this is especially the case for the low molecular weight polymers.
(42) The difference between these styrene systems and styrene Ia and Ib is the fact that we do not observe a significant broadening of the molecular weight distribution in time, which would be the case for significant catalyst poisoning.
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