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Direct Observation of Cobalt−Carbon Bond Formation in the Catalytic Chain Transfer Polymerization of Methyl Acrylate Using Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

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ABSTRACT: A preliminary study into the mechanism of catalytic chain transfer polymerization of methyl acrylate with BF_2-bridged cobaloxime is reported. The reaction kinetics indicate two distinct phases of the reaction: an induction time followed by a steady-state polymerization. In the polymerization phase chain transfer occurs. Low molecular weight polymer chains formed during the induction period were isolated and analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI). The MALDI spectra clearly indicated poly(methyl acrylate) chains bound to a single cobaloxime molecule. The poly(methyl acrylate)−Co chains were then further reacted with α-methylstyrene at 60 °C. MALDI analyses of the polymer from the second reaction stage indicated a displacement of cobaloxime from the chain end by an α-methylstyrene unit.

Introduction

Catalytic chain transfer polymerization of methacrylates and styrenic derivatives using cobalt complexes is now well established as a powerful synthetic route to functionalized oligomers.[1−4] This technique is based upon the fact that certain low-spin Co(II) complexes, such as cobaloximes, catalyze the chain transfer to monomer reaction, via a mechanism that is generally believed to consist of two consecutive steps.[1−4] First, a growing polymeric radical, $R_n^\bullet$, undergoes a hydrogen-transfer reaction with the Co(II) complex to form a dead polymer chain, P_n, and a Co(III)H complex (eq 1). This Co(III)H complex subsequently reacts with a monomer molecule, M, to produce the original Co(II) complex and a monomeric radical, $R_1^\bullet$ (eq 2).

$$R_n^\bullet + \mathrm{Co(II)} \rightarrow P_n + \mathrm{Co(III)H} \qquad (1)$$

$$\mathrm{Co(III)H} + M \rightarrow \mathrm{Co(II)} + R_1^\bullet \qquad (2)$$

Catalytic chain transfer is most efficacious for tertiary propagating radicals, from which a hydrogen atom is abstracted from the α-carbon atom in the substituent. This chain transfer process appears to operate at a diffusion-controlled rate.[5,6] However, for secondary radicals such as styrene, the chain transfer reaction is less effective, and this has been (at least partly) ascribed to reversible cobalt−carbon bond formation,[6,7] a concurrent reaction that reduces the free active Co(II) catalyst in the reaction (eq 3).

$$R_n^\bullet + \mathrm{Co(II)} \rightleftarrows R_n{-}\mathrm{Co(III)} \qquad (3)$$

The cobalt−carbon bond formation in acrylates has been exploited by Harwood and co-workers[8] and Wayland et al.[9,10] to induce “living” radical polymerization, using experimental conditions where the competing chain transfer reaction is suppressed.

The primary evidence for cobalt−carbon bond formation with secondary radicals (in a polymerizing system) has come from indirect analytical methods such as electron spin resonance measurements of the free Co(II) concentration, polymerization induction times, and changes in the UV/vis spectrum of the polymerizing mixture with time/conversion.[7,11] Furthermore, the presence of Co−C bonds has been shown by Gridnev et al.[12] in their work involving reactions between porphyrins and unsaturated compounds via nuclear magnetic resonance studies. The work presented in this paper describes the application of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) to analyze poly(methyl acrylate) chains formed by a catalytic chain transfer polymerization, thereby permitting the direct observation of the cobalt−carbon bonding phenomenon in acrylate polymerization.

Experimental Section

Materials. Methyl acrylate (MA) (Aldrich, 99%) and α-methylstyrene (AMS) (Aldrich, 99%) were purified by passing through a column of activated basic alumina to remove inhibitor. Toluene (Aldrich) was used direct from the manufacturer without further purification. The monomers/solvent were sparged with nitrogen for 30 min prior to use in polymerization reactions. The initiator, azobis(isobutyronitrile) (AIBN), was purified by recrystallization from methanol. The catalytic chain transfer agent, the bis(methanol) complex of bis[(difluoroboryl)dimethylglyoximato]cobalt(II), was prepared according to the method of Bakac et al.[13] In the remainder of this paper we will use COBF as an abbreviation of the bis(methanol) complex of the catalyst.

Polymerizations for MALDI Analyses. COBF (0.0051 g, 1.14×10^{-5} mol) and AIBN (0.0466 g, 2.81×10^{-4} mol) were placed in a Schlenk flask that was then sealed with a rubber septum. The flask was then consecutively evacuated and purged with nitrogen three times. An oxygen-free solution of 8 g of methyl acrylate (9.3×10^{-2} mol) in 12 g of toluene (1.3×10^{-1} mol) was charged into the flask using standard syringe

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techniques, ensuring the exclusion of oxygen. This reaction mixture was then split into four equal volumes in modified reaction ampules, and each was placed in a water bath maintaining isothermal reaction conditions at 60 °C. After 20 min, two of the ampules were removed, and the polymer/oligomer product mixture was isolated by drying the mixtures in vacuo at 30 °C for 12 h (i.e., procedure A). The remaining two ampules were quenched in iced water and connected to a vacuum line in order to remove the remaining monomer and solvent (i.e., procedure B). Deoxygenated α-methylstyrene (3.5 g, 3.0×10^{-2} mol) was then added to the product oligomer/polymer via a syringe, and the resealed ampules were again placed in an isothermal water bath at 60 °C for a further 2 h. The product polymer/oligomer was then isolated according to procedure A as described above.

Polymerizations for Rate Data. COBF (~0.007 g, 1.6×10^{-5} mol) and AIBN (~0.25 g, 1.5×10^{-3} mol) were charged to a 250 mL round-bottom flask equipped with a Schlenk tap and a magnetic stirrer bar prior to sealing with a septum. The flask was then consecutively evacuated and purged with nitrogen three times. A solution of 50 g of methyl acrylate (0.58 mol) and toluene (100 mL, 0.94 mol) was charged into the flask via a cannular. The flask, equipped with a stirrer, was placed in an isothermal water bath (two experiments at 50 and 60 °C). Samples were taken using standard syringe techniques maintaining oxygen-free conditions and placed in preweighed aluminum pans. Conversion was measured by gravimetry.

Molecular Weight Analyses. Molecular weight distributions were determined by size exclusion chromatography (SEC) using a Shimadzu LC-10 AT VP pump, a Shimadzu SIL-10AD VP autoinjector, a column set consisting of a Polymer Laboratories 5.0 μm bead-size guard column (50×7.5 mm) followed by three linear PL columns (10^5, 10^4 and 10^3 Å), and a Shimadzu RID-10A 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 poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range $200-1.6 \times 10^6$). Molecular weights were transformed via the known[14] Mark–Houwink–Sakurada (MHS) constants for poly(methyl acrylate) in tetrahydrofuran, viz., $K = 19.5 \times 10^{-5}$ dL g^{-1} and $\alpha = 0.72$. This calibration procedure is subject to some error because the MHS constants should only be used for a specified molecular weight range; at low molecular weights the MHS constants are a function of chain length.[15] However, the exact measurement of molecular weight is not crucial to the conclusions of this work (vide infra).

Matrix-Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry Analysis. MALDI analyses were carried out using positive ion detection on either a Perseptive Biosystems, Voyager DERP instrument operated in reflectron mode or a Kratos Kompact III MALDI-TOF-MS operated in linear mode. The matrix used was 2,5-dihydroxybenzoic acid (DHB, 10 mg), with NaCl (1 mg) as the cation source. The matrix and cations were dissolved in 1 mL of a methanol/water mixture (1/1 v/v). The analyte polymers were dissolved in tetrahydrofuran at a concentration of approximately 5 mg/mL. Equal parts of the matrix and polymer solution were mixed together and deposited on the target slide and stirred until dry.

Results and Discussion

As stated in the Introduction, cobalt-mediated free radical polymerization involving secondary propagating radicals is thought to be strongly influenced by the formation of cobalt–carbon bonds (eq 3). In the case of styrene polymerization, the Co–C bond formation induces an induction period followed by a growth in molecular weight with conversion until a critical conversion (dictated by the cobalt concentration) when the system becomes chain transfer dominated. The molecular weight distribution remains constant thereafter.[7] The induction period is explained by the fact that the primary radicals which result from the decomposition of AIBN and any subsequent larger radicals will bind with the free Co(II) until the equilibrium of eq 3 has been established. Subsequent polymerization kinetics and molecular weight evolution can be explained in terms of a simple kinetic model which predicts “living”-like features in the early stages of polymerization (i.e., an almost linear increase of molecular weight with conversion), after which the chain transfer process starts to dominate. The overall effect of this entire process is a reduction in the effective catalyst concentration, which in terms of the practical application of the catalytic chain transfer synthetic method is thought to be the primary reason the chain transfer constant, C_s, is about 2 orders of magnitude lower in styrene than in methacrylates.[6,7]

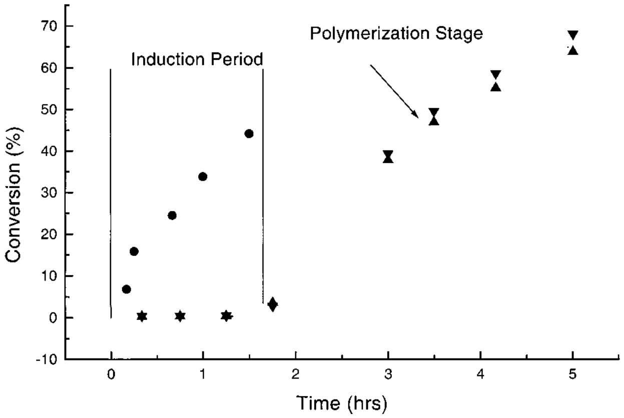


Figure 1. Conversion versus time plots for methyl acrylate polymerization in the absence of cobaloxime (●) and two replicate experiments in the presence of cobaloxime at 1.4×10^{-4} mol/L (▲ and ▼).

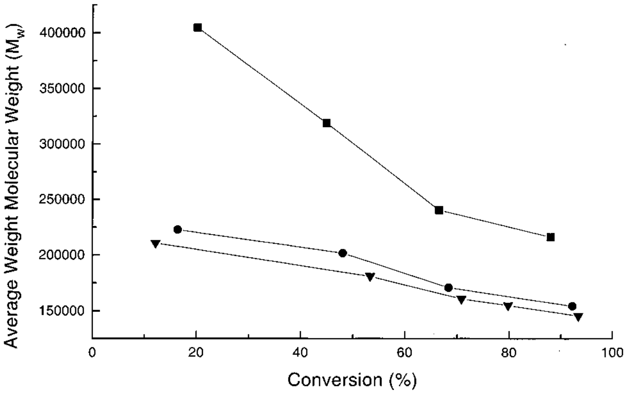


Figure 2. Plots of weight-average molecular weight versus conversion for methyl acrylate polymerization in the absence of cobaloxime (■) and two replicate experiments in the presence of cobaloxime at 9.9×10^{-5} mol/L (● and ▼).

The efficacy of catalytic chain transfer in acrylate polymerization is known to be very poor,[16] and a hypothesis can be proposed attributing this to even stronger Co–C bond formation. Because of the commercial importance of acrylate systems in coatings and resins applications,[17] we investigated the kinetics and mechanism of catalytic chain transfer in acrylate systems. The essential features of conversion/time behavior for cobalt-mediated methyl acrylate polymerization are shown in Figures 1 and 2. Figure 1 shows that a significant induction period is followed by polymerization. The molecular weight in the cobalt-mediated reactions is significantly reduced, as shown in Figure

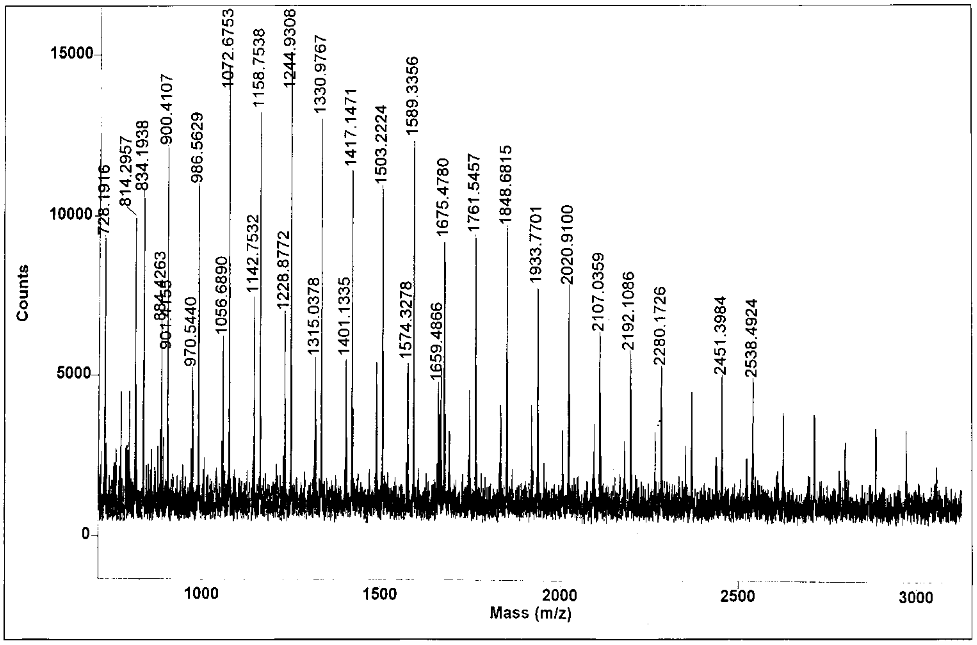


Figure 3. A MALDI-MS spectrum of poly(methyl acrylate) prepared by catalytic chain transfer polymerization, formed during the induction period shown in Figure 1. The assignment of peaks is listed in Table 1.

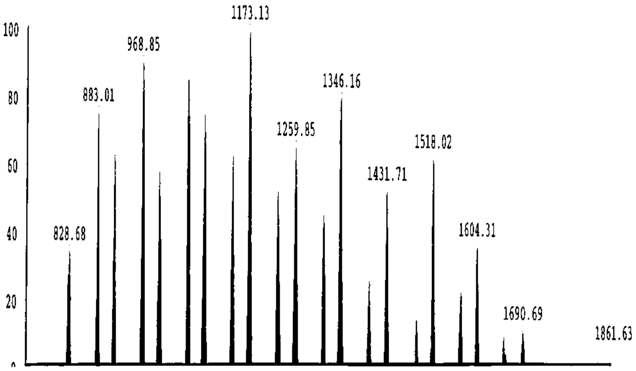


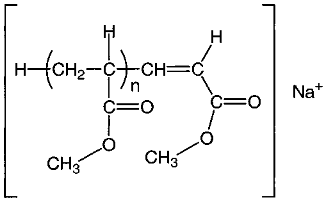
Figure 4. A MALDI-MS spectrum of poly(methyl acrylate) prepared by catalytic chain transfer polymerization after subsequent reaction with α-methylstyrene (see text for full explanation). The assignment of peaks is listed in Table 1.

Table 1. Theoretical and Experimental Peak Assignments of the Polymeric Species in Figures 3 and 4

origin		theor mass (Da)	actual mass (Da)
$MA_{13}Na^+$	1	1141.25	1142.7532
$MA_{14}Na^+$		1227.27	1228.8772
$MA_{15}Na^+$		1313.29	1315.0378
$MA_{16}Na^+$		1399.31	1401.1335
$COBF_1MA_{19}Na^+$	2	2106.17	2107.0359
$COBF_1MA_{20}Na^+$		2192.19	2192.1086
$COBF_1MA_{21}Na^+$		2278.21	2280.1726
$COBF_1MA_{23}Na^+$		2450.25	2451.3984
$AMS_1MA_{12}Na^+$	3	1173.41	1173.13
$AMS_1MA_{13}Na^+$		1259.43	1259.85
$AMS_1MA_{14}Na^+$		1345.45	1346.16
$AMS_1MA_{15}Na^+$		1431.47	1431.71

2, indicating that chain transfer is playing a significant role in this polymerization. In Figure 2, the M_w value is plotted, as this tends to be the most reliable molecular weight moment accessible via SEC for low molecular weight polymers.[18] In all cases (except the lowest molecular weight) the polydispersity was approximately two—as expected in a (catalytic) chain transfer dominated process.[6,19] Overall, methyl acrylate polymerization seems to behave in a fashion similar to that observed previously in styrene polymerization, as briefly described above.[7]

The methyl acrylate chains formed in the cobalt-mediated polymerization analyzed by MALDI are shown in Figures 3 and 4. The MALDI spectrum in Figure 3 shows polymer chains formed during the induction period. There are two distinct series of chains, as listed in Table 1. The first series shows chains with no initiator fragments, which is consistent with the known products of catalytic chain transfer reactions (**1**).[2] The second series is consistent with methyl acrylate chains capped with the cobalt catalyst, COBF (**2**). To provide further proof that we are indeed observing Co−C bonding in these chains, these samples were further reacted by heating under oxygen-free conditions in the presence of α-methylstyrene. Once again, the products were isolated and analyzed by MALDI; the resulting spectrum is shown as Figure 4. The original series is still present; however, the second series, which we attributed to cobalt-terminated chains, has now completely disappeared and been replaced by a series of chains with molecular masses consistent with poly-



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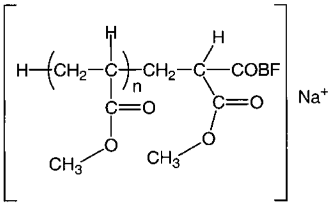
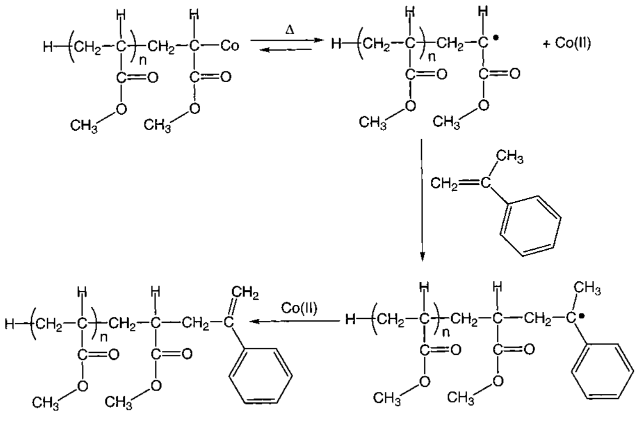
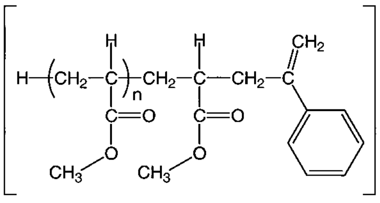


2

Scheme 1



(methyl acrylate) capped with one α-methylstyrene unit (**3**). This result is consistent with the earlier spectral assignment, showing that at elevated temperatures the Co−C bond is broken and radical addition to α-methylstyrene occurs. As the newly formed α-methylstyrene derived tertiary radical is very slow to propagate,[20] it almost exclusively undergoes catalytic chain transfer to yield a methyl acrylate oligomer with an unsaturated α-methylstyrene end group[18,21] as depicted in Scheme 1. Overall, these observations are entirely consistent with earlier studies on styrene that indicated the presence of reversible Co−C bonding; polymerization commences once an equilibrium concentration of Co(II) is attained. However, free Co(II) is present throughout the reaction, and as seen in Figure 2 there is a substantial decrease in molecular weight, which is consistent with this mechanism. At 60 °C the apparent C_s value for COBF in methyl acrylate is about 10−20,[22] indicating that the apparent elementary rate coefficient, k_{tr}, is 2 orders of magnitude lower in methyl acrylate compared to methyl methacrylate. It is still not entirely clear whether this low C_s value is solely indicative of Co−C bonding (hence a low free Co(II) concentration) or whether other factors are operative in this system.



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Conclusions

The cobalt-mediated free radical polymerization of methyl acrylate is fully consistent with a mechanism and kinetic model previously published for styrene polymerization.[7] The application of MALDI has permitted the direct observation of Co−C bonds in the catalytic chain transfer polymerization of methyl acrylate. These Co−C bonds have a profound effect on the initial rate of polymerization and on the efficiency of the catalytic chain transfer reaction, reducing the apparent C_s by orders of magnitude in comparison with a tertiary propagating radical (such as a methacrylate). The true C_s value in acrylate systems is still unknown, and further studies involving quantitative electron spin resonance are required before this can be known with any certainty.

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(22) The exact value of the apparent C_s for methyl acrylate cannot be quoted with certainty as the extent of Co−C bonding will affect the equilibrium Co(II) concentration, which as a result will be dependent on the radical concentration and (at the initial stages) the conversion. The C_s range of 10−20 quoted in the paper is the result of one experiment and should only be seen as a general indication of the magnitude of C_s for the chain transfer reaction of COBF with methyl acrylate.

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