Competition between β-Scission of Macromonomer-Ended Radicals and Chain Transfer to Cobalt(II) in Catalytic Chain Transfer Polymerization (CCTP)

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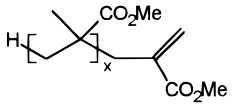
Introduction. The use of low-spin Co(II) macrocycles as extremely efficient catalytic chain transfer agents is a very effective means of producing methacrylic oligomers. This chemistry, first described in the Russian literature,[1,2] has been the subject of numerous patents describing the chemistry,[3−5] process, and applications of the products.[6,7] However, the mechanism of the reaction and an understanding of the role of Co(II) is not completely clear. The nature of the termination step is chain transfer to Co(II) yielding Co(III)−H and an unsaturated methacrylic polymer of structure **1** or macromonomer. The presence of very high levels of terminal unsaturation has been demonstrated by NMR[8] and TGA[9−11] and more recently by matrix-assisted laser desorption ionization (MALDI) Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS).[12]

Due to the very high chain transfer constants of this system it is relatively easy to prepare macromonomers of very low molecular weights down to dimer, trimer, and tetramer, etc. The vinyl group in the macromonomers of structure **1** makes them susceptible to radical



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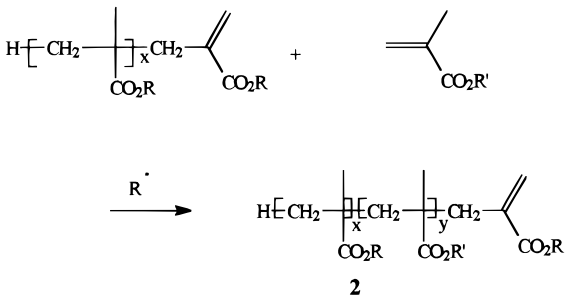
addition to form macromonomer-ended polymer radicals. This radical can undergo a β-scission reaction in addition to normal propagation and termination which compete in free radical polymerization. β-Scission results in the ultimate unit of the macromonomer terminating the propagating radical, the remainder of the radical being released as a new propagating radical giving products of general formula **2**, Scheme 1.

Macromonomers of structure **1** have been shown not to homopolymerize due to this β-scission.[13] There is indirect evidence for β-scission being the exclusive fate of the macromonomer-ended radicals when added to the polymerizations of methacrylates. In contrast when these macromonomers are added to the polymerization of monomers which propagate via radicals centered on a secondary carbon, such as styrene and acrylates, copolymerization has been observed along with β-scission.[13−15]

During the course of a catalytic chain transfer polymerization, chain transfer via β-scission is in direct competition with chain transfer to Co(II). We have been investigating the mechanism of CCTP and in particular the relative importance of these two predominant modes of termination.

The approach we have taken is to prepare pure methyl methacrylate dimer, trimer, and tetramer mac-

Scheme 1



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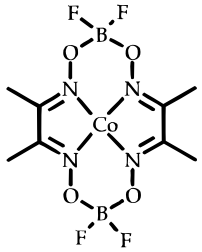
romonomers by CCTP with **3**[16] and subsequent isolation



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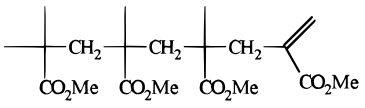
by vacuum distillation. These have been added to a catalytic chain transfer polymerization of butyl methacrylate in the presence of **3**. The combination of methyl methacrylate macromonomer with butyl methacrylate allows us to directly observe methyl methacrylate incorporation into poly(butyl methacrylate) by matrix-assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectrometry (MS), the residual mass of MMA being 100.12 and of BMA 142.20. MALDI-TOF-MS allows the resolution of molecular species that differ by approximately 4−5 Da; MALDI is a very soft ionization technique which results in little or no fragmentation.

Results and Discussion. The methyl methacrylate tetramer of structure **4** was prepared from MMA by use of **3** as a catalytic chain transfer agent.[16] Macromonomer **4** was shown to be essentially a pure macromonomer by both high-field ^{1}H and ^{13}C NMR with no detectable contamination of saturated product.



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Macromonomers of structure **4** or similar will act as effective chain transfer agents in methacrylate polymerizations even in the absence of Co(II) catalytic chain transfer agent. The free radical polymerization of butyl methacrylate in the presence of 33 weight % **4** (with respect to BMA) by AIBN in butanone solution was carried out in the presence of varying amounts of catalytic chain transfer agent **3**.[17] Table 1 summarizes the experiments along with molecular weight data on the products as measured by size exclusion chromatography relative to PMMA narrow molecular weight standards on a Polymer Laboratories 15 cm mixed E column with thf elutant at 1 cm min^{-1}. All SEC results are distorted by the presence of unreacted tetramer which is not separated from the reaction products, and

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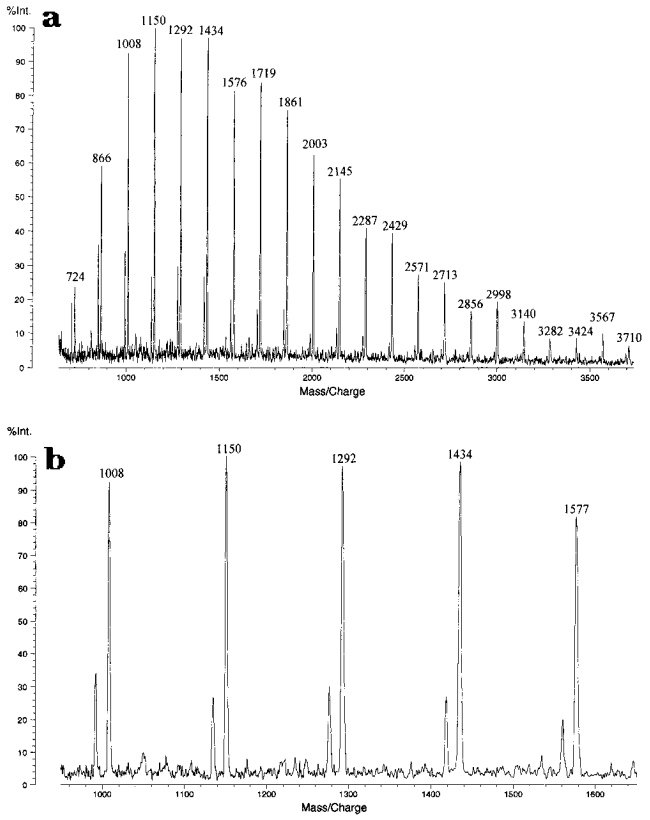

Figure 1. (a) MALDI-TOF-MS from experiment A, no Co(II) present, showing K^+ adducts of BMA_xMMA_4 with spacings of 142.20. (b) Selected area of spectrum, smaller peaks at 16 Da lower than main peaks from Na^+ adducts arising from residual Na^+.

Table 1. Reaction Conditions and Molecular Weight Data for Polymerization of Butyl Methacrylate in the Presence of MMA Tetramer and Varying Amounts of 3

	MEK/mL	nBMA/g	**3**/mg	**1**/g	AIBN/mg	Mn	PDI
A	3.00	1.350	0	0.675	7.50	1240	3.3
B	3.00	1.350	0.025	0.675	7.50	1010	2.5
C	3.00	1.350	0.075	0.675	7.50	760	1.5
D	3.00	1.350	0.15	0.675	7.50	580	1.2

chromatograms were analyzed so as to include the tetramer in the analysis.

Figure 1 shows the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of A, the reaction in the absence of catalytic chain transfer agent, **3**. We observe an envelope of molecular ions at M + 39 (K^+) separated by 142 Da, the repeat unit for PBMA. Each peak corresponds to a molecular formula of *x*BMA + 4MMA + 39, i.e. *x*(142.20) + 400.48 + 39. For example, the peak at 1861 has the molecular structure of 10 BMA units and 4 MMA units initiated by H and terminated with an unsaturated end group. The smaller peaks observed at 16 Da lower than the main series are due to Na^+ adducts arising from residual Na^+ in the sample. There is no evidence for MMA monomer, dimer, or trimer incorporation. Also there are no peaks corresponding to BMA_xMMA_8 from the incorporation of two macromonomers into the propagating chain from copolymerization of **4**. When the reaction is carried out in the presence of **3** at [BMA]:[tetramer]:**3** of 170 250:30 300:1 (mole ratio), four main poly(butyl methacrylate) polymers are clearly seen in the MALDI-TOF spectrum, Figure 2, each with the characteristic repeat unit of 142 Da, as would be expected for PBMA. The same series as observed in the absence of **3** is seen at, for example, 1434 (BMA_7MMA_4 + K^+), 1577 (BMA_8MMA_4 + K^+), etc. We also observe

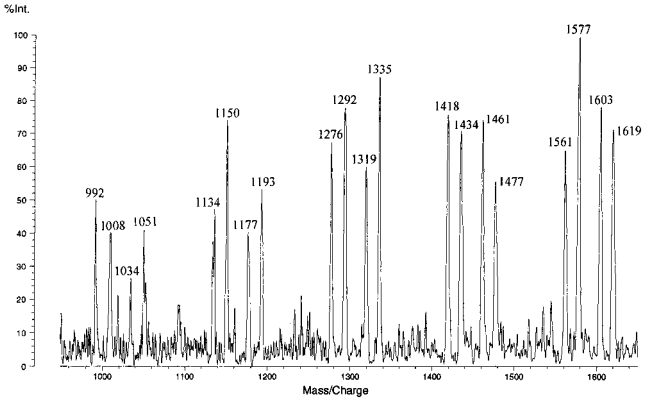

Figure 2. MALDI-TOF-MS from experiment B showing BMA_x, BMA_xMMA_1, BMA_xMMA_3, and BMA_xMMA_4 in approximately equal proportions.

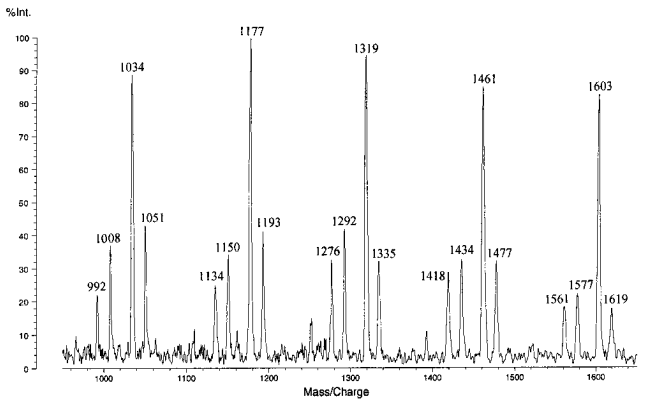

Figure 3. MALDI-TOF-MS from experiment C, the predominant species corresponds to BMA_x.

trimer incorporation, e.g. 1335 (BMA_7MMA_3 + K^+) (continuation of the above series should give a peak at 100.12 Da higher, the repeat unit of MMA, i.e. 1334) and 1477 (BMA_8MMA_3 + K^+), MMA monomer incorporation, e.g. 1134 (BMA_7MMA_1 + K^+) and 1276 (BMA_8MMA_1 + K^+), and zero MMA incorporation, e.g. 1034 (BMA_7 + K^+) and 1177 (BMA_8 + K^+). However there is no evidence for two MMA units incorporated, which would occur at 1234 (BMA_7MMA_2 + K^+) and 1376 (BMA_8MMA_2 + K^+) for the two series discussed above. As the levels of **3** are increased, we still see the same four PBMA polymers above but in different relative proportions. For both C and D the predominant macromolecular species corresponds to PBMA with no MMA macromonomer incorporation, for example 1034 (BMA_7 + K^+), Figures 3 and 4. Again there is no evidence for species corresponding to BMA_xMMA_2. A small peak is observed at 16 Da lower than the predominant peak due to Na^+ adducts from residual Na^+, as shown in Figure 4.

In no instance do we observe macromolecules which contain primary radical fragments derived from AIBN which would occur at 68 Da higher than the H-initiated polymer. This illustrates the effectiveness of **1** as a catalytic chain transfer agent. Scheme 2 summarizes the reactions that can occur in this system. However, it is more surprising that in the absence of Co(II) we observe that the macromonomer products, synthesized by Co(II) CCTP, are themselves very effective catalytic chain transfer agents and that although each kinetic chain is initiated by conventional means, i.e. by AIBN, the number of macromolecules containing this fragment is very small, reactions 1−6. Indeed, the molecular weight of the product in the absence of **3** is very low, only a factor of 2 higher than in experiment D with the highest amount of **3** present.

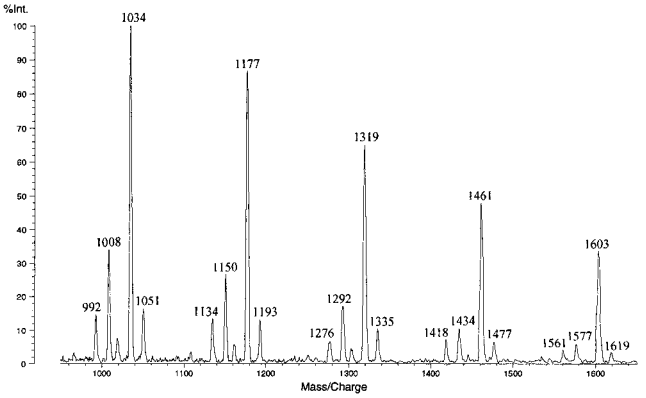

Figure 4. MALDI-TOF-MS from experiment D. Small peak 16 Da lower than mass of predominat species is due to Na^+ adduct from residual Na^+.

Scheme 2

Primary Radical Reaction Products

		AIBN	→	2R•		(1)*
R•	+	xBMA	→	R-BMA$_x$•		(2)*
R-BMA$_x$•	+	Co(II)	→	R-BMA$_x$	+ Co(III)-H	(3)
R-BMA$_x$•	+	MMA$_4$	→	R-BMA$_x$MMA$_4$•		(4)*
R-BMA$_x$MMA$_4$•		(β-scission)	→	R-BMA$_x$MMA	+ MMA$_3$•	(5)*
R-BMA$_x$MMA$_4$•	+	Co(II)	→	R-BMA$_x$MMA$_4$	+ Co(III)-H	(6)

Reinitiation Products

Co(III)-H	+	xBMA	→	H-BMA$_x$•	+ Co(II)	(7)
H-BMA$_x$•	+	Co(II)	→	H-BMA$_x$	+ Co(III)-H	(8)
H-BMA$_x$•	+	MMA$_4$	→	H-BMA$_x$MMA$_4$•		(9)
H-BMA$_x$MMA$_4$•		(β-scission)	→	H-BMA$_x$MMA	+ MMA$_3$•	(10)
H-BMA$_x$MMA$_4$•	+	Co(II)	→	H-BMA$_x$MMA$_4$	+ Co(III)-H	(11)
MMA$_3$•	+	xBMA	→	MMA$_3$BMA$_x$•		(12)*
MMA$_3$BMA$_x$•	+	MMA$_4$	→	MMA$_3$BMAxMMA$_4$•		(13)*
MMA$_3$BMA$_x$•	+	Co(II)	→	MMA$_3$BMA$_x$	+ Co(III)-H	(14)
MMA$_3$BMA$_x$MMA$_4$•		(β-scission)	→	MMA$_3$BMA$_x$MMA	+ MMA$_3$•	(15)*
MMA$_3$BMA$_x$MMA$_4$•	+	Co(II)	→	MMA$_3$BMA$_x$MMA$_4$	+ Co(III)-H	(16)

Equations 7−16 summarize the possible reactions assuming initiation is predominantly by the secondary radical. We observe no evidence for the incorporation of 7 MMA units within PBMA, the product of chain transfer to cobalt(II) from MMA trimer initiated and MMA tetramer terminated radical, (16). Therefore we can assume that the relative rate of β-scission relative to transfer to Co(II) from the macromonomer-terminated propagating radical is large. Thus reactions 6 and 11 will also be slow relative to (5) and (10), respectively. Hence we would not expect any macromolecules of the general structure BMA_xMMA_4, AB block copolymers, but $MMA_3BMA_xMMA_1$ ABA triblock copolymers arising from β-scission, (15). In the absence of Co(II) the only possible reactions from secondary radicals are (12), (13), and (15), labeled with an asterisk, and the only product obtained is the ABA block copolymer, MMA_3BMA_x-MMA_1, as would be expected from β-scission. A combination of transfer to Co(II) and β-scission results in both BMA_xMMA_1 and MMA_3BMA_x macromolecules in equal number, as seen in Figures 2−4. No reactions in this scheme result in macromolecules of the general formula MMA_2BMA_x, in agreement with the experimental observations.

In conclusion we have used MALDI-TOF-MS to directly demonstrate that in copolymerization of methacrylates with methacrylate macromonomers from CCTP, β-scission is indeed the predominant reaction pathway for the macromonomer-ended propagating radical. We see no evidence for copolymerization of these macromonomers and indeed no evidence for chain transfer to Co(II) by macromonomer-ended radicals. The macromonomers themselves are effective CCTA's with the predominant product being an ABA triblock copolymer from a radical polymerization. In the presence of **3** chain transfer to Co(II) from propagating PBMA competes with macromonomer addition followed by β-scission. Thus a competition between β-scission and chain transfer to Co(II) will always be present in Co(II)-mediated methacrylic polymerization, especially during the later stages of the reaction as it approaches high conversion.

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Supporting Information Available: Full mass range MALDI-TOF-MS from experiments A−D, Figures 5−8. Peaks below 500 Da are due to matrix fragments and residual cations e.g. Na^+ and K^+ (5 pages). Ordering information is given on any current masthead page.

References and Notes

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(16) MMA (150 mL), **3** (45 mg), and dimethyl 2,2′-azobis-(isobutyrate) (700 mg) were dissolved in degassed butanone (150 mL). The reaction mixture was heated to 75 °C for a period of 24 h, after which time the solvent and excess monomer were removed using a rotary evaporator. SEC of the products at this stage showed a mixture of MMA oligomers which were subsequently separated by Kugelrohr distillation. MMA dimer was collected at a pressure of 1.2×10^{-1} mbar and a temperature of 130 °C, MMA trimer was collected at 1.2×10^{-1} mbar and 170 °C, and in a separate experiment, MMA tetramer was removed at 6×10^{-2} mbar and 150 °C.
(17) In a typical polymerization reaction a stock solution was made up by dissolving *n*-butyl methacrylate (6.0 mL), AIBN (30 mg), and the required amount of MMA oligomer (e.g. 2.70 g of MMA tetramer) in butanone (12 mL). The stock solution was then deoxygenated by performing three freeze−pump−thaw cycles in liquid nitrogen. Equal volumes of solution were then removed to be used for polymerization reactions, with the required amount of **3** being added from a separate stock solution. Reactions were heated to 60 °C for a period of 24 h.
(18) MALDI-TOF-MS was carried out on a Kratos Kompact Maldi III (Manchester, U.K.) using 2,5-dihydroxybenzoic acid as the matrix with KCl added as a source of K^+.

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