Macromolecules **2004,** *37,* 6667−6669 **6667**

New Thiolate−Cobalt(II) Complexes for Catalytic Chain Transfer Polymerization of Methyl Methacrylate

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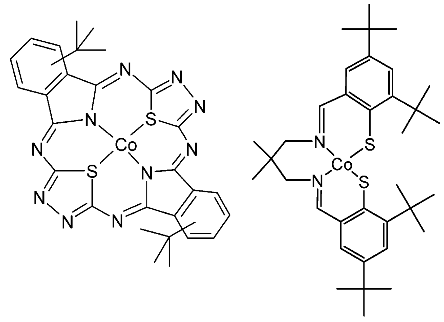
Received April 15, 2004
Revised Manuscript Received July 20, 2004

Introduction. The control of molecular weight in methacrylate polymerization by the introduction of catalysts that can influence the process of chain transfer is well established.[1,2] Catalytic chain transfer (CCT) reactions that employ low-spin Co^{II} complexes as catalysts are the most efficient routes to molecular weight reduction in homogeneous[3−14] and heterogeneous systems without the use of stoichiometric chain terminators.[15−19] CCT reactions usually lead to the synthesis of a large variety of structured monofunctional macromonomers that are terminated by a vinylic functionality.[20−24] This terminal group creates the potential for synthesizing a wide variety of polymeric products which may be used to develop novel structured materials. This versatility has led to the application of CCT polymerization in the automotive, paper, and printing industries where materials with high-quality finishes are required.[20−24] For example, the copolymerization of macromonomers with other smaller monomers can lead to graft copolymers or α,ω-telechelic materials. In addition, star-shaped polymers or even branched and hyperbranched systems can be synthesized.[23] All of these rely upon the availability of a wide range of macromonomer species.

The nature of the products obtained from CCT polymerization in the presence of Co chelates depends strongly upon the steric and electronic properties of the ligand.[20−24] While Co catalysts chelated by ligands containing four coordinating N donors have been employed extensively in CCT polymerization reactions, few Co complexes containing S ligation have been evaluated as potential catalysts for CCT.[23,25] The incorporation of S atoms into the phthalocyanin-like macrocyclic ligand in compound **1** (Scheme 1) significantly decreases the catalytic chain transfer activity (compound **1** transfer constant $C_T < 50$).[23] Thus, the incorporation of S donors into the coordination sphere of the Co center may be used to moderate the activity of the Co catalyst and thereby control the product distributions of CCT reactions. We report herein the synthesis, characterization, and evaluation of a novel (N_2S_2) sulfur-ligated Co^{II} complex [CoL_S] (compound **2** in Scheme 1) as a catalyst for CCT polymerization reactions.

Experimental Section. a. Materials. Methyl methacrylate (MMA, Aldrich) was dried over CaH_2 for 48 h and distilled just before use under reduced pressure. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, 98%, Acros) was purified by recrystallization from THF. [ZnL_S] was prepared directly from $Zn(OAc)_2$ (Supporting Information). All solvents were distilled and degassed under dinitrogen prior to use. All reactions were carried out in a dinitrogen atmosphere unless otherwise stated using standard Schlenk line techniques.

Scheme 1



Compound 1 **Compound 2**

b. Synthesis of [CoL_S]·$2H_2O$. A solution of Co$(OAc)_2$·$4H_2O$ (0.054 g, 0.22 mmol) in methanol (10 mL) was added dropwise to a solution of [ZnL_S] (0.126 g, 0.2 mmol) in chloroform (30 mL) and the mixture stirred at room temperature for 10 min by which time a bright red precipitate had formed. An excess of methanol was added and the crude product collected by filtration, recrystallization from chloroform gave red [$Co^{II}L_S$] (0.097 g, 0.16 mmol, 78%).

[CoL_S]·$2H_2O$: MS (ES+): 623 ($C_{35}H_{52}N_2S_2Co$ = [CoL_S]$^+$ requires 623). IR (KBr pellet): 2960 s, 2909 s, 2870 s, 1629 s, 1588 s, 1522 m, 1466 s, 1386 s, 1362 s, 1266 s, 1200 m, 1154 m, 1059 m, 949 m, 763 m, 683 m cm^{-1}.

Microanalysis (CHN): [$Co^{II}L_S$] requires C 67.38%, H 8.40, N 4.49%; found C 67.42%, H 8.70%, N 4.37%.

c. Typical Polymerization. Known amounts of [CoL_S] (6 mg) and AIBN (0.1 g) were added to a glass tube (100 mL) fitted with a three-way stopcock connected to a dinitrogen line and a vacuum pump. The glass tube was pump-filled with dinitrogen before being charged with known amounts of MMA (20 mL) and butanone (20 mL). The polymerization reactions were conducted at 70 °C with vigorous stirring. Samples were withdrawn throughout the polymerization by syringe, and monomer conversion was calculated by ^1H NMR spectroscopy. The polymer sample was dissolved in THF, the solution was filtered, and the polymer was precipitated in heptane, separated by filtration, and dried under vacuum.

d. Polymer Characterization. Molecular weight data were obtained by gel permeation chromatography with two PLgel 5 μm Mixed-D columns (Polymer Laboratories, M_w range 200−400 000) and an evaporative light scattering detector (Polymer Laboratories) using chloroform as the solvent at 50 °C. Calibration was accomplished with PMMA narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1 mL min^{-1}. ^1H NMR data were collected on a Bruker 300 MHz NMR spectrometer in $CDCl_3$. Infrared data were collected on a Nicolet 730 IR spectrometer using OMNIC software.

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10.1021/ma049267z CCC: $27.50

Table 1. Molecular Weight and Monomer Conversion for the Polymerization of Methyl Methacrylate in Butanone at 70 °C[a]

entry	$[Co(II)L_S]$ [M] $\times 10^{-4}$	AIBN [M] $\times 10^{-2}$	reaction time (h)	yield (%)	M_n[b]	M_w[b]	PDI[b]
1	2.4	1.5	1	27	55 000	81 000	1.42
2	2.4	1.5	4	65	47 000	69 000	1.47
3	4	1.5	1	25	37 000	53 000	1.43
4	4	1.5	4	67	32 000	47 000	1.45
5	4	0	4	<1			
6	0	1.5	1	22	102 000	144 000	1.43
7	0	1.5	4	73	105 000	170 000	1.62

[a] [MMA] = 4.7 M. [b] Measured using GPC relative to PMMA standards.

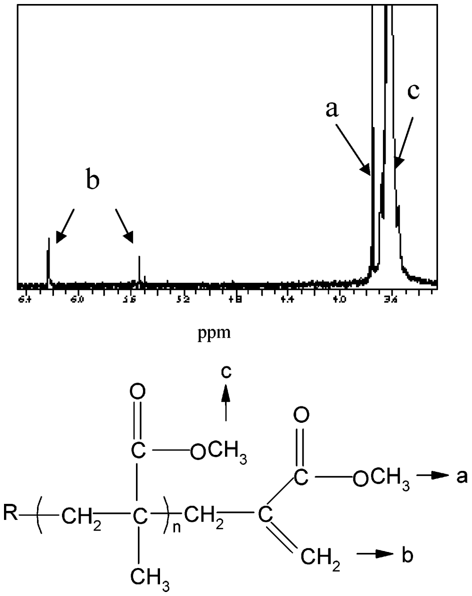

Figure 1. ^{1}H NMR spectrum of MMA macromonomer (Table 1, entry 4); $M_{n,NMR} = 29\,000$.

Results and Discussion. The transmetalation of $[ZnL_S]$ with $Co(OAc)_2{\cdot}4H_2O$ affords the corresponding Co^{II} complex $[Co(L_S)]$ in 78% yield. We have been unable to confirm the molecular structure of $[CoL_S]$ by X-ray crystallography although our available evidence, together with comparisons with the chemistry of Co^{III} with $[L_S]^{2-}$ and with the X-ray crystal structures of $[ML_S]$ (M = Ni, Cu, Pd, Zn),[26] suggests a monomeric formulation for $[CoL_S]$ in which Co^{II} is coordinated by the N_2S_2 coordination sphere of one $[L_S]^{2-}$ ligand. $[Co^{II}L_S]$ is stable to air in the solid state, but in dichloromethane solution $[Co^{II}L_S]$ decomposes, presumably to a Co^{III} species that results from the rapid oxidation of $[Co^{II}L_S]$ by dioxygen. Support for this decomposition process derives from the synthesis of $[Co^{III}L_S(OAc)]$ which can be achieved by the reaction of $[ZnL_S]$ with $Co(OAc)_2{\cdot}4H_2O$ in air in dichloromethane solution.[27]

When a solution of methyl methacrylate, $[Co^{II}L_S]$, and AIBN in butanone is maintained under dinitrogen at reaction temperature (70 °C), the viscosity of the solution can be seen to progressively increase. This solution is red-orange and homogeneous, which indicates that $[Co^{II}L_S]$ is soluble in the polymerization medium. Under these conditions there is a molecular weight change with monomer conversion that results from radical polymerization (Table 1, entries 1–4). However, comparison to the radical polymerization in the absence of metal catalyst (Table 1, entries 6 and 7) clearly shows that the molecular weight of PMMA in the presence of $[Co^{II}L_S]$ has been dramatically reduced. Furthermore, it is clear that the rate of polymerization is independent of the concentration of $[Co^{II}L_S]$, and no polymerization occurs in the absence of AIBN (Table 1, entry 5). These experimental data suggest that the radical polymerization of MMA is controlled and that $[Co^{II}L_S]$ enhances the chain transfer reaction. The ^{1}H NMR spectrum of the low molecular weight product (Table 1, entry 4) shows vinyl resonances (peak b in Figure 1). Integration of these vinyl resonances against the bulk methoxy resonance of the PMMA chain (peak c) demonstrates that the molecular weight data obtained from NMR ($M_{n,NMR} = 29\,000$) do indeed match closely the GPC data ($M_n = 32\,000$, entry 4 in Table 1).

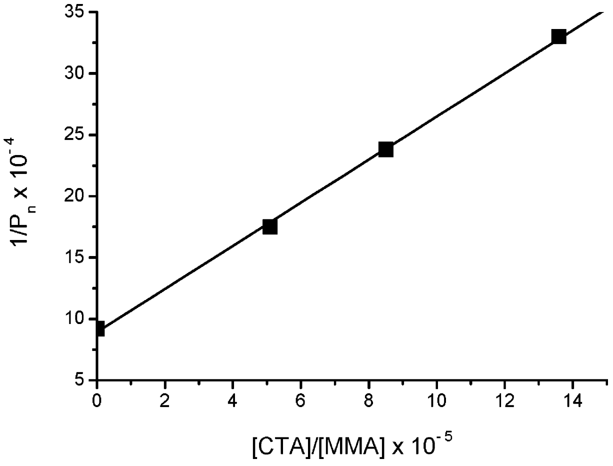

Figure 2. Mayo plot for the polymerization of MMA at 70 °C in the presence of $[Co(II)Ls]$.

The activity of transfer agent is defined in the terms of their chain transfer constant ($C_T = k_{tr}/k_p$; k_{tr} is the rate constant for chain transfer by a growing polymer chain, and k_p is the rate constant for addition of an additional monomer unit to a growing polymer chain). Traditionally, chain transfer constants can be evaluated by applying the Mayo equation (eq 1).[2,28–30]

$$\frac{1}{P_N} = \frac{1}{P_{N0}} + \frac{k_{tr}}{k_p}\frac{[CTA]}{[MMA]} \qquad (1)$$

where P_N is the number-average degree of polymerization, P_{N0} is the number-average degree of polymerization in the absence of chain transfer agent, and [CTA] and [M] are the concentrations of transfer agent and monomer, respectively. Low conversion polymerizations (<10% conversion) were performed with a range of concentrations of $[Co^{II}L_S]$ (from 0 to 6.4×10^{-4} M) at a constant concentration of AIBN ([AIBN] = 0.015 M). A plot of $1/P_N$ vs [CTA]/[MMA] (Figure 2) yields a chain transfer constant, C_T, of 17.5, which is much lower than those for typical N_4 CCT catalysts [CoL_N transfer constant (C_T) > 10^3]. Thus, with easily accessible and measurable loadings of ca. 100–400 ppm of the $[CoL_S]$ catalyst, it is very easy to generate high yields of high molecular weight macromonomers in the region of M_n 10 000−100 000. By contrast, if the same macromonomers were to be targeted using the traditional N_4 catalysts, then the concentration of catalyst required would need to be accurately measured to extremely low levels.

Conclusions. A novel N_2S_2 donor Co^{II} complex ([CoL_S]) incorporating two thiophenolate donors has been synthesized. The replacement of two nitrogen atoms with sulfur in the coordination center significantly influences the catalytic chain transfer activity. [CoL_S] is a much milder as a chain transfer agent ([CoL_S] transfer constant (C_T) is ca. 17.5) than the typical corresponding N_4 complexes (typically (C_T) > 10^3). While this diminution in activity is well-known,[23] we have shown here for the first time that the decreased catalytic chain transfer activity of [CoL_S] can be used to produce controlled high molecular weight macromonomer species at readily accessible and practical concentrations of CCT catalyst.

Acknowledgment. We gratefully acknowledge The University of Nottingham Institute of Materials (UNIMAT), the EPSRC, CONACYT, and DGAPA-UNAM, and Uniqema (SRF award) for support. We thank also Prof. Andrew Harrison for a measurement with SQUID magnetometry at University of Edinburgh. S.M.H. is a Royal Society−Wolfson Research Merit Award Holder.

Supporting Information Available: Synthesis and characterization of [ZnL_S] complexes and experimental data for measurement of C_T. This information is available free of charge via the Internet at http://pubs.acs.org.

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MA049267Z