Metal-Mediated Polymerization of Acrylates: Relevance of Radical Traps?

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Introduction. Metal-mediated vinyl insertion polymerization of polar monomers, especially acrylates, is an area of great current interest because of the control over polymer microstructure, molecular weight, and polydispersity that such systems are expected to provide.[1] Recently, several reports have appeared claiming insertion polymerization of acrylates by late transition metal-based systems.[2–4] The common feature of these systems is that they employ methylaluminoxane (MAO) as the activator. The primary evidence cited against an alternative radical mechanism has been the failure of radical traps to halt the polymerization. While the reliability of phenolic radical traps, such as di-*tert*-butylphenol, has been questioned,[5] stable radicals such as galvinoxyl, DPPH, and TEMPO have been used as benchmark traps for probing the intermediacy of radicals in polymerizations. The test is based on the hypotheses that the radical trap reacts only with radical species in the medium and is not affected by other species. However, as illustrated below for a copper-based system, this may not hold for systems where the possibility of deactivation of the trap, for example by reduction to the anion, exists. Our work calls into question the widespread use of radical traps for probing reaction mechanism in metal-based systems employing MAO.

Experimental Section. a. Synthesis of [1,2-Bis-(4,4-dimethyl-2-oxazolin-2-yl)ethane]copper(II) Dichloride. In a round-bottom flask $CuCl_2\cdot 2H_2O$ (3.7 mmol) was dissolved in anhydrous ethanol (35 mL) at room temperature. This was followed by the addition of triethylorthoformate (4 mL). To this solution, 1,2-bis-(4,4-dimethyl-2-oxazolin-2-yl)ethane (DMOX) (1.2 mmol) (Aldrich, used as received) was then added. A bright yellow precipitate formed almost immediately. The precipitate was collected by vacuum filtration, washed with pentane, and dried under high vacuum. Yield: 50%. C, H, N, Cl analyses were satisfactory.

b. Polymer Synthesis and Characterization. Polymerizations were performed using oven-dried glassware in a drybox. For those carried out with the copper compound, a vial was charged with a stirbar and Cu(DMOX)Cl_2 (0.022 mmol) followed by the addition of distilled chlorobenzene (5 mL) to form a yellow solution. Subsequently, MMA (0.01 mol) was added to this solution. A 30% MAO solution was prepared separately by the addition of dry MAO (300 mg) to chlorobenzene (700 mg). To the Cu(DMOX)Cl_2/MMA solution, 80 mg of the MAO solution was added, thus inducing a quick color change from yellow to green to colorless. The reaction was then sealed and allowed to react at the appropriate temperature for 21 h. The formed polymer was precipitated in a large excess of 5% HCl in methanol and stirred overnight to dissolve any catalyst residues. The insoluble polymer was filtered and dried under vacuum overnight. For those reactions initiated with other metal species or AIBN, similar procedures were followed.

NMR spectra of polymers were recorded on a Bruker DPX 300 MHz spectrometer to determine the tacticity from triad distributions. Polymer molecular weights were determined against a polystyrene standard by gel permeation chromatography on either a Waters Associates 600 using Millenium 32 software or a Shimadzu chomatograph using EZSTART 7.2 software. Each of these instruments contained three Waters Styragel HR columns at 35 °C in chloroform (1 mL/min).

c. EPR Experiments. EPR spectra were measured with a Bruker ECS 106 with a modulation amplitude and modulation frequency of 60 G and 100 kHz, respectively. The spectra were measured at 77 K. Four samples were prepared. The first three were prepared in a nitrogen-filled glovebox and contained chlorobenzene (1), chlorobenzene, MMA and Cu(DMOX)Cl_2 (2), chlorobenzene, MMA, Cu(DMOX)Cl_2, and MAO (3), and finally (3) was exposed to air causing reoxidation of the copper (4). Signals were only observed for samples (2) and (4), indicating the presence of copper(II). The absence of signal for sample (3) indicated that all of the copper had been reduced to the EPR silent Cu(I).

To test for the presence of a galvinoxyl signal, a solution of galvinoxyl (4.3 mM) was prepared in chlorobenzene, giving a very deep purple color. The EPR of this solution gave a single, strong signal for the organic radical. A second solution was prepared by the addition of Cu(DMOX)Cl_2 (0.022 mmol) to chlorobenzene (5 mL), followed by the addition of MMA (0.01 mmol). To this solution, a 30% MAO solution (80 mg) was then added turning the color from yellow to colorless. There was no EPR signal for this solution. The solution was briefly allowed to stir before the addition of galvinoxyl (0.021 mmol), which resulted in a solution that was once again 4.3 mM in galvinoxyl, and bright red in color. This sample was capped, quickly removed from the glovebox, and placed in liquid nitrogen. An EPR spectrum of this second sample showed no signal, indicating the presence of EPR-silent Cu(I), as was observed previously, and also the complete disappearance of the galvinoxyl radical. EPR experiments with other metal compounds were carried out analogously.

For reactions of radical traps with MAO only, 0.02 mmol of galvinoxyl, DPPH, and TEMPO were separately dissolved in chlorobenzene. The EPR spectrum showed an organic radical peak in each case. To each solution, 30% MAO solution (80 mg) was then added. These solutions were then allowed to stir for several minutes, and once again EPR spectra were taken. In all cases, there was a complete disappearance of the original EPR signal.

Results and Discussion. The compound Cu(DMOX)Cl_2 is an air-stable, distorted tetrahedral complex, whose crystal structure is shown in Figure 1. At a relatively low MAO to copper ratio of 20, an active system for the homopolymerization of methyl methacry-

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Table 1. Methyl Methacrylate Homopolymerization[a]

entry	initiator/catalyst	cocatalyst[b]	inhibitor[c]	temp (°C)	yield (%)	$M_w{}^d \times 10^{-3}$	$M_w/M_n{}^d$	tacticity[e] (%)		
								mm	mr	rr
1	$Cu(DMOX)Cl_2$	MAO		50	55	316	4.3	5.3	26.6	68.1
2	$Cu(DMOX)Cl_2$	MAO		60	60	278	3.8	4.6	29.9	65.5
3	$Cu(DMOX)Cl_2$	MAO		70	48	389	4.4	5.3	30.6	64.1
4	$Cu(DMOX)Cl_2$	MAO		80	42	257	3.7	5.9	31.6	62.5
5	$Cu(DMOX)Cl_2$			40	NR					
6	$Cu(DMOX)Cl_2$	MAO	galvinoxyl	40	41	131	4.2	5.4	30.6	63.9
7	AIBN		galvinoxyl	60	NR					
8	AIBN			60	77	73	1.9	5.3	34.4	60.4
9	AIBN			70	77	62	1.5	7.0	34.5	58.2
10	AIBN			80	81	32	1.5	6.3	36.4	57.3
11	AIBN	MAO		60	72	114	1.3	4.9	33.9	61.2
12	$Cu(OAc)_2$	MAO		60	25	170	3.9	5.9	37.9	56.2

[a] Conditions: AIBN (0.030 mmol) or Cu compound (0.022 mmol); PhCl, 5 mL; MMA, 0.01 mol; 21 h in drybox. [b] 80 mg of 30% MAO solution (0.42 mmol). [c] 1 equiv of galvinoxyl. [d] Determined by GPC against polystyrene standards using refractive index detector. [e] Calculated from ^{1}H NMR integration of α-methyl resonances.[9]

Table 2. Methyl Acrylate Homo- and Coolymerization[a]

comonomer	temp (°C)	MA conv (%)	alkene incorp (mol %)[b]	M_w ($\times 10^{-3}$) (M_w/M_n)[c]	tacticity[d] (%)		
					threo	racemic	erythro
	50	50		126 (1.7)	25.2	48.6	26.2
	60	49		122 (1.8)	25.8	48.3	25.7
	70	47		105 (3.2)	25.5	49.6	24.9
ethene (500 psi)	40	20	16.4	126 (2.1)			
propene (2 g)	60	27	22.5	257 (3.7)			

[a] Conditions: $Cu(DMOX)Cl_2$, 0.022 mmol; 30% MAO solution, 0.42 mmol (80 mg); PhCl, 5 mL; 0.01 mol of MA; 21 h in drybox. [b] Calculated from integration of ^{1}H NMR resonances. [c] Determined by GPC against polystyrene standards using refractive index detector. [d] Calculated from ^{1}H NMR integration of methylene resonances.[10]

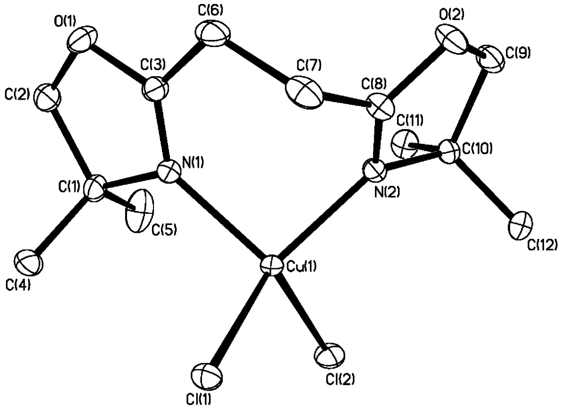

Figure 1. An ORTEP view of $Cu(DMOX)Cl_2$, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu(1)−N(1), 1.9914(17); Cu(1)−N(2), 1.9940(16); Cu(1)−Cl(1), 2.2221(5); Cu(1)−Cl(2), 2.2306(6); N(1)−Cu(1)−N(2), 93.91(7); N(1)−Cu(1)−Cl(1), 99.42(5); N(2)−Cu(1)−Cl(1), 134.57(5); N(1)−Cu(1)−Cl(2), 135.82(6); N(2)−Cu(1)−Cl(2), 100.18(5); Cl(1)−Cu(1)−Cl(2), 99.75(2).

late (MMA) is formed from this species (Table 1). Polymerizations were carried out at various temperatures from ambient to 80 °C with good monomer conversions. A comparison with the polymers obtained using either the radical initiator AIBN or a combination of AIBN and MAO showed that the polymers formed by the copper-based system were slightly more syndiotactic (e.g., rr dyad was 5−8% higher) for all three temperatures examined (60, 70, and 80 °C) (see Table 1). The system is also effective for the homopolymerization of methyl acrylate (MA) and its copolymerization with ethene and propene (Table 2). However, the poly(methyl acrylate) obtained is atactic. The introduction of ethene or propene into the MA homopolymerization system resulted in the formation of acrylate-rich copolymers in greatly reduced yields. Additionally, the level of alkene incorporation in the copolymers was similar to that observed by us and others for well-documented radical polymerization systems.[6−8] $Cu(OAc)_2$ was tested with our system and yielded PMMA with significantly lower yield and syndiotacticity than that observed with $Cu(DMOX)Cl_2$ (see Table 1), thereby demonstrating the importance of the ligand.

The addition of MAO to the EPR-active $Cu(DMOX)Cl_2$ resulted in the formation of an EPR-silent Cu(I) species. This occurred on the same time scale as the onset of polymerization, suggesting that the reduction of Cu(II) to Cu(I) alkyl is necessary for polymerization. No further change in EPR spectrum occurred in the course of the polymerization; however, the Cu(I) species was reoxidized to Cu(II) upon exposure of the polymerization system to air.

To examine whether free radicals were involved in the polymerization process, 1 equiv of galvinoxyl per Cu was added to the reaction mixture. As shown in Table 1, a similar yield of PMMA was obtained. In contrast, an equivalent amount of galvinoxyl totally quenched the polymerization activity of AIBN. The above results with galvinoxyl posed a dilemma. The polymerization profile, specifically the failure to homopolymerize unactivated alkenes (e.g., ethene or 1-alkenes) or to incorporate them in significant amounts in copolymerizations, clearly suggested a radical mechanism; initiation of radical polymerization by metal-based systems is quite common.[7,8] In contrast, the strongest (and the most widely accepted) evidence against a radical mechanism was the failure to stop or slow the MMA homopolymerization by adding galvinoxyl. However, we observed the disappearance, at ambient temperature, of the EPR signal of galvinoxyl (0.021 mmol) when a solution of it in chlorobenzene was added to a solution prepared by dissolving $Cu(DMOX)Cl_2$ (0.022 mmol) and MMA (0.01

mol) in chlorobenzene (5 mL) followed by the addition of a 30% MAO solution (80 mg). To probe the generality of the deactivation of galvinoxyl by the combination of a metal species and MAO, $Cu(OAc)_2$, $Ni(acac)_2$, $Co(acac)_2$, and $Fe(OAc)_2$ were also employed under similar reaction conditions. In every case the EPR signal of galvinoxyl disappeared, and polymer (PMMA) formation was observed.

The above experiments led us to suspect that MAO was responsible for the deactivation of galvinoxyl through reduction. Indeed, EPR experiments demonstrated that the radical signal of galvinoxyl, as well as two other commonly employed radical traps DPPH and TEMPO, *disappeared* upon the addition of excess MAO. Additionally, we observed that AIBN-initiated homopolymerization of MMA was completely halted when any one of the above radical traps was added, *but polymer was obtained when MAO was also present in the reaction mixture* (conditions: MMA, 10 mmol; AIBN, 0.024 mmol; galvinoxyl, DPPH, or TEMPO, 0.021−0.026 mmol; PhCl, 5 mL; 18 h, 60 °C, 80 mg of 30% MAO in PhCl).

Finally, to ascertain the fate of galvinoxyl in its reaction with MAO, galvinoxyl (0.021 mmol) was mixed with 30% MAO in PhCl (80 mg). After stirring for 10 min at ambient temperature, the mixture was added to an excess of 0.1 M aqueous HCl, and the resultant diamagnetic organic product was isolated. Mass spectral analysis suggested a phenol derived from galvinoxyl (*m*/*z*, 423 (MH^+)), formed by the reduction of the latter to the anion by MAO, a strong reducing agent.

Conclusion. The use of radical traps such as galvinoxyl, DPPH, and TEMPO as probes for radical mechanism in metal-based systems employing MAO can lead to the wrong conclusion. We had earlier reported that radical traps can react with metal hydrides and halt or slow down metal-centered nonradical reactions.[11] Now, we show that radical traps may fail to intercept even radical reactions that proceed in the presence of MAO. Clearly, it is necessary to rely on several independent lines of evidence before coming to a firm mechanistic conclusion. For example, the formation of copolymers whose compositions vary significantly from that predicted from the radical reactivity ratios must be demonstrated before a nonradical mechanism can be invoked.

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Supporting Information Available: Details of crystal structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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