*Macromolecules* **2006,** *39,* 5555−5558

# Notes

## Unfavorable Coordination of Copper with Methyl Vinyl Ketone in Atom Transfer Radical Polymerization

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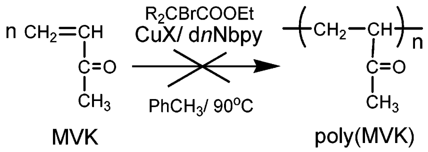
*Received February 18, 2006*
*Revised Manuscript Received May 25, 2006*

Atom transfer radical polymerization (ATRP) has recently become one of the well researched areas of polymer science.[1−4] Copper-catalyzed ATRP is a robust technique that provides tailor-made vinyl polymers through radical polymerization. Although a wide range of monomers have been used in copper-mediated ATRP,[5] vinyl acetate (VAc) is difficult to polymerize in a controlled manner.[6,7] Unlike methyl methacrylate (MMA) and styrene, VAc lacks conjugation and, thus, its radicals are highly reactive, less stable and more prone to termination and transfer. The difficulty encountered in ATRP of VAc is also attributed to a low equilibrium constant ($K_{eq}$).[8] Several attempts to polymerize VAc in a controlled manner by nitroxide- and copper-mediated radical polymerizations have resulted only in a partial control.[8−10]

Methyl vinyl ketone undergoes classical free radical polymerization using AIBN as initiator at 60 °C in ethanol, producing poly(methyl vinyl ketone) in moderate yield.[11,12] However, there has been no prior report of a controlled radical polymerization of methyl vinyl ketone. An ability to polymerize methyl vinyl ketone in a controlled fashion followed by a polymer analogous Baeyer−Villiger oxidation of the ketone group may offer an interesting and indirect approach to the preparation of poly(vinyl acetate) (PVAc) of controlled structure. With this motivation in mind, we first established the feasibility of polymer analogous Baeyer−Villiger oxidation of poly(methyl vinyl ketone) (PMVK). The PMVK was synthesized by free radical polymerization as reported elsewhere.[11,12] The obtained PMVK exhibited $M_{n,SEC} = 17\,500$ g/mol ($M_w/M_n = 2.77$), which was subjected to Baeyer−Villiger oxidation using *m*-chloroperbenzoic acid as the oxidant. The resulting product was characterized as a poly(VAc-*co*-MVK) copolymer with 15:85 mol % of VAc: MVK as determined by $^1$H NMR (Figure S1, Supporting Information).

We, then, proceeded to study the polymerization of methyl vinyl ketone (MVK) via copper-mediated ATRP using various initiator/CuX/ligand/solvent systems (Table S1, Supporting Information). The ligands such as *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), *N*-(*n*-propyl)-2-pyridylmethanimine (NPPI), 2,6-bis[1-(2,6-diisopropyl phenylimino)ethyl]pyridine (BPIEP), 4,4′-di(*n*-nonyl)2,2′-bipyridine (d*n*Nbpy), and 2,2′-bipyridine (bpy) were used in the presence of CuX (X = Cl or Br) with [MVK]:[I]:[CuX]:[ligand] = 127:1:1:2. Experiments were conducted in different solvents, such as diphenyl ether, THF, and anisole, and also in bulk at 90 °C for several hours (3−24 h).

**Scheme 1. Non-polymerizing Nature of Methyl Vinyl Ketone (MVK) Due to Its Strong Coordination with Copper Catalyst**



During the polymerization, the color of the reaction mixture changed to reddish-brown or green depending on the nature of ligands used for the reaction. However, the reaction mixture when poured into hexane after passing through a short alumina column did not produce any polymer. GC studies revealed that the reaction mixture contained a large amount of unreacted MVK in all the reactions. Disappointingly, no polymer could be obtained in all of the ATRP reactions. Experiments carried out in the presence of low concentration of ligand and in the absence of ligand have also failed to produce polymer (Table S1, entries 8 and 9, Supporting Information). This clearly shows that the MVK is competing for complexation with CuBr. Upon scanning several initiating systems such as ethyl-2-bromoisobutyrate (EB*i*B), 3-bromo-3-methylbutanone-2 (BMB),[13] and AIBN/$CuX_2$ (reverse ATRP), it was confirmed that none of the copper-containing initiating systems could polymerize MVK (Scheme 1). This confirms that MVK could not be polymerized using copper-mediated ATRP. The fact that the radical polymerization of MVK produces polymer and the copper-mediated ATRP initiating system does not produce polymer indicates that the copper catalyst is the cause for the inhibition of polymerization.[14]

Vinyl monomers having donor atoms such as N or O could coordinate with transition metal catalyst and could complicate the ATRP. Matyjaszewski and co-workers have shown that an interaction of monomer with copper having tetraphenylborate counterion led to the formation of the $\pi$-complex.[15] Moreover, Haddleton and co-workers have shown that the reactivity of aminoethyl methacrylate differs significantly due to a strong monomer-coordination with catalyst in ATRP.[16] In an attempt to examine the complexation of copper with MVK, an admixture of MVK and copper halide was prepared by adding a small amount of CuBr (∼10 mg) in 10 mL of MVK and kept the mixture stirring for 1 h at 30 °C. The CuBr completely dissolved in MVK and the solution becomes homogeneous. After an hour, excess MVK was pumped off under vacuum ($10^{-4}$ Torr) for 4−5 h. A transparent pale yellow viscous residue was obtained, which was subjected to FT-IR, NMR, and UV−vis spectroscopic analysis.

If there were no interaction between CuBr and MVK, the residue should contain only CuBr free from MVK. However, the residue showed the presence of signals corresponding to MVK in IR and $^1$H NMR. The $^1$H NMR spectrum of the MVK−

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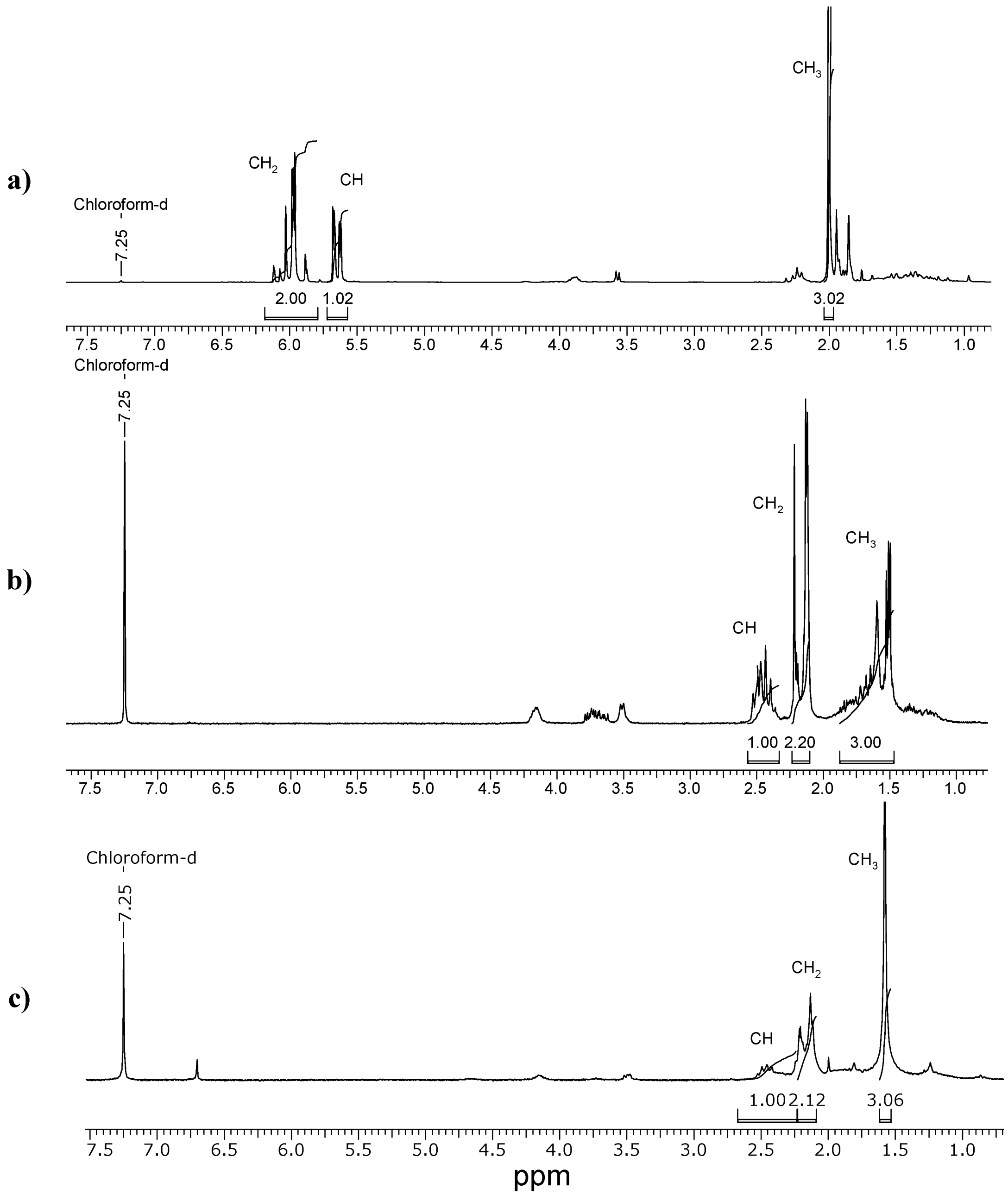

**Figure 1.** $^1$H NMR spectra of the admixture residue after removing excess of MVK in $CDCl_3$. Key: (a) neat MVK, (b) residue of 1:1 mixture of MVK and CuBr, and (c) residue of CuBr mixed with excess of MVK.

**Table 1. IR, UV and $^1$H NMR Shifts$^a$ on Mixing Methylvinyl Ketone and Copper Bromide**

| substrate | IR$^b$ stretching ($\nu$ or $\Delta\nu$, cm$^{-1}$) | | | UV$^c$ ($\lambda$ or $\Delta\lambda$, nm) | $^1$H NMR$^d$ ($\delta$ or $\Delta\delta^e$ ppm) | | |
|---|---|---|---|---|---|---|---|
| | C=C | C=O | C−H | C=O | $CH_2$= | CH= | $COCH_3$ |
| MVK | 1618 | 1683 | 2925 | 325 | 5.91 | 6.19 | 2.25 |
| MVK−CuBr | −106 | −27 (1236)$^f$ | −12 | −4 | +3.78 | +3.73 | +0.67 |
| $Me_2CO$ | | 1742 | 2977 | Nd$^g$ | | | 2.16 |
| $Me_2CO$−CuBr | | +27 | +50 | Nd$^g$ | | | +0.92 |

[a] Shift ($\Delta\nu$ or $\Delta\lambda$ or $\Delta\delta$) = value before complexing − value after complexing with CuBr. [b] Performed using KBr pellet. [c] UV performed in chloroform. [d] $^1$H NMR recorded on 200 MHz spectrometer using $CDCl_3$ as solvent. [e] Shift is calculated based on the $\delta$ value of an intense peak. [f] New peak due C−O stretching. [g] Not done.

CuBr complex showed a huge upfield shift of vinyl and $CH_3$ protons of MVK indicating an enhanced $\pi$-electron interaction of vinyl groups with copper (Figure 1). The vinyl protons are shifted to 2.3 and 2.4 ppm from 5.2 and 6.0 ppm (Figure 1c). Similarly, the methyl protons are seen at 1.6 ppm in the complexed MVK. The huge upfield shift of vinyl and methyl protons is attributed to the delocalization of pi-electron participating in the coordinative complex formation with copper halide. In the case of 1:1 admixture of MVK−CuBr, the signals corresponding to the upfield splitting patterns of $CH_2$=CH− are also seen adjacent to $-CH_3$ signals at 1.5 ppm which supports the point that the coordination of copper with MVK is progressive in nature depending upon the concentration. The presence of coordinative complex between MVK and CuBr can

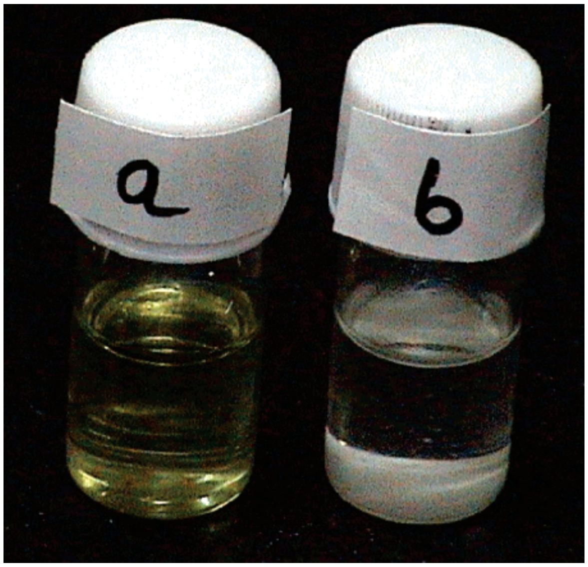

**Figure 2.** Solutions of CuBr (a) homogeneous in excess MVK (4 mg/mL) and (b) heterogeneous in excess MMA (5 mg/mL).

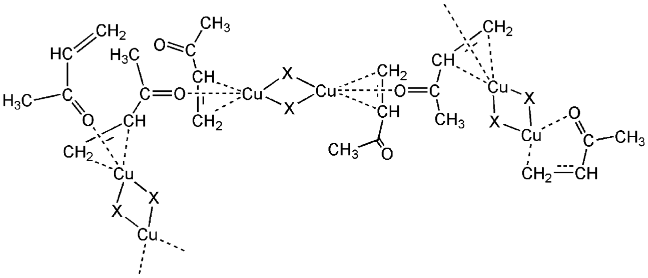

**Figure 3.** Proposed extended-coordinative structure of $(MVK)_m-(CuBr)_n$ based on the X-ray crystal structure of MVK−CuX.[18] The structure shows both trans confirmation, and inter/intramolecular MVK coordination with the CuX dimer.

also be seen in the FT-IR which showed the vinyl, carbonyl and $CH_3$ peaks of MVK had a substantial shift ($\Delta\nu$) −106, −12, and −27 cm$^{-1}$, respectively (Table 1). In addition, a new peak at 1236 cm$^{-1}$ has appeared which corresponds to the C−O stretching frequency similar to the ones present in carboxylic acids.[17] This confirms the presence of extended coordinative complex between MVK and CuBr (Figure S2, Supporting Information). A similar shift in IR frequency was also observed in acetone−CuBr admixture suggesting the coordination of copper is present in all ketones (Table 1). In the case of MVK, the vinyl group also participates in the coordination as seen in $^1$H NMR (Figure 1).

The UV−vis spectra of the MVK−CuBr complex in chloroform had a blue shift corresponding to n → $\pi^*$ transition indicating a relatively strong interaction of carbonyl chromophore with copper (Table 1). The exact nature of the coordination of copper with vinyl and ketone of MVK is clearly not known. A crystalline tetrameric complexes of MVK with copper(I) chloride has been reported at low temperature (−100 °C).[18,19] A physical mixture of CuBr in excess MVK and MMA produces homogeneous and heterogeneous solutions respectively indicating the presence of a strong ketone coordination as compared to ester coordination in MMA (Figure 2). After removal of free MVK, the residual admixture of MVK−CuBr is viscous at room temperature, which also suggests that the nature the coordination with CuBr is nonstoichiometric and the coordination could be an extended network. Thermogravimetric analysis (TGA) of the residue showed 95 wt % loss at $T_{max}$ ~ 154 and ~403 °C, which were attributed to the decomposition of MVK and thermally polymerized MVK, respectively. The residue at 500 °C was around 5 wt % corresponding to CuBr (Figure S3, Supporting Information). This indicates a 0.97:0.03 mole ratio of $(MVK)_m-(CuBr)_n$ in the complex, which confirms that the coordination of MVK to CuBr is nonstoichiometric in nature. On the basis of the results obtained through spectroscopy and the TGA, we propose an extended-coordination structure for $(MVK)_m-(CuBr)_n$ (Figure 3).

It has been reported by van Koten that a decrease in stretching frequency of C=O was noticed in MMA from 1720 to 1580 cm$^{-1}$ due to a monomer-coordination with catalyst.[20] The presence of monomer-coordination has also been observed in ATRP of *N*,*N*-dimethylacrylamide (NDMA).[21,22] In all these cases, the presence of monomer coordination with metal catalyst did not suppress the polymerization. The coordination of copper with monomer would influence the equilibrium of activation and the deactivation processes in ATRP, and thus, it could

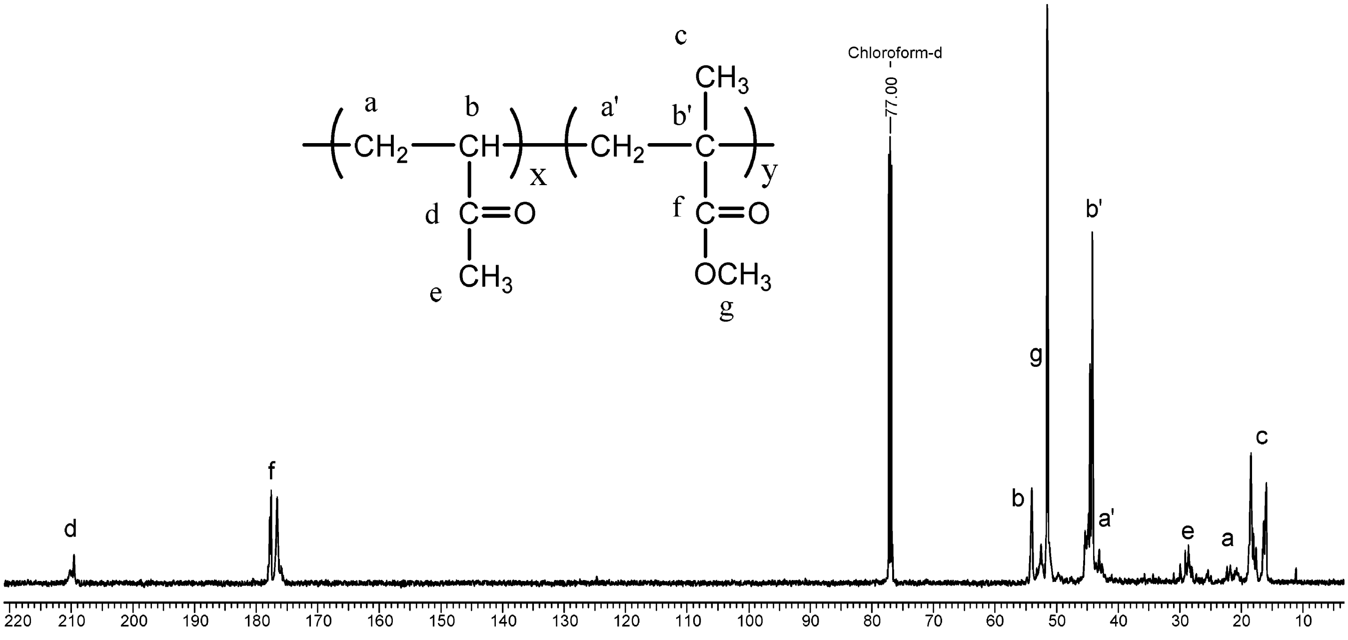

**Figure 4.** $^{13}$C NMR spectrum of the poly(MMA-*co*-MVK) obtained by reverse ATRP in $CDCl_3$.

significantly alter the kinetics of the polymerization. In the case of MVK, the coordination of copper appears to be very strong and extensive, and it completely inhibited the polymerization. On the basis of the literature and the present study, the monomer coordination with copper catalyst in ATRP is very strong in MVK than in NDMA and MMA monomers.

The extended coordination of copper with MVK renders the monomer non-reactive for the polymerization. In the case of ATRP, it appears that the catalyst is not available for the redox process with the initiator due to the monomer coordination. In the case of reverse ATRP, the formed initial radicals (initiator or oligomeric) could have added to copper coordinated MVK and then become inactive either before or after undergoing a single redox cycle. Nevertheless, the copolymerization of MVK (0.5 mL) and MMA (1.8 mL) using AIBN (39 mg) as initiator and $CuCl_2$(66 mg) as catalyst in bulk produced copolymer. Unlike the homopolymerization, the copolymerization proceeded in bulk and produced polymer with $M_w/M_n = 1.7$ (70% yield), which indeed, was a copolymer containing both MMA and MVK repeat units as confirmed by $^1$H and $^{13}$C NMR (Figure 4). This indicates that the copper coordinated MVK may be in equilibrium with free MVK which under goes copolymerization with MMA via reverse ATRP. However, the poly(MMA-*co*-MVK) showed that the content of MVK is very low. The composition of MMA in the copolymer was found to be six times higher than the composition of MVK as shown in Figure 4.

In summary, the copper-mediated ATRP of MVK failed to produce polymers. Unsuccessful polymerization of MVK in the presence of copper catalyst is attributed to the presence of extended coordination of MVK with copper as identified by the admixture complexes of MVK and CuBr in FT-IR, $^1$H NMR, and UV−vis spectroscopic studies. However, the copper-coordinated MVK was found to undergo copolymerization with MMA in reverse ATRP.

**Acknowledgment.** D.B. acknowledges the National Chemical Laboratory for a start-up grant (MLP 007926) and A.M. thanks CSIR for the award of senior research fellowship.

**Supporting Information Available:** Text giving the details of Experimental Section, figures showing the SEC eluogram of poly(MVK) and $^1$H NMR of copoly(VAc-*co*-MVK) after oxidation of the homopolymer, FTIR spectra of MVK and MVK−CuBr, and TGA of $(MVK)_m-(CuBr)_n$, and a table containing data related to the unsuccessful polymerization of methyl vinyl ketone using copper-mediated ATRP and reverse ATRP processes with different initiator/ligand/catalyst systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA060365P