Atom Transfer Radical Polymerization of Methyl Acrylate with Molybdenum Halides as Catalysts in an Ionic Liquid

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ABSTRACT: The atom transfer radical polymerization of methyl acrylate in 1-butyl-3-methylimidazolium hexafluorophosphate was studied with a molybdenum halide catalytic system. A combination of a bromine-containing initiator (ethyl-2-bromopropionate) with a chloride-containing catalyst $[MoCl_3(PMe_3)_3/MoCl_4(PMe_3)_3]$ led to a controlled polymerization, and matrix-assisted laser desorption/ionization time-of-flight analysis of the polymers indicated that the reversibly deactivated macromolecules contained both bromine and chloride end groups. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 278–281, 2007

Key words: atom transfer radical polymerization (ATRP); catalysts; MALDI; ionic liquids

INTRODUCTION

Atom transfer radical polymerization (ATRP) is the most versatile method of controlled radical polymerization.[1–5] ATRP is a catalytic process based on a reversible activation–deactivation cycle involving a low-oxidation metal-state complex reacting with alkyl halide to generate radicals and a corresponding higher oxidation state metal complex, as shown in Scheme 1.

Most commonly, the metal complexes are copper halides, but many other transition metal complexes have been successfully used, including ruthenium and iron complexes. Recently, the application of molybdenum-based catalysts for the ATRP of styrene has been reported.[6,7]

Not all of these complexes are well soluble in bulk monomers or typical organic solvents. This has stimulated interest in the use of ionic liquids as solvents for ATRP processes. Ionic liquids are organic salts that are liquid at ambient temperatures; a typical example is 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]; Scheme 2).[8–10]

Ionic liquids are nonvolatile solvents that readily dissolve many inorganic compounds, including those that are used as ATRP catalysts. Some monomers that can polymerize by ATRP (e.g., styrene) show, however, only limited solubility in typical ionic liquids. Other typical monomers, such as methyl acrylate and methyl methacrylate (as well as their polymers), are miscible with [bmim][PF$_6$].

It has been shown that conducting ATRP of methyl methacrylate or methyl acrylate in [bmim][PF$_6$] offers the advantage of good solubility of the catalyst (therefore, the reaction mixture is homogeneous, and residual catalyst can be easily separated from the polymer after polymerization) and may, in some instances, favorably affect the kinetics. Thus, in the radical polymerization of methyl methacrylate, it has been shown that the rate constant of propagation is higher and the rate constant of termination is lower then in bulk polymerization,[11] which creates more favorable conditions for controlled polymerization.[12,13] The ATRP of acrylate esters is shown in Scheme 3.

The studies of ATRP of (meth)acrylates in ionic liquids have been limited to the most commonly used catalytic system, namely, the CuBr/CuBr$_2$/amine ligand. In this article, we report on attempts to perform the ATRP of methyl acrylate in [bmim][PF$_6$] with molybdenum-based catalysts, which was successfully used by two of us for the ATRP of styrene in toluene solvent.[7] Preliminary results on the application of this catalytic system for the ATRP of acrylates were presented at the American Chemical Society meeting.[14]

The structure of the catalyst used in this work is shown in Scheme 4.
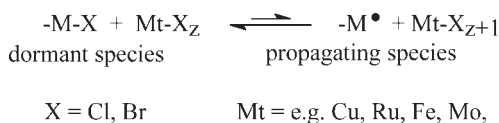
EXPERIMENTAL

Chemicals

Ethyl 2-bromopropionate was purchased from Aldrich and was used as received. Methyl acrylate

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This article is dedicated to the memory of Professor Marian Kryszewski.

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$$-M\text{-}X + Mt\text{-}X_Z \rightleftharpoons -M^{\bullet} + Mt\text{-}X_{Z+1}$$
dormant species   propagating species

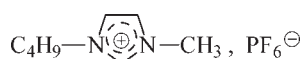X = Cl, Br   Mt = e.g. Cu, Ru, Fe, Mo,

Scheme 1

(from Aldrich) was purified by distillation under argon. [bmim][PF$_6$] was obtained according to a procedure described in the literature[15] starting from 1-methylimidazol, butyl chloride, and aqueous (60%) hexafluorophosphoric acid. MoCl$_3$(PMe$_3$)$_3$, MoBr$_3$ (PMe$_3$)$_3$, MoBr$_4$(PMe$_3$)$_3$, and MoCl$_4$(PMe$_3$)$_3$ were obtained as described earlier.[16–19]
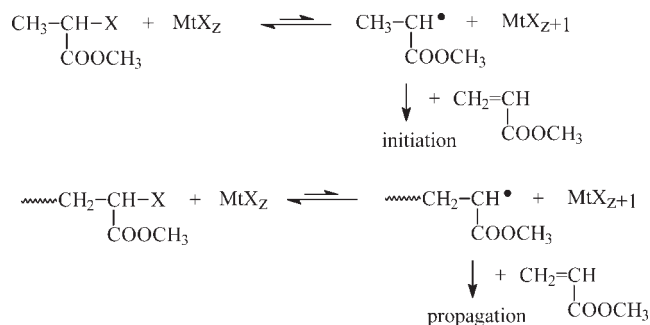
Polymerizations

All polymerizations were carried out under dry and oxygen-free conditions (*in vacuo* or under argon). The monomer and the molybdenum complex(es) were dissolved in [bmim][PF$_6$] (the volume ratio of monomer to [bmim][PF$_6$] was 2 : 1). Ethyl 2-bromopropionate was then introduced to the stirred reaction mixture under an argon atmosphere. The flask (*in vacuo* or under argon) was then immersed in an oil bath heated at the desired temperature. Samples of the polymerization mixture were withdrawn at different time intervals. A portion of the sample was dissolved in deuterated chloroform, and the monomer conversion was determined by means of ^{1}H-NMR spectroscopy. The remaining portion was extracted with chloroform [the chloroform extraction gave practically colorless polymer solutions, which after the evaporation of the solvent, were used for the gel permeation chromatography (GPC) measurements].

Characterization

^{1}H-NMR spectra were recorded on a Bruker 300MSL 300-MHz spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra were taken on a Voyager Elite MALDI-TOF spectrometer with dihydroxybenzoic acid as a matrix and nitrogen laser desorption at 337 nm. Sodium iodide was used as a cationating agent. GPC measurements were performed with an LKB 2150 HPLC pump and a set of TSK-GEL G2000 HXL and G40000 HXL columns with CH$_2$Cl$_2$ as the eluent. Double refractive index (RI) and multi-angle light scattering detectors were used for the determination of the absolute values of the average molecular weights.

$$C_4H_9-\overset{\oplus}{N}\underset{}{\frown}N-CH_3 , \; PF_6^{\ominus}$$

Scheme 2

$$CH_3\text{-}CH\text{-}X + MtX_Z \rightleftharpoons CH_3\text{-}CH^{\bullet} + MtX_{Z+1}$$
COOCH$_3$ COOCH$_3$

$\downarrow + CH_2=CH$
initiation   COOCH$_3$

$$\sim\sim\sim CH_2\text{-}CH\text{-}X + MtX_Z \rightleftharpoons \sim\sim\sim CH_2\text{-}CH^{\bullet} + MtX_{Z+1}$$
COOCH$_3$ COOCH$_3$

$\downarrow + CH_2=CH$
propagation   COOCH$_3$

Scheme 3

RESULTS AND DISCUSSION

Methyl acrylate–CH$_3$CH(COOEt)Cl–MoCl$_3$(PMe$_3$)$_3$/MoCl$_4$(PMe$_3$)$_3$ system

ATRP of methyl acrylate was conducted with CH$_3$CH(COOEt)Cl as the initiator and MoCl$_3$(PMe$_3$)$_3$/MoCl$_4$(PMe$_3$)$_3$ as a catalytic system at a [Monomer]$_0$/[Initiator]$_0$/[Mo^{III}]$_0$/[Mo^{IV}]$_0$ ratio equal to 470: 11 : 1 : 1.1. At 60°C, polymerization proceeded quickly (57% conversion after 10 min), and the number-average molecular weight (M_n) of the polymer ($M_n \approx 10^5$) was well above the calculated value. In the subsequent experiment, the concentration of MoCl$_3$ was reduced five times, whereas concentration of MoCl$_4$ was increased ([Monomer]$_0$/[Initiator]$_0$/[Mo^{III}]$_0$/[Mo^{IV}]$_0$ = 470 : 11 : 0.2 : 1.8) Increasing the concentration of MoCl$_4$(PMe$_3$)$_3$ to shift the equilibrium, as shown in Scheme 1, more to the left-hand side and to reduce the instantaneous concentration of growing radicals improved the outcome only slightly. The rate of polymerization indeed decreased (35% conversion after 3 h, 82% after 19 h), but the molecular weight was still considerably higher ($M_n \sim 6\times10^4$) than calculated for the controlled polymerization. It seems, therefore, that under typical ATRP conditions no control could be achieved with this catalytic system in the polymerization of methyl acrylate.

Methyl acrylate–CH$_3$CH(COOEt)Br –MoBr$_3$(PMe$_3$)$_3$/MoBr$_4$(PMe$_3$)$_3$ system

Replacing chlorine by bromine in both the initiator and catalyst led to significant improvement. Thus, in the polymerization conducted at a [Monomer]$_0$/[Initiator]$_0$/[Mo^{III}]$_0$/[Mo^{IV}]$_0$ ratio of 500 : 10 : 1 : 1.7 at 60°C, almost complete conversion was reached in 24 h. M_n was only slightly higher then the calculated value (calcd M_n = 4480, GPC M_n = 5730), but the dispersity was still relatively high. To improve the

MoCl$_3$(PMe$_3$)$_3$, MoCl$_4$(PMe$_3$)$_3$, MoBr$_3$(PMe$_3$)$_3$, MoBr$_4$(PMe$_3$)
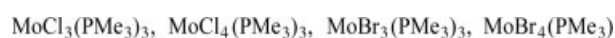
Scheme 4
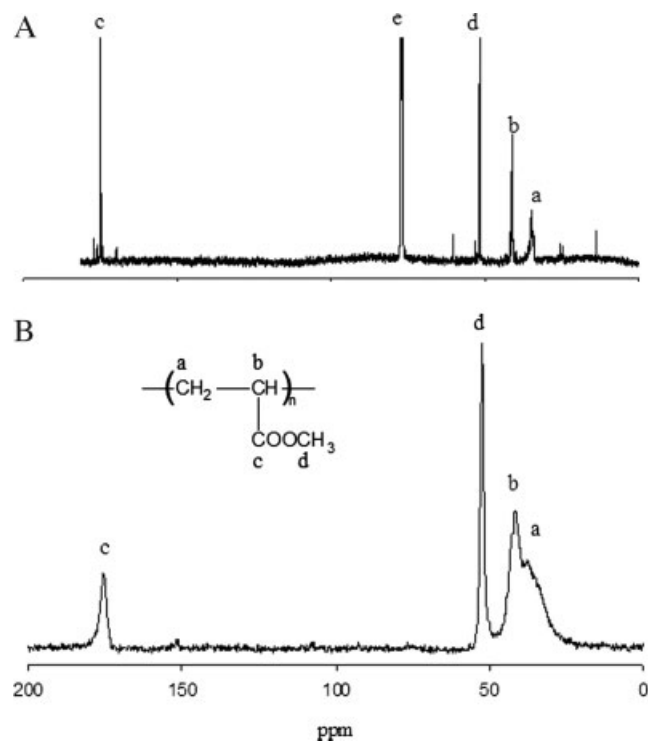
Figure 1 (A) ^{13}C-NMR solution (in CDCl$_3$) spectrum of poly(methyl acrylate) obtained by a conventional ATRP process. (B) ^{13}C CP–MAS spectrum of solid insoluble product obtained in the polymerization of methyl acrylate catalyzed by the MoBr$_3$(PMe$_3$)$_3$/MoBr$_4$(PMe$_3$)$_3$ system.

control, the concentration of MoBr$_4$(PMe$_3$)$_3$ was increased in subsequent experiments. This, however, led to an unexpected result. Polymerization proceeded in the ionic liquid phase, as evidenced by the increasing viscosity of the solution, but at the same time, significant quantities of the white solid formed on the walls of ampule. The recovered solid was insoluble in common organic solvents. Solid-state NMR [^{13}C cross-polarization/magic-angle spinning (CP–MAS)] showed four signals characteristic for carbon atoms in the methyl acrylate unit. In Figure 1, ^{13}C CP–MAS spectrum of solid product is compared

with the typical spectrum of poly(methyl acrylate) (obtained by conventional ATRP in bulk) recorded in solution in CDCl$_3$.

Also, the results of elemental analysis were essentially consistent with the assumption that the insoluble solid was indeed poly(methyl acrylate) (C: found 56.00%, calcd 55.80%; H: found 7.20%, calcd 8.13%). The polymer isolated from solution had a molecular weight considerably higher than that obtained at a lower concentration of MoBr$_4$ (polymer isolated at 30% conversion had $M_n = 28,400$ as compared to the calculated $M_n = 1500$). MALDI-TOF analysis of the polymer isolated from the solution showed the presence of two populations of macromolecules. In Table I, the m/z values of the signals appearing in the spectrum are shown, and the assignments are given.

In a control experiment, the catalyst [MoBr$_3$ (PMe$_3$)$_3$/MoBr$_4$(PMe$_3$)$_3$] was added to the solution of methyl acrylate in ionic liquid in the absence of initiator. Significant quantities of insoluble polymer were formed in this system in addition to small amounts of soluble, very high-molecular-weight polymer. This confirmed that an unknown side reaction occurred between MoBr$_4$ and [bmim][PF$_6$] (no formation of insoluble polymer was observed when MoBr$_3$ was used in the absence of MoBr$_4$, but polymerization in this system was not controlled), and the products of this reaction were able to initiate the polymerization of methyl acrylate and led to the formation of a branched high-molecular-weight polymer in solution and eventually to crosslinked polymer. The formation of insoluble polymer on the walls of the reaction vessel implied that some volatile products were involved. At present, we do not have enough data to speculate on the exact nature of this side reaction.

Methyl acrylate–CH$_3$CH(COOEt)Br–MoCl$_3$(PMe$_3$)$_3$/MoCl$_4$(PMe$_3$)$_3$ system

We showed earlier that in the ATRP of styrene in toluene, MoCl$_3$/(PMe$_3$) is a more active catalyst

TABLE I
m/z Values of the Signals Appearing in the MALDI-TOF Spectrum of Poly(methyl acrylate) Obtained with the CH$_3$CH(COOEt)Br–MoBr$_3$(PMe$_3$)$_3$/MoBr$_4$(PMe$_3$)$_3$ System

m/z			m/z		
Found	Calcd	Formula	Found	Calcd	Formula
4767	4767	In–[MA]$_{53}$–Br	4804	4804	bmim–[MA]$_{53}$–Br
4852	4853	In–[MA]$_{54}$–Br	4891	4890	bmim–[MA]$_{54}$–Br
4939	4939	In–[MA]$_{55}$–Br	4977	4976	bmim–[MA]$_{55}$–Br
5025	5025	In–[MA]$_{56}$–Br	5063	5062	bmim–[MA]$_{56}$–Br
5111	5111	In–[MA]$_{57}$–Br	5149	5148	bmim–[MA]$_{57}$–Br
5197	5197	In–[MA]$_{58}$–Br	5235	5236	bmim–[MA]$_{58}$–Br

The m/z values for a selected fragment of the spectrum are shown. The same pattern was observed for the whole spectrum. In– denotes a head group derived from the initiator [In = CH$_3$CH(COOC$_2$H$_5$)—], bmim– denotes a head group derived from the 1-butyl-3-methylimidazolium moiety, MA denotes a methyl acrylate unit, and Br denotes a bromine terminal group.

than MoBr$_3$/(PMe$_3$) (the corresponding apparent rate constants of polymerization at 90°C were equal to 1.42×10^{-4} and 5.49×10^{-5} min^{-1}, respectively).[7] Both catalysts, however, were capable of catalyzing the controlled polymerization of styrene, although the higher rate observed for MoCl$_3$/(PMe$_3$) implied a higher concentration of growing radicals. In the case of methyl acrylate polymerization in [bmim] [PF$_6$], MoCl$_3$/(PMe$_3$), even in the presence of an excess of MoCl$_4$/(PMe$_3$), gave a fast polymerization to high-molecular-weight polymer. Apparently, the deactivation reaction in this system was not effective, and polymerization proceeded as a conventional radical polymerization.

The MoBr$_3$(PMe$_3$)$_3$/MoBr$_4$(PMe$_3$)$_3$ system seemed to be much more effective for the control of methyl acrylate polymerization in [bmim][PF$_6$], but the side reaction involving MoBr$_4$ led to deviation from the controlled polymerization scheme.

Thus, in the subsequent series of experiments, the mixed system was applied involving a bromine-containing initiator [CH$_3$CH(COOEt)Br] and a chloride-containing catalyst [MoCl$_3$(PMe$_3$)$_3$/MoCl$_4$(PMe$_3$)$_3$]. The polymerization conducted at a [Monomer]$_0$/[Initiator]$_0$/[Mo^{III}]$_0$/[Mo^{IV}]$_0$ ratio equal to 500 : 10 : 1 : 2 at 60°C was terminated at 80% conversion. There was good agreement between the experimental and theoretical molecular weights (GPC M_n = 3500, calcd M_n = 3640), and the dispersity was relatively narrow (M_w/M_n = 1.38). MALDI-TOF analysis of the polymer indicated the presence of two main populations of macromolecules, one containing the CH$_3$CH(COOEt)— moiety as the head group and —Br as the end group and the other containing the same head group and a —Cl end group. In addition, a third minor series was observed. Macromolecules of this series contained the same head group and saturated —CH$_2$—CH$_2$(COOCH$_3$) formed by irreversible termination. It is interesting to note that the intensities of the signals corresponding to the macromolecules terminated with bromine and chlorine were similar. At a [CH$_3$CH(COOEt)Br]$_0$/[MoCl$_3$]$_0$/ [MoCl$_4$]$_0$ ratio equal to 10 : 1 : 2, the proportion of bromine and chlorine introduced with the initiator and catalyst was 10 : 11.

This observation was a little unexpected because catalytic systems containing chloride and bromine behave differently, which could indicate that the positions of activation–deactivation equilibria were different in both cases. In the system in which chloride and bromide were present in nearly equal proportion, however, the molybdenum compounds formed mixed halides (MoCl$_n$Br$_{3-n}$ and MoCl$_n$Br$_{4-n}$), and the efficiency of such mixed halides in the control of activation–deactivation equilibria may not be simply related to the efficiency of catalysts containing either chloride or bromine.

CONCLUSIONS

It was shown earlier that the ATRP of methyl acrylate can be advantageously conducted in [bmim] [PF$_6$] with a CuBr/CuBr$_2$/pentametyldiethylenetri-amine system. The situation was more complex with molybdenum based catalytic systems, which proved to be effective in the ATRP of styrene. MoCl$_3$/MoCl$_4$ was not effective in conjunction with a chloride-containing initiator, whereas for a MoBr$_3$/MoBr$_4$ catalyst in conjunction with a bromine-containing initiator, a side reaction (that of MoBr$_4$ with a cationic fragment of ionic liquid) obscured the results. Combination of a bromine-containing initiator with a chloride-containing catalyst led to controlled polymerization, and MALDI-TOF analysis of the polymers indicated that the reversibly deactivated macromolecules contained both bromine and chlorine end groups.

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