A New Initiator Cholesteryl Chloroformate for Cupper-Based Atom Transfer Radical Polymerization of Methyl Methacrylate

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The polymerization of metyl methacrylate (MMA) was studied in detail by use of CuCl/L as a catalyst and cholesteryl chloroformate (CC) as an initiator. It was found that the atom transfer radical polymerization of MMA could proceed when L equals to a multidentate aliphatic amine ligand, *N,N,N',N'',N''*-penta(methyl acrylate)diethylenetriamine (MA$_5$-DETA), and no polymerization was occurred while L＝2,2'-bipyridine and 1,10-phenanthroline. The linear proportionality of the molecular weights to the conversions and straight lines observed in ln[M]$_0$/[M] versus time plots indicated that the present polymerization system had the typical controlled polymerization characteristics.

Keywords   ATRP, initiator, polymethyl methacrylate, cholesteryl chloroformate

Introduction

The atom transfer radical polymerization (ATRP) is the most effective method not only for getting a polymer with well-controlled molecular weights and narrow molecular weight distribution, but also for synthesis of a functionalized polymer with well-controlled architecture and molecular weights.[1] Therefore, the study on ATRP has received much attention in recent years.[2] ATRP has been successfully applied to the synthesis of well-defined gradient, comb, star and dendritic macro-moleculars[3] by the metal catalyst. Thus, the choice of an initiator is essential for getting a fast polymerization rate and good controllability of the system. Especially, when the initiator with a functionalized group was used, an *α*-end functionalized polymer with a predicted molecular weight could be formed.[4] Low polydispersive polystyrenes with pyrene (Py-PS) or naphthalene (Na-PS) at one end of the chain, were synthesized by ATRP.[5]

As a result, the study on searching a new suitable initiator is always one of the important topics in ATRP field. Until now, a variety of initiators have been explored and most of them can be divided into two classes: one is alkyl halides containing an activated C—X bond and the other is sulfonyl halides bearing an active S—X bond.[6] Recently, *N*-chlorosulfonamides,[7] *α*-chloroacetyl polystyrene macroinitiator and 5-norborn-2-enylmethyl chloroacetate were reported to be the initiators for the ATRP of acrylate[8] and/or styrene and methyl methacrylate[9] respectively.

The cholesteryl chloroformate contains a chloroformyl group in its molecule, which might be decomposed into an active radical species by metal complex, and cholesterol itself has liquid crystal character. These features of cholesteryl chloroformate induced us to try to use it as an initiator in the ATRP of methyl methacrylate to see whether the addition of cholesteryl group to the end of the polymer will give the polymer with liquid crystal character. The preliminary results show that cholesteryl chloroformate together with cuprous chloride and MA$_5$-DETA can catalyze the ATRP of metyl methacrylate, giving a polymer with narrow polydispersity. In this report we would like to present the results.

Experimental

Materials

Cholesteryl chloroformate (99.5%, white powder) was commercially available and used without further purification.
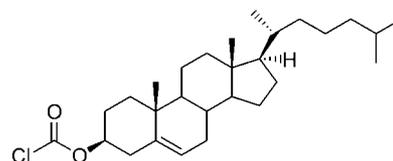
Cuprous chloride was prepared by cupric chloride and sodium sulfite according to the published method.[10] 2,2'-Bipyridine and 1,10-phenanthroline were commercially available and used as received. Methyl methacrylate (MMA) was vacuum distilled after being dried by

Polymethyl methacrylate

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anhydride magnesium sulfate before polymerization. *N,N,N',N'',N'''*-penta(methyl acrylate) diethylenetriamine (MA$_5$-DETA) was synthesized in our lab by a slightly modified method of Johnson.[11,12]

Polymerization

A typical polymerization procedure was as follows. The CuCl cholesteryl chloroformate (CC), MA$_5$-DETA, MMA were added into a Schlenk tube in turn. The tube was sealed and degassed by three freeze-pump-thaw cycles and finally immersed in an oil bath and heated at the desired temperature under stirring. After a certain time, the tube was opened and diluted with dichloromethane. The solution was precipitated into methanol and the resultant polymer was filtrated and dried in vacuum.

Measurements

The monomer conversion was determined gravimetrically. Molecular weight and molecular weight distribution were measured by a Waters 1515 /GPC apparatus, using THF as eluent and calibrated with polystyrene as standard. ^{1}H NMR was recorded on an INOVA 400 MHz NMR spectrometer using CDCl$_3$ as solvent.

Results and discussion

Effect of ligand on the polymerization

Because ClCOO$^-$ group in CC is labile, CACE is expected to be able to initiate copper mediated ATRP of MMA. In view of fact that the two complexes of CuX-2,2'-bipyridine and CuX-1,10-phenanthroline are well known the good catalyst for most of the ATRP systems with a variety of initiators,[13,14] thus the bulk polymerization of MMA was first conducted by use of CuCl-2,2'-bipyridine and CuCl-1,10-phenanthroline as the catalyst respectively and CC as the initiator. It was surprising that no polymerization was occurred for both systems under the wide range of reaction conditions. Considering the fact that the ligand around the metal has a great effect on the catalytic activity and the tridentate amine is a better ligand than bidentate one in most cases, we tried again with MA$_5$-DETA as the ligand, which was found to be a suitable ligand in iron-based ATRP of styrene and/or MMA in our laboratory.[15] Indeed, the bulk polymerization took place and the process was controlled (see later section). This result demonstrated obviously that the suitable combination of the metal complex and an initiator was essential for getting an active ATRP system.

ATRP of MMA catalyzed by CuCl/MA$_5$-DETA/CACE in bulk

In order to get more information about the present catalytic system, the polymerization was first studied at different temperature. The results are listed in Table 1. As can be seen from Table 1, the reaction temperature has great effect on the polymerization rate and the polydispersity of the resulting polymer, which both in-

crease with increasing temperature. The polymer with the narrowest molecular weight distribution was obtained at 90 ℃.

Table 1 Bulk polymerization of MMA initiated by CuCl/MA$_5$-DETA/CC

No.	T/℃	Conv./%	$M_{n\,(GPC)}$	M_w/M_n
1	120	47	125400	2.23
2	115	43	107400	1.96
3	110	38	97800	1.75
4	105	28	92600	1.86
5	100	21	67500	1.68
6	95	14	51400	1.47
7	90	5.0	13900	1.15
8	85	1.0	6500	1.34
9	80	—	—	—

Reaction conditions: time, 1.5 h; CC : CuCl : MA$_5$-DETA : MMA＝1 : 1.5 : 3 : 200 (molar ratio).

The ratio of $[M]_0/[I]_0$ had effects not only on the polymerization rate but also on the initiation efficiency. The polymerization rate increased with the decrease of $[M]_0/[I]_0$. The monomer conversion reached to 68% in 1.5 h at a lower $[M]_0/[I]_0$ ratio (50/1), while the conversion decreased to 28%, when the ratio of $[M]_0/[I]_0$ was increased to 400. The initiation efficiency increases with the increase of $[M]_0/[I]_0$, even the initiation efficiency for the present catalyst system was low (Table 2). The polymerizations of MMA in the range of $[M]_0/[I]_0$＝50—700 all afforded the polymers with narrow molecular weight distributions (M_w/M_n＝1.22—1.51) under the conditions of CuCl/MA$_5$-DETA/CACE ＝ 1.5/3/1 (molar ratio) and at 90 ℃ (Table 2).

Table 2 Effect of $[M]_0/[I]_0$ on the ATRP of MMA initiated by CuCl/MA$_5$-DETA/CC

No.	$[M]_0/[I]_0$	Conv./%	$M_{n\,(th)}$	$M_{n\,(GPC)}$	M_w/M_n
1	700	27	19270	114200	1.33
2	600	13	8200	45500	1.15
3	500	18	9400	57600	1.25
4	400	28	11600	95600	1.35
5	300	21	6700	61100	1.21
6	200	24	5200	56800	1.42
7	150	55	8700	226600	1.64
8	100	68	7200	216400	1.84
9	80	31	2900	82000	1.55
10	50	68	3800	104900	1.50

Reaction conditions: CC 1 mmol, CuCl 1.5 mmol, MA$_5$-DETA 3 mmol, T＝90 ℃. The theoretical molecular weight in Table 2 are calculated using the following equations: $\overline{M}_{n\,(th)}$ ＝$[M]_0/[I]_0$× Conv.% × M_{MMA}＋M_I. The efficiency of initiation was determined by rate of the measured molecular weights and the theoretical values: f＝$M_{n\,(th)}/M_{n\,(GPC)}$.

Polymerization kinetics and mechanism

In order to better understand the process, the bulk polymerization kinetic of MMA was measured. The results are shown in Figure 1, and the relationship between molecular weights and molecular weight distributions and conversion are illustrated in Figure 2. The straight semilogarithmic plot of $\ln[M]_0/[M]$ versus time was obtained. The linear relationship demonstrated that the polymerization was first-order with respect to monomer consumption and the concentration of growing radicals kept constant in the system. Figure 2 showed that the molecular weight of the polymer increased with the increase of monomer conversion linearly and the molecular weight distributions kept narrow and almost unchanged. These results indicated that the polymerization system was controlled one.
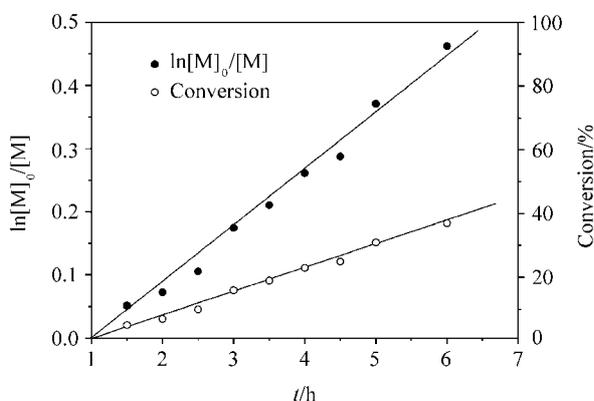

Figure 1 Plots of conversion and $\ln[M]_0/[M]$ versus time.
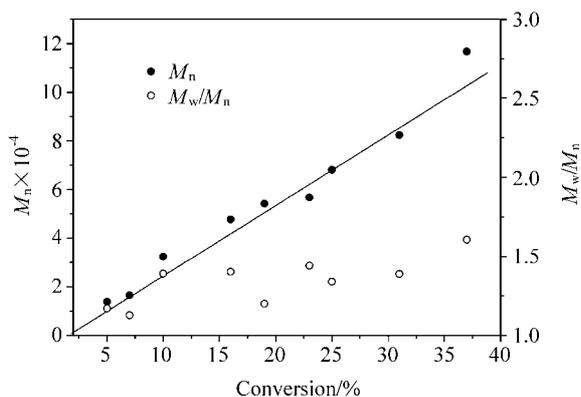

Figure 2 Dependence of molecular weight and polydispersity on conversion.

To confirm further its living nature, the block copolymerization of PMMA-St was performed by use of the macroinitiator of PMMA ($M_{n\ (GPC)}$＝54271, PDI＝1.18) obtained by the system CACE/CuCl/MA$_5$-DETA/MMA in the ratio of 1∶1.5∶3∶200. The block copolymer of PMMA-St ($M_{n\ (GPC)}$＝264587, PDI＝1.76) was obtained by the system PMMA/CuCl/MA$_5$-DETA/St in the ratio of 1∶1.5∶3∶800.

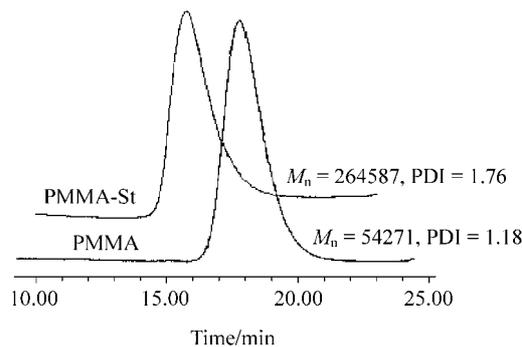The GPC curves for the macroinitiator and the copolymer are shown in Figure 3.

Figure 3 GPC curves of the macroinitiator and the copolymer.

In order to give a supporting datum for the ATRP mechanism, the analysis of the end-group of the polymer was determined by ^{1}H NMR. The sample to be measured was prepared by solution polymerization in anisol under the conditions of CACE/CuCl/MA$_5$-DETA/MMA＝1/1.5/3/200 (molar ratio) at 90 ℃. Figure 4 shows the ^{1}H NMR of the resulting polymer.

The peaks δ 5.39 and δ 0.67 are associated respectively with the protons h and f in CC and those within δ 1—2 with other corresponding protons of CC. The peak at δ 1.87 should belong to the methyl group d, which located at the other end of the polymer. The shift of the peak δ 1.87 to the lower field δ 2.03 and 3.74 was caused by the electron-drawing effect of the chlorine atom.

As discussed above, it would be concluded that CACE is a new initiator, which can really initiate the ATRP of MMA catalyzed by CuCl-MA$_5$-DETA. However, the initiation efficiency, according to the rate of the measured molecular weight by GPC and the theoretical one, is low, especially in the case of $[M]_0/[I]_0$＝50. The low initiation efficiency leads to the formation of a high molecular weight PMMA and high viscosity of the polymerization system, which may be the reason for that the polydispersity for the polymers obtained at $[M]_0/[I]_0$＝50 and 100 is the highest (Table 2 Entries 6 and 7). The low initiation efficiency of CC may be ascribed to the high cleavage energy of the Cl—C bond of ClCOO group.

The mechanism of the ATRP of MMA with CC as an initiator can be supposed as follows:
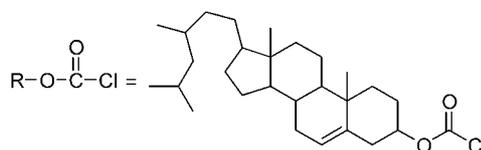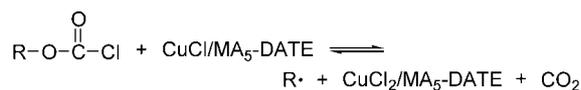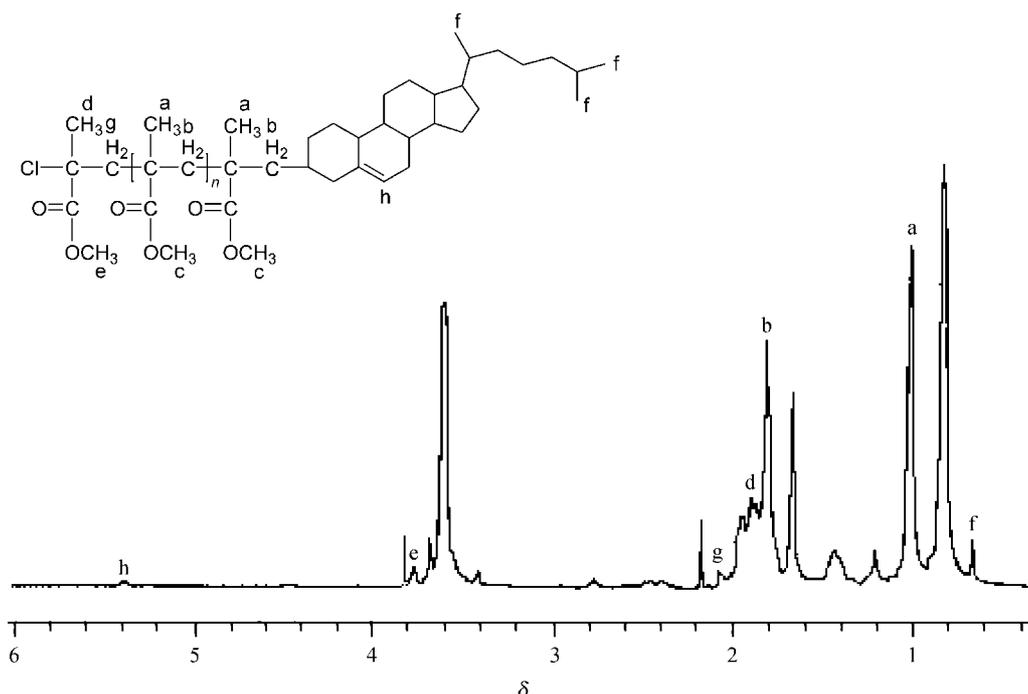
Figure 4 ^{1}H NMR spectrum of PMMA initiated by CC.

Conclusion

This paper demonstrated a new initiator CC for CuCl-based ATRP of MMA. Several parameters including the kind of the ligand, the polymerization temperature, the molar ratio of the catalyst to monomer, have great effect on the polymerization behavior. The living/controlled polymerization of MMA with the catalyst system CuCl/MA$_5$-DETA/CC was successfully performed in bulk at 90 ℃. The polymerization mechanism was proposed.

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