

Atom Transfer Radical Polymerization of Methyl Methacrylate with α,α -Dichlorotoluene or α,α,α -Trichlorotoluene as Initiator

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Abstract: The atom transfer radical polymerization (ATRP) of methyl methacrylate using α,α -dichlorotoluene or α,α,α -trichlorotoluene as the initiator and CuCl/2,2'-bipyridine complex as the catalyst was investigated. α,α -Dichlorotoluene gave good control of molecular weight with high initiation efficiency and low polydispersity. While α,α,α -trichlorotoluene gave very slow polymerization rate, which could be improved by the addition of Cu (0) to the system.

Keywords: atom transfer radical polymerization (ATRP), methyl methacrylate, initiator.

In Atom Transfer Radical Polymerization (ATRP), which is a new “living”/controlled radical polymerization technique developed independently by Matyjaszewski *et al*¹ and Sawamoto *et al*², any alkyl halide with activated substituents on α -carbon such as aryl, carbonyl or allyl can be used as initiator³. Benzyl halide and polymers with benzyl halide end group were reported to be efficient initiator or macroinitiator for the ATRP of styrene^{4,5}. However, when benzyl halide was used to initiate MMA polymerization, it was found that the initiation efficiency was very low in our laboratory⁶. This communication will report that two new initiators, α,α -dichlorotoluene and α,α,α -trichlorotoluene, can give relative high initiation efficiency in the ATRP of MMA.

Experimental

MMA from was vacuum distilled and stored at -15°C . 2,2'-Bipyridine (bipy), copper powder, α,α -dichlorotoluene and α,α,α -trichlorotoluene (Aldrich) were used as received. CuCl (98%) was purified according to the literature procedure⁷.

The general procedure for the polymerization was as follows. To a 50ml taper glass flask were added initiator, ligand, CuX, and monomer. The solution was degassed by bubbling argon for 10 min. The flask was sealed with rubber stopper under argon atmosphere, and then immersed in an oil bath heated at desired temperature. After a certain time, the flask was opened and THF was added to dissolve the polymer.

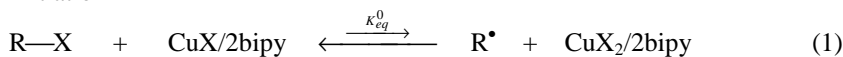
Monomer conversions were determined gravimetrically. Molecular weight averages and molecular weight distributions were measured by Waters 150C gel permeation chromatography (GPC) using columns SHODEX A803-A805. Polystyrene standards were used to calibrate the columns.

Results and Discussion

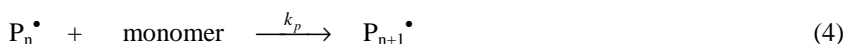
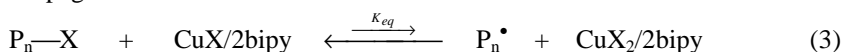
The ATRP using RX/CuX/bipy (X=halide, such as Cl or Br) initiation system has been proposed to occur by the mechanism⁸ illustrated in **Scheme 1**. It consists of a halogen atom transfer equilibrium at both the initiation and propagation steps and addition of radicals to monomer at both the initiation and propagation steps.

Scheme 1

Initiation



Propagation



According to the above mechanism, a key factor that must be taken into consideration for the proper choice of the alkyl halide (RX) is the ratio of the apparent rate constant of initiation ($k_i^{\text{app}}=k_iK_{\text{eq}}^0$, where k_i and K_{eq}^0 refer to the absolute rate constant of addition of the initiating radical to the monomer and the equilibrium constant for the initiating species, respectively.) to the apparent propagation rate constant ($k_p^{\text{app}}=k_pK_{\text{eq}}$, where k_p and K_{eq} refer to the absolute propagation rate constant and the equilibrium constant for the polymer species, respectively.). If $k_i^{\text{app}} \ll k_p^{\text{app}}$, initiation is incomplete, molecular weight is higher than the theoretical one, and polydispersity is high⁹.

When the structure of alkyl group R is similar to the structure of the growing chain, such as ethyl 2-bromobutyrate initiating MMA polymerization and 1-phenylethyl halide initiating styrene polymerization, $k_i^{\text{app}}=k_p^{\text{app}}$, and the initiation efficiency is high. This might be due to the fact that the bond dissociation energy of C-X in initiator is equal to that in polymer.

Because the bond strength of C-Cl in benzyl chloride is higher than that in PMMA-Cl, its initiation efficiency should be low, which has been confirmed by our previous study⁶. When the hydrogen atoms on the α -carbon of benzyl chloride is substituted by chloride atom, the bond strength of C-Cl will decrease greatly, thus resulting in faster initiation rate and higher initiation efficiency.

Figure 1 illustrates the kinetic data obtained for bulk polymerization of MMA at 95°C using α,α -dichlorotoluene as initiator and CuCl/bipy complex as catalyst. The linear plot of $-\ln(1-x)$ versus polymerization time indicates that the concentration of growing radicals remains constant during propagation and termination is not significant. The number average molecular weight (M_n, exp) increases linearly with conversion and the the molecular weight distribution is fairly narrow ($M_w/M_n=1.2\sim 1.26$) (**Figure 2**).

The $M_{n,exp}$ is very close to the theoretical one. These results indicate that α,α -dichlorotoluene acts as an efficient initiator.

Figure 1. Relationship of $-\ln(1-x)$ versus time.

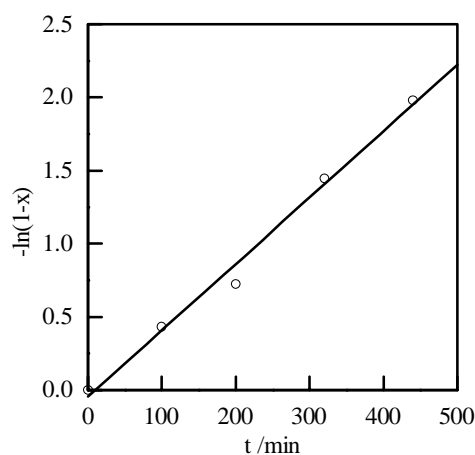
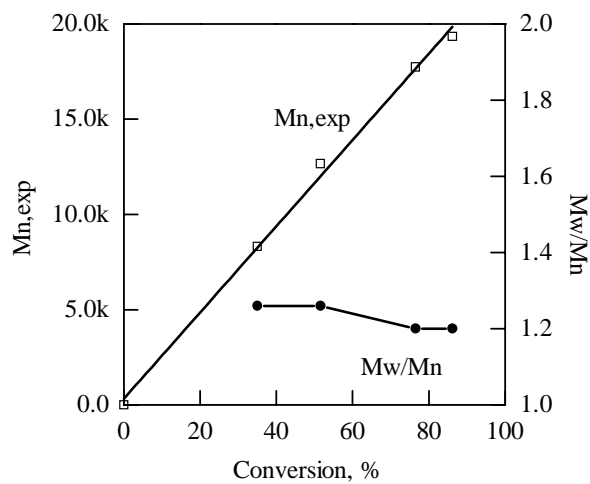


Figure 2. Dependence of M_n and M_w/M_n on conversion.



The C–Cl bond dissociation energy in α,α,α -trichlorotoluene is lower than that of α,α -dichlorotoluene. Therefore it was also used to initiate the polymerization of MMA. However, the polymerization rate was very slow (monomer conversion is below 5% after 12 hours with α,α,α -trichlorotoluene/CuCl/bipy/MMA = 1/1/2/200 mmol at 90 °C). This may be due to the fact that α,α,α -trichlorotoluene is so easy to be activated by the Cu^I complex to form radicals in relatively high concentration that radical-radical termination occurs at a significant rate early in the polymerization, irreversibly

generating an excess of Cu^{II} species. Matyjaszewski *et al.*¹¹ ever reported an acceleration of the metal halides catalyzed ATRP in the presence of Cu (0). We also added some copper powder to the reaction system to accelerate the polymerization rate. The results of the ATRP of MMA with α,α,α -trichlorotoluene/CuCl/Cu (0)/bipy as the initiating system are shown in **Table 1**.

Table 1. Results of MMA ATRP initiated by α,α,α -trichlorotoluene/CuCl/Cu/bipy

Time, min	Conversion,%	Mn,th	Mn,exp	Mw/Mn
125	45.7	9400	13920	1.25
250	62.3	12600	18110	1.20
500	90.3	18200	24060	1.24

From **Table 1**, it can be seen that Mn,exp is somewhat higher than Mn,th. This shows that termination indeed occurs in the early stage of polymerization when α,α,α -trichlorotoluene acts as initiator. This polymerization system also has living characteristics: Mn,exp increases linearly with monomer conversion and the polydispersity (Mw/Mn) is much lower than conventional radical polymerization.

References

- 1 J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **1995**, *117*, 5614.
- 2 M. Kato, M. Kamigaito, M. Sawamoto, *et al.*, *Macromolecules*, **1995**, *28*, 1721.
- 3 J. S. Wang and K. Matyjaszewski, *Macromolecules*, **1995**, *28*, 7901.
- 4 K. Matyjaszewski, S. Coca, Y. Nakagawa, *et al.*, *Polym. Mater. Sci. Eng.*, **1997**, *76*, 147.
- 5 M. R. Leduc, W. Hayes and J. M. J. Frechet, *J. Polym. Sci.: Part A: Polym. Chem.* **1998**, *36*, 1.
- 6 Z. Fu, Y. Shi and S. Jiao, *J. Beijing Univ. Chem. Techn.*, **1998**, *25*(2), 17.
- 7 R. N. Kelle and H. D. Wycoff, *Inorg. Synth.*, **1946**, *2*, 1.
- 8 K. Matyjaszewski, T. E. Patten and J. Xia, *J. Am. Chem. Soc.*, **1997**, *119*, 674.
- 9 K. Matyjaszewski, *Polym. Prep.*, **1997**, *38*(1), 736.
- 10 K. Matyjaszewski, S. Coca, S. G. Gaynor, *et al.*, *Macromolecules*, **1997**, *30*, 7348.

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