Atom Transfer Radical Polymerization of Methyl Methacrylate with α,α,α',α'-Tetrachloroxylene as an Initiator

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The homogeneous ATRP of methyl methacrylate (MMA) using α,α,α′,α′-tetrachloroxylene (TCX)/CuCl/N,N,N′,N″,N″–pentamethyldiethylenetriamine (PMDETA) as the initiating system has been successfully carried out. The kinetic plots showed first order relationship vs. monomer concentration. Well-controlled polymerizations with low polydispersities ($M_w/M_n = 1.15 - 1.25$) polymers have been achieved. The molecular weights increased linearly with monomer conversions and were close to the theoretical values, indicating high initiation efficiency. The polymerization rate increased significantly with an increase of TCX concentration. The rate of polymerization was about 0.6 orders with respect to the concentration of initiator. The polymerization rate increased significantly with an increase of CuCl concentration. The dependence of $\ln k_p^{app}$ on $\ln ([CuCl]_0)$ indicated a 0.91 order. The apparent activation energy was calculated $\Delta E_{app}^{\neq} = 43.3\,KJ/mol$, and the enthalpy of the equilibrium, ΔH_{eq}^{0}, was estimated to be 21.1 KJ/mol. The structure of obtained PMMA was analyzed by means of ^1H NMR spectroscopy. The result proved that the TCX acted as a bifunctional initiator for ATRP of MMA.

Keywords α,α,α′,α′-tetrachloroxylene (TCX), atom transfer radical polymerization, methyl methacrylate

Introduction

Atom transfer radical polymerization (ATRP) is one of the most convenient methods for the large range of vinyl monomers and complex architectural polymers (1–13). It is based on a fast equilibrium where a transition metal complex reversibly activates a dormant polymer chain via an atom transfer event. As a multi-component system, ATRP is composed of the monomer, an initiator with a transferable halogen, and a catalyst (composed of a transition metal species with suitable ligand). Bifunctional initiators may provide chain growth in two directions and be used for preparation of telechelic and ABA block polymers. α,α′-*p*-Dihaloxylene is a difunctional initiator for the copper-catalyzed living radical polymerizations of styrene, MA, nBA, and *p*-acetoxystyrene to give telechelic polymers with controlled molecular weights and

narrow molecular weight distributions (2, 14–18). The telechelics could further be employed as macroinitiators for ABA-type block copolymers. The copper-catalyzed radical polymerization of MMA using 9,10-bis(chloromethyl)anthracene as an initiator and CuCl/2,2-bipyridine as a catalyst gave polymers with narrow molecular weight distributions ($M_w/M_n = 1.2$) but with low initiation efficiency (ca. 13%) (19). The obtained PMMA possesses one anthracene unit in the middle of the polymer backbone. Anthrathene-labeled polystyrene can be synthesized with the copper-catalyzed polymerizations initiated by 9,10-bis (1-bromoethylcarbalkoxymethyl) anthracene (ANTDBr). The initiation efficiency of ANTDBr was 100% and the polymerization proceeds in a controlled fashion, proving low-polydispersity polystyrenes with one anthracene chromophore in the middle of the main chain (20). The ATRP polymerizations of styrene and methyl methacrylate with α,α-dichlorotoluene (**DCT**) as an initiator result in the respective chlorotelechelic polymers. However, the polymerization of styrene and methyl methacrylate showed a different behavior: for the polymerization of styrene, **DCT** is a difunctional, while for the polymerization of methyl methacrylate, it is a monofunctional initiator due to the low reactivity of the second C-Cl bond after the initiation (21). A haloketone (dichloroacetophenone) induced living radical polymerization of MMA in the presence of ruthenium catalysts to give polymers with extremely narrow molecular weight distributions ($M_w/M_n < 1.1$) (22). As it turned out, both of the carbon-chlorine bonds in the initiator initiate living polymerization (23). Ester-type bifunctional initiators, such as bis (2-bromopropionyloxy) ethane and 1,4-(2′-bromo-2′-methylpropionato) benzene, can readily be prepared by a reaction of dialcohols or diphenols with haloacyl halides and have been used successfully in ATRP to give telechelic polymers (23–33). Dibromoacetates (dimethyl 2,6-dibromoheptanediate and diethyl *meso*-2,5-dibromoadipate) are commercially available and effective for methacrylates, acrylates, and styrene with nickel and copper catalysts (34–38). These telechelic polymers can further be employed as bifunctional macroinitiators for ABA (25, 27–29, 35–37) and CBABC (38) block copolymers. Bifunctional initiators with bipyridine units such as bis(chloromethyl) bipyridine induced the living radical polymerizations of styrene, 4-bromostyrene and MMA with copper catalysts to give polymers that carry a coordination site at the middle of the chain (39–43). Bifunctional initiators with oligophenylenes as a rigid spacer unit generate rigid/flexible triblock copolymers of styrene (44). Aryl disulfonyl chloride initiators such as phenoxybenzene-4,4′-disulfonyl chloride are effective bifunctional initiators for various monomers including methacrylates, acrylates, and styrenes (45, 46). Others reported the use of difunctional macroinitiators in the synthesis of triblock ABA copolymers with narrow polydispersities and controlled number average molecular weights (47–50).

However, to the best of our knowledge, the atom transfer radical polymerization (ATRP) of MMA using $\alpha,\alpha,\alpha',\alpha'$-tetrachloroxylene (TCX) as an inintiator has not been reported yet. In this article, we report a kinetic investigation of the homogeneous solution ATRP of MMA using $\alpha,\alpha,\alpha',\alpha'$-tetrachloroxylene (TCX, Figure 1) as a bifunctional inintiator and CuCl/N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) as catalyst.

Experiment

Materials

Methyl methacrylate (MMA) (chemically pure, from Shanghai Chemical Reagent Co. Ltd., China) was washed with 5% sodium hydroxide aqueous solution, and with deionized water until neutralization. After being dried with sodium sulfate anhydrous
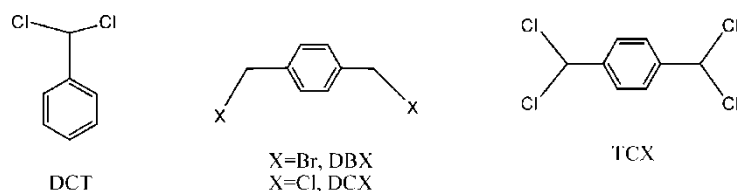
Figure 1. Bifunctional benzylic halides initiators.

overnight, the MMA distillated under vacuum. N,N,N′,N″,N″-pentamethyldiethylene-triamine (PMDETA) (98%, from Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4Å molecular sieves and distillated under vacuum. $\alpha,\alpha,\alpha',\alpha'$-Tetrachloroxylene (TCX) (97%, from Jiangsu Jiangdu Chemical Factor, China) was recrystallized twice from ethanol. Copper (I) chloride (CuCl) (analytical reagent, from Shanghai Zhenxin Chemical Reagent Factory, China) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with absolute ethanol, and dried under vacuum. N,N-Dimethyl formamide (DMF) and tetrahydrofuran (THF) (analytical reagent, Shanghai Chemical Reagent Co. Ltd., China), hydrochloric acid (HCl) (36–38%, Analytical Reagent, Jiangsu Jincheng Chemical Reagent Co. Ltd., China), and methanol (commercially available, Suzhou China) were used as received.

General Procedures of Polymerization

The typical polymerization is showed below. A dry glass tube was filled with TCX (31.2 mg, 0.142 mmol), CuCl (14 mg, 0.142 mmol), PMDETA (73.7 mg, 0.142 mmol), MMA (6 mL, 56.8 mmol) and DMF (2 mL) ($V_M/V_{DMF} = 3:1$), and then the homogeneous mixture was degassed under vacuum and charged with nitrogen for three times. Then the tube was sealed and immersed in an oil bath held by a thermostat at 80°C. At timed intervals, the tube was cooled by ice water bath and opened. Afterwards, the contents were dissolved in THF, precipitated into a large amount of methanol. The polymer was obtained by filtration and dried under vacuum overnight at room temperature. Conversion of monomer was determined by gravimetry.

Characterizations

The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatograph (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 column with molecular weight in the range 100–500,000 calibrated with PMMA standard samples. Tetrahydrofuran was used as the eluent at a flow rate of $1.0\,\text{mL}\,\text{min}^{-1}$ operated at 30°C. ^{1}H-NMR spectra of the polymers were recorded on a INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using dimethyl-d6 sulfoxide as a solvent and tetramethylsilane (TMS) as the internal standard.

Results and Discussion

Effect of Catalyst Concentration

The kinetic plots of homogeneous solution ATRP polymerization of MMA initiated by TCX/CuCl/ PMDETA at different catalyst concentrations are displayed in Figure 2,
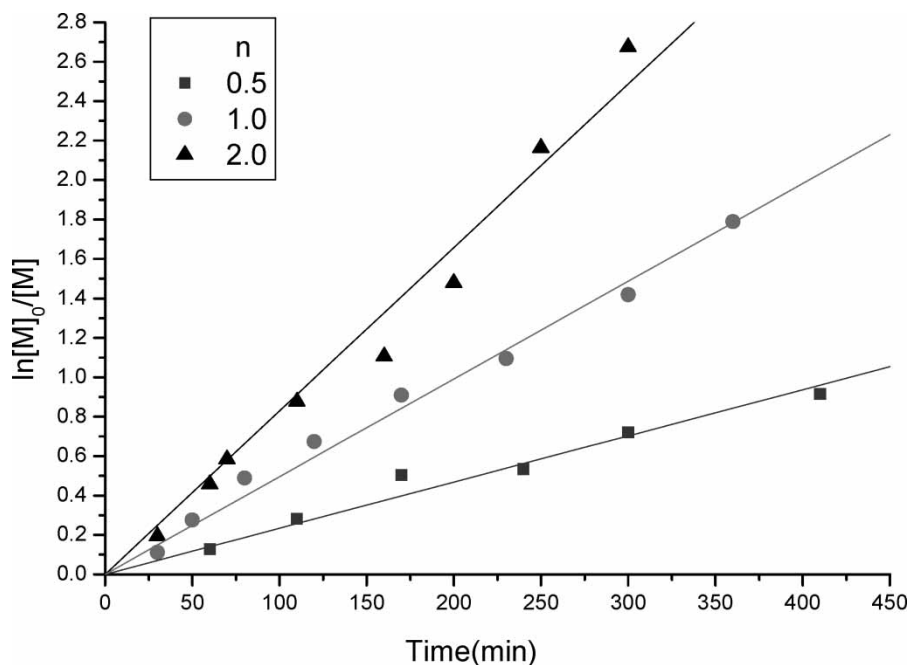
Figure 2. Effect of CuCl concentration on the homogeneous solution ATRP of MMA at 80°C. Conditions: $[MMA]_0 : [TCX]_0 : [CuCl]_0 : [PMDETA]_0 = 400 : 1 : n : 3n$, VMMA/ VDMF = 3 : 1.

and the plots of number-average molecular weights ($M_{n(GPC)}$) and molecular weight distributions vs. conversions are shown in Figure 3. As shown in Figure 2, the kinetics was first-order vs. monomer, indicating a constant concentration of growing radicals. The polymerization rate increased significantly with the increase of CuCl concentration. As shown in Figure 3, the $M_{n(GPC)}$ values increased linearly with conversions and polydispersities remained in relatively low ($M_w/M_n < 1.25$) ranges, indicating a well-controlled polymerization process. The $M_{n(GPC)}$ values were close to the $M_{n(th)}$ values which indicating a high apparent initiator efficiency. The $M_{n(th)}$ calculated on the assumption that one initiating radical generated one growing polymeric chain (Equation 1) for all initiator concentrations for different concentrations of CuCl. Figure 3 also shows that molecular weights were dependent on [TCX] and not on [CuCl] when the concentration of CuCl was varied. The experimental molecular weights were slightly higher than the calculated ones at higher conversion ($>70\%$) when the $[TCX]_0/[CuCl]_0$ ratio of 1 : 2 was used.

$$M_{n(th)} = ([MMA]_0/[TCX]_0) \times MW_{MMA} \times conversion \qquad (1)$$

The relationship between the rate of polymerization and the concentration of CuCl was investigated. Figure 4 illustrates the dependence of $\ln k_p^{app}$ on $\ln ([CuCl]_0)$ which showed that the rate of polymerization follows first order (slope = 0.91) with respect to the concentration of CuCl. This is similar to the study on the effect of $[CuCl]_0$ on the apparent rate constant k_p^{app} for homogeneous ATRP of MMA initiated with p-TsCl in diphenyl ether at 90°C, which indicated the first order (slope = 0.94) dependence of the rate on the concentration of CuCl (51). However, this is different from the 0.80 order dependence of the polymerization rate on the concentration of CuCl observed for
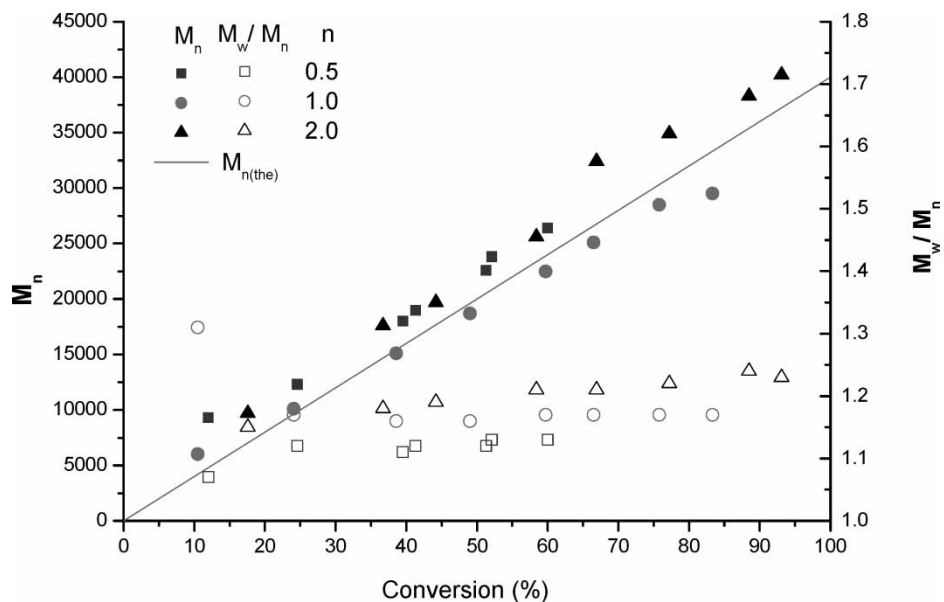
Figure 3. Dependence of molecular weights and polydispersities on conversion in homogeneous solution ATRP of MMA at different concentrations of catalyst. Conditions the same as Figure 2.
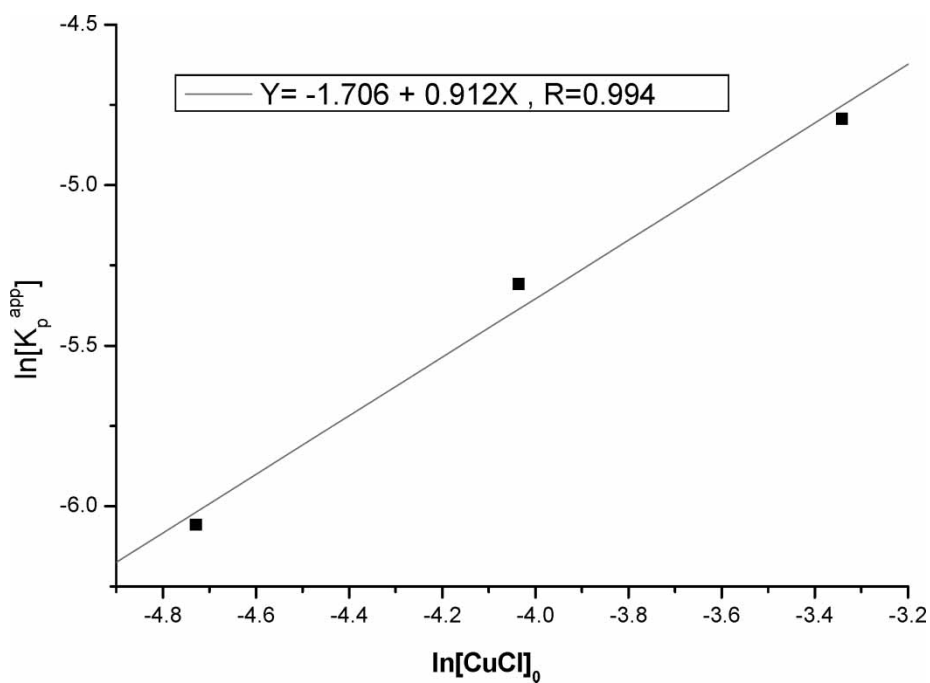

Figure 4. Dependence of ln(Kpapp) on ln([CuCl]$_0$) for the homogeneous solution ATRP of MMA at T = 80°C, VMMA/VDMF = 3 : 1.

homogeneous ATRP of MMA in 4-methoxybenzenesulfonyl chloride/CuCl/4,4-dinonyl-2, 2-bipyridine initiation system (52).

Effect of Initiator Concentration

To examine the effect of initiator concentration on polymerization, a series of homo-geneous solution ATRP of MMA initiated by TCX/CuCl/PMDETA at different initiator concentrations were carried out at 80°C. The experimental results were shown in Figure 5. Figure 5 shows the effect of initiator concentration on the kinetic of homo-geneous ATRP of MMA. The kinetic plots of ln ([M]$_0$/[M]) vs. reaction time are linear throughout the reaction at all initiator concentrations, suggesting that the radical concen-trations in all cases maintained at a constant value throughout the polymerization. A plot of ln (k_P^{app}) vs. ln ([TCX]$_0$) shows that the rate of polymerization is linear (slope = 0.60) with respect to the concentration of initiator (Figure 6). This is different from the first-order and 0.37 order dependence of the polymerization rate on the initiator concentration observed for ATRP of MMA in p-TsCl/CuCl/dNbpy initiation system (51) and in 4-methoxybenzenesulfonyl chloride/CuCl/4,4-Dinonyl-2,2-bipyridine initiation system (52), respectively.

Figures 7 and 8 show the dependence of the molecular weights and molecular weight distributions on the monomer conversion at various initiator concentrations. In the cases of [MMA]$_0$/[TCX]$_0$ ratios of 400 : 1.0 and 400 : 0.5, the molecular weights (M$_{n(GPC)}$) increased linearly with monomer conversion and were close to the theoretical values (M$_{n(th)}$), and the molecular weight distributions are relatively narrow (M$_w$/M$_n$ lower than 1.25), all these results indicated that the polymerizations are well controlled. For the case of very high ratios of [MMA]$_0$/[TCX]$_0$ (like 400 : 0.125), the molecular
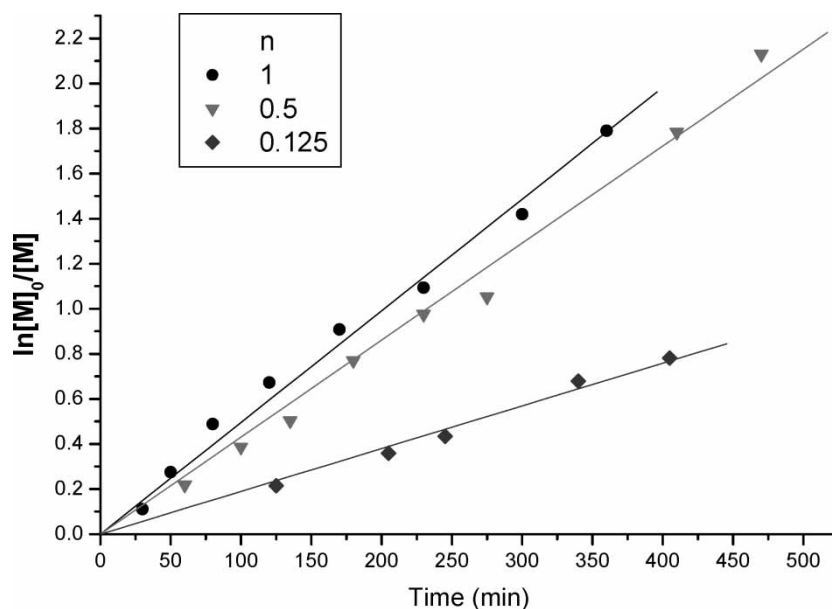

Figure 5. Effect of initiator concentration on the homogeneous solution ATRP of MMA at 80°C. Conditions: [MMA]$_0$: [TCX]$_0$: [CuCl]$_0$: [PMDETA]$_0$ = 400 : n : 1 : 3, VMMA/VDMF = 3/1.
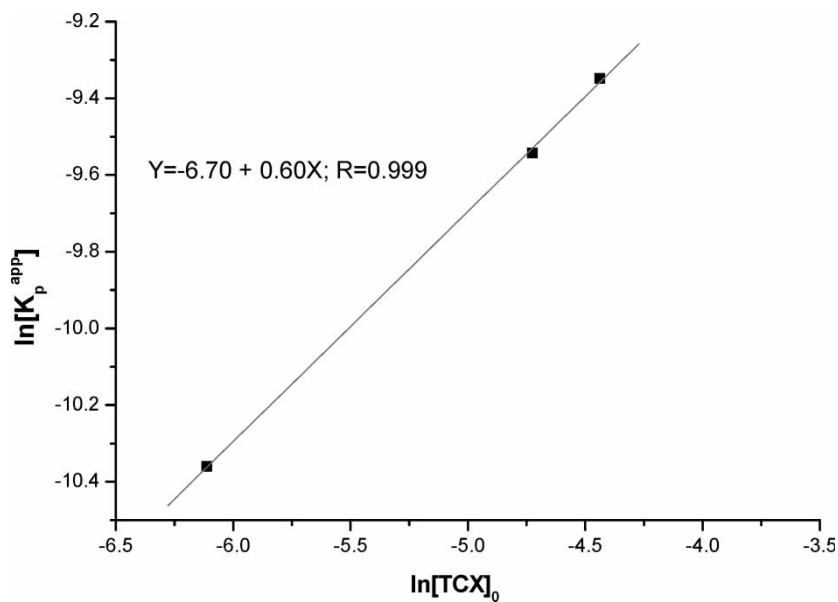
Figure 6. Dependence of $\ln[k_p^{app}]$ on $\ln[TCX]$ 0 for homogeneous ATRP of MMA in DMF. Conditions: VMMA/VDMF = 3/1, T = 80°C.
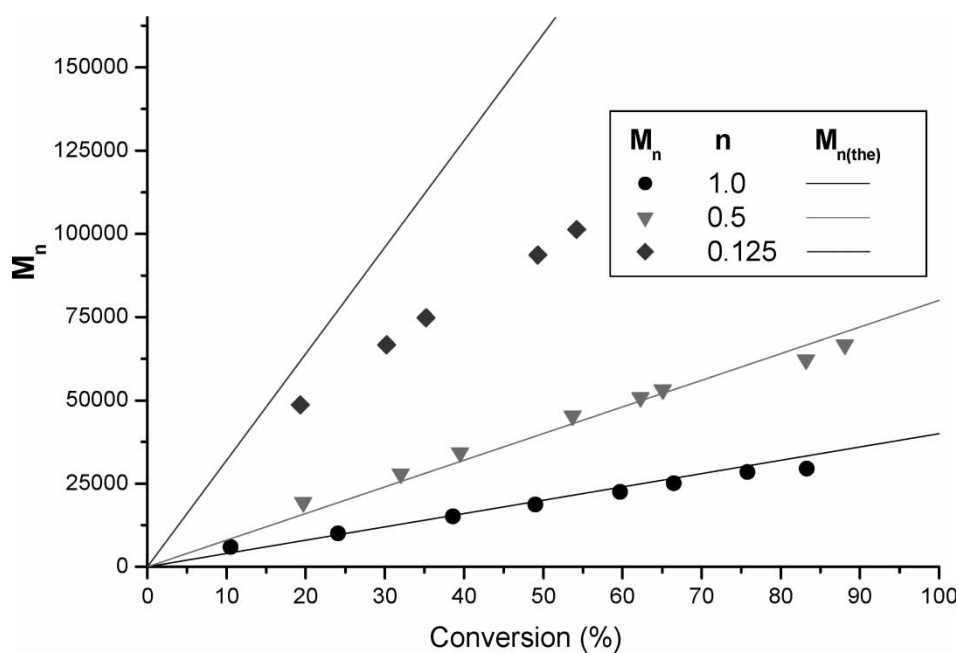

Figure 7. Dependence of the molecular weights on conversion at different concentrations of initiator. Conditions the same as Figure 5.
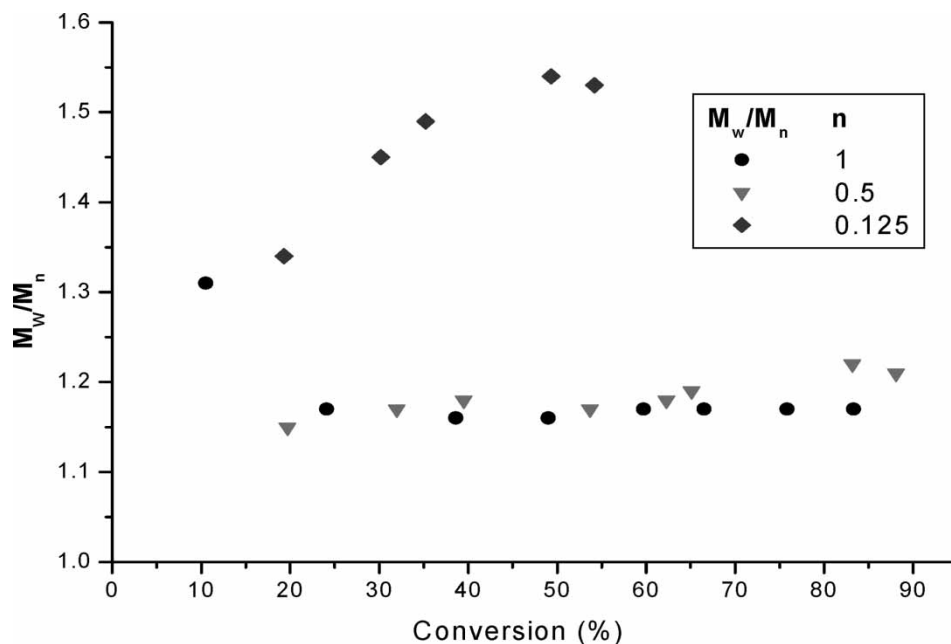
Figure 8. Dependence of molecular weight distributions on conversion at different concentrations of initiator. Conditions the same as Figure 5.

weights are a deviation from the theoretical values, and the molecular weight distributions are broad ($M_w/M_n = 1.33–1.54$), the reason for this may be lie in the termination and other side reactions which become prominent as higher molecular weight polymers are targeted (6, 53).

Effect of Reaction Temperature

The temperature effect on the rate of polymerization for the homogeneous ATRP of MMA initiated by TCX/CuCl/PMDETA (1 : 1 : 3) was investigated, and the result is shown in Figure 9 (the result at 80°C have been shown in Figure 2). The corresponding plots of $\ln([M]_0/[M])$ vs. time were linear for all temperatures, indicating the first order kinetics with respect to monomer, the propagating radical concentration was constant and with no significant termination reactions during the polymerization. No induction time was found in all temperatures. The rate of polymerization increased significantly with an increasing of polymerization temperature.

On the basis of the Arrehnius plot in Figure 10, the apparent activation energy was calculated $\Delta E_{app}^{\neq} = 43.3\,\text{KJ/mol}$ for the homogeneous ATRP of MMA initiated by TCX/CuCl/PMDETA (1 : 1 : 3), which was lower than the result (62.7 kJ/mol) for p-TsCl/CuCl-initiated ATRP of MMA reported by Wang et al. (51) and the result (105.8 KJ/mol) for 4-methoxybenzenesulfonyl chloride/CuCl/4,4-Dinonyl-2,2-bipyridine -initiated ATRP of MMA reported by Percec et al. (52), respectively.

The activation energy for MMA propagation is known to be $\Delta E_{prop}^{\neq} = 22.2\,\text{kJ/mol}$ (54). The relation between the enthalpy of the equilibrium, the activation energy of propagation, and the apparent activation energy is shown in Equation (2). The enthalpy of the
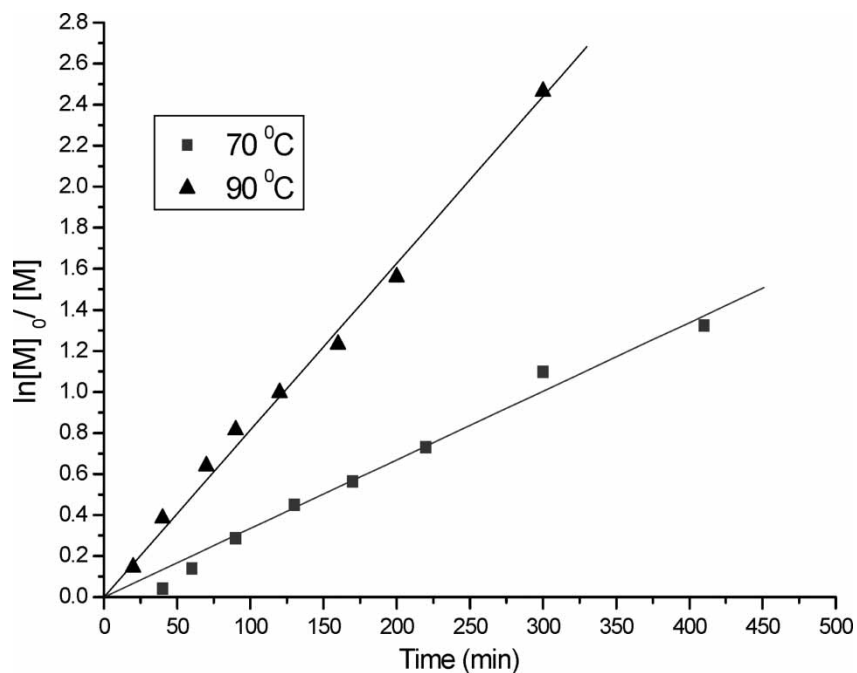
Figure 9. Kinetic plots for the homogeneous ATRP of MMA at different temperatures in DMF. Conditions: $[MMA]_0 : [TCX]_0 : [CuCl]_0 : [PMDETA]_0 = 400 : 1 : 1 : 3$, VMMA/VDMF $= 3/1$.
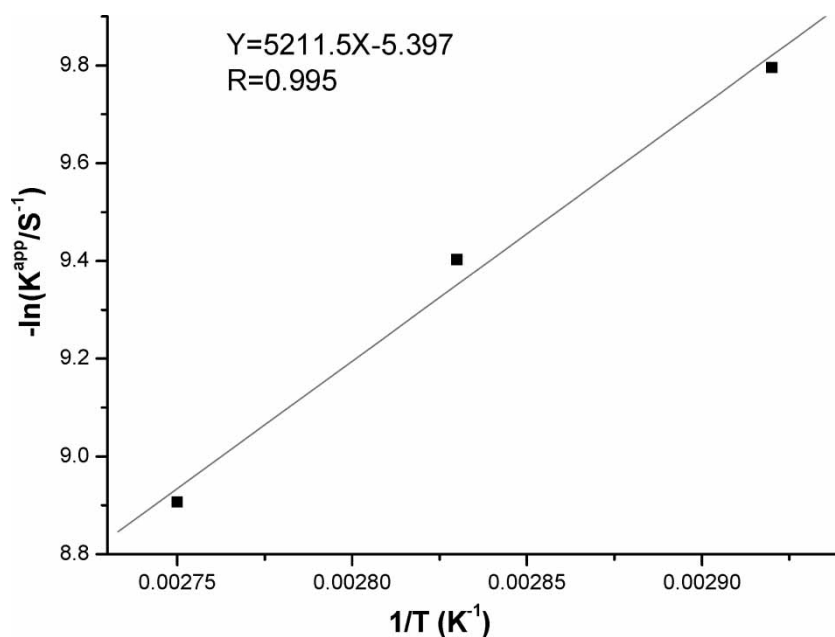

Figure 10. Arrhenius plots for the ATRP of MMA in DMF conditions same as Figure 9.

equilibrium, ΔH_{eq}^0, was therefore estimated to be 21.1 KJ/mol for the homogeneous ATRP of MMA initiated by TCX/ CuCl/ PMDETA (1 : 1 : 3).

$$\Delta H_{eq}^0 = \Delta E_{app}^{\neq} - \Delta E_{prop}^{\neq} \qquad (2)$$

Figure 11 shows the dependence of the molecular weights and molecular weight distributions on monomer conversion. In all cases, the molecular weights increased linearly with monomer conversion and were close to the theoretical values, and the molecular weight distributions were relatively narrow (most molecular weight distributions were lower than 1.2). The results suggest that the reactions proceed in a controlled way at all temperatures, and the reaction temperature had little influence on the molecular weights and molecular weight distributions.

Analysis of Polymer Structure

There are two halogen atoms at each direction of the initiator; to determine how much halogen atoms have the action of initiation, we analyzed the ^{1}H-NMR spectrum of obtained polymer (Figure 12). The signals at $0.75 \sim 1.15$ ppm (d) are assigned to protons of methyl groups of $-C(CH_3)(COOCH_3)$, the signals from $1.45 \sim 1.90$ ppm (c) are attributed the methylene group of $-CH_2$-, and the peak at 3.56 ppm (e) corresponds the methoxy groups in the main chain. The small peaks at 7.40 (b) and 5.13 ppm (a) correspond to the aromatic protons and residual alkyl protons of initiator, and the integration ratio is 2/1. It is because the residual alkyl protons of initiator are next to the halogen atoms that make its peak at 5.13 ppm. However, if all halogen atoms of initiator have the initiation action, there will be no halogen atoms next to the residual alkyl protons of initiator and its peaks should be lower than 5.13 ppm. This
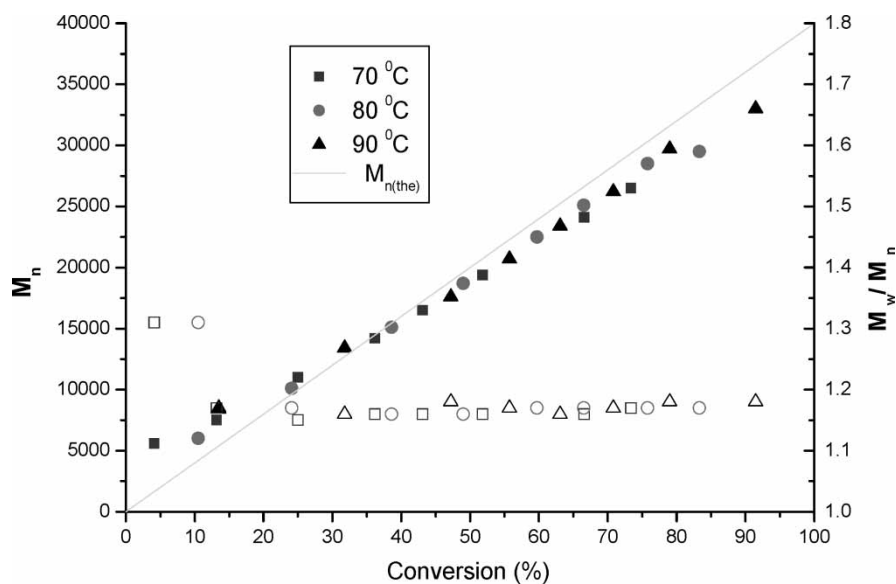

Figure 11. Dependence of M_n and M_w/M_n on monomer coversion for the homogeneous ATRP of MMA in DMF at different temperatures. Conditions the same as Figure 9.
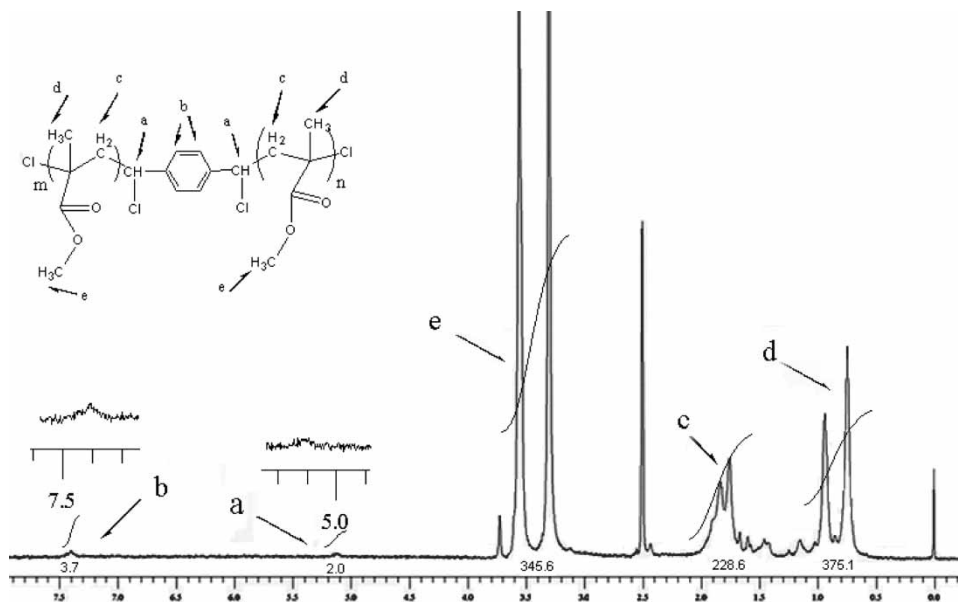
Figure 12. ^{1}H-NMR for PMMA ($M_{n(GPC)} = 5800$, $M_w/M_n = 1.30$) prepared by MMA/TCX/CuCl/PMDETA in DMF, $V_{MMA}/V_{DMF} = 3:1$.

result indicated that the TCX acts as a bifunctionsal initiator for ATRP of MMA, and the result is consistent with the result reported by Hocker (21) that PhCHCl$_2$ acts as a mono-functional initiator. The $M_{n(NMR)}$ values for PMMA can be calculated using its ^{1}H-NMR data according to the equation [$M_{n(NMR)} = (2 \times I_e \times M_m)/(6 \times I_a) + M_i$], where M_m and M_i are the molar masses of the monomer and initiator, respectively. The value is calculated as 5940, which is close to the $M_{n(GPC)}$ value (5800). This result suggests that TCX is a bifunctional initiator for ATRP of MMA. A similar method was used in other reports (55–57, 55–57), to analyze the polymer structure whether it is star polymer or not.

Chain Extension

As shown by ^{1}H-NMR analysis, the obtained PMMA was functionalized with halogen atoms and can be used as a macroinitiator to advance a chain-extension reaction with a fresh MMA monomer. Figure 13 shows GPC curves of PMMA before and after chain-extension. As shown in Figure 13, the molecular weight increased form 11600 to 32900 with the conversion of 89.4%. The molecular weight of the extended polymer is close to the theoretical value (31230). The molecular weight distribution is low (1.21). The success of the chain-extension polymerization further verifies the active nature of the precursor chain end.

Conclusions

In summary, the homogeneous ATRP using TCX/CuCl/PMDETA as the initiating system has been successfully carried out for methyl methacrylate. The kinetic plots were first order vs. monomer. Well-controlled polymers with low polydispersities ($M_w/M_n = 1.15–1.25$) have been achieved. The molecular weights increased linearly with
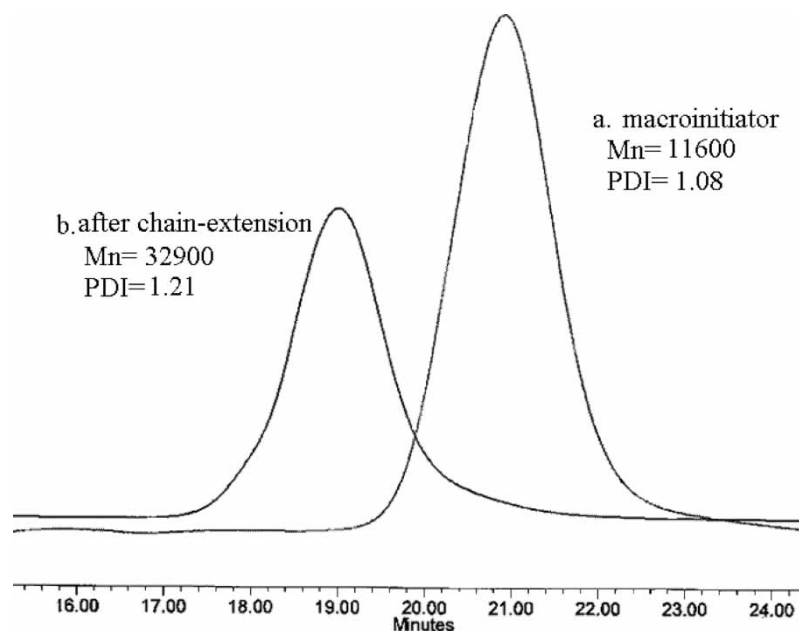
Figure 13. GPC traces of (a) the macroinitiator and (b) the chain-extended polymer. Conditions: $[MMA]_0/[Macroinitiator]_0/[CuCl]_0/[PMDETA]_0 = 227:1:1:3$; $V_{MMA}/V_{DMF} = 1/1$; Temperature $= 90°C$; Conversion $= 85.4\%$.

monomer conversion and were close to the theoretical values, indicating a high apparent initiator efficiency. To examine the effect of initiator concentration on polymerization, a series of homogeneous ATRP polymerization of MMA initiated by TCX/CuCl/ PMDETA at different initiator concentrations were carried out at 80°C. The polymerization rate increased significantly with an increase of TCX concentration. A plot of the apparent rate constant k_p^{app} vs. the initial initiator concentration ($[TCX]_0$), showed that the rate of polymerization was about 0.6 order with respect to the concentration of initiator. The polymerization rate increased significantly with an increase of [CuCl] concentration. The dependence of $\ln k_p^{app}$ on $\ln [CuCl]_0$ indicated a 0.91 order. On the basis of the Arrehnius plot, the apparent activation energy was calculated $\Delta E_{app}^{\neq} = 43.3$ KJ/mol, and the enthalpy of the equilibrium, ΔH_{eq}^0, was estimated to be 21.1 KJ/mol for the homogeneous ATRP of MMA initiated by TCX/CuCl/PMDETA (1:1:3). It was proved that TCX acted as a bifunctional initiator for ATRP of MMA through the ^{1}H-NMR spectroscopy characterization of obtained PMMA. The feasibility of TCX as an initiator for the facile preparation of ABA block copolymer or star shape polymer via ATRP is currently under investigation.

Acknowledgement

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