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Controlled radical polymerization of methyl methacrylate in the presence of CuX/phen complexes and alkyl halides

Guang Lou Cheng, Chun Pu Hu, Sheng Kang Ying*

Laboratory of Living Polymerization, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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Abstract

The polymerization behaviour of methyl methacrylate (MMA) in *p*-xylene in the presence of CuCl/L [L = 1,10-phenanthroline (phen) or 4,7-diphenyl-1,10-phenanthroline (DPP)] and tetrachlorocarbon has been studied. For the CCl_4/CuCl/phen/MMA/*p*-xylene system, the linear relationship between the number-average molecular weight of the resulting poly(methyl methacrylate) (PMMA) and MMA conversion, as well as between $\ln[M]_0/[M]$ and time, demonstrate the 'living' nature of this system. When phen is replaced by DPP the polymerization becomes slower, but the molecular weight and molecular weight distribution are better controlled. The stereochemistry of PMMA synthesized in the CCl_4/CuCl/DPP/MMA/*p*-xylene system indicates that the MMA monomer adds to the living polymer chain end in an atactic fashion. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Controlled radical polymerization; Methyl methacrylate; Copper complexes

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1. Introduction

Well-defined polymers have been synthesized successfully by use of living polymerization techniques such as ionic polymerization, coordination polymerization and group-transfer polymerization [1]. However, for these techniques, the rigorous exclusion of moisture and other impurities is required and the choice of suitable monomers is limited. With controlled/'living' radical polymerization, on the other hand, it is possible to overcome these problems by establishing a reversible equilibrium between active species and dormant species [2–10]. One of the approaches to the controlled radical polymerization of styrene or acrylates is atom-transfer radical polymerization (ATRP) with RX/CuX/2,2′-bipyridine (bpy) as initiator and catalyst system [8,9]. Phenanthroline (phen) is less expensive and a more rigid molecule compared with bpy, having a flexible C(2)–C(2′) bond that is able to rotate. In addition, the oxidation–reduction potentials for bpy and phen complexes [the redox potentials of $Cu(bpy)_2Cl$ and $Cu(phen)_2Cl$ are +120 mV and +174 mV, respectively] show that phen stablizes the Cu(1) state better than bpy, possibly because the former has a more delocalized electronic structure of which the π^* orbitals contribute more to π-backbonding interaction [11]. So it was found that $Cu(phen)_2Cl$ always shows higher catalytic activity and selectivity than $Cu(bpy)_2Cl$ in ATRA reactions [12].

Against from this background, it is encouraging to investigate the feasibility of ATRP catalysed by CuX/phen complexes. In previous papers we reported that RX/CuX/1,10-phenanthroline (phen) is also an effective system to control the polymerization of styrene [13–15]. Since then, Destarac et al. also reported the controlled behaviour of styrene polymerization by using the (1-PE)Cl/CuCl/phen system [16]. In this work, the controlled polymerization of methyl methacrylate (MMA) initiated and catalysed with CCl_4/CuCl/phen and CCl_4/CuCl/4,7-diphenylphenyl-1,10-phenanthroline (DPP) systems was investigated. The number-average molecular weight (M_n) of the resulting poly(methyl methacrylate) (PMMA) was well controlled and the polydispersities of the PMMA synthesized were quite narrow (at around 1.20).

2. Experimental

2.1. Materials

MMA was vacuum distilled twice from CaH_2 just prior to use. CCl_4 and *p*-xylene were distilled under argon just before use. CuX was purified according to a known

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* Corresponding author. Tel.: +86-21-642-5318; Fax: +86-21-642-53539

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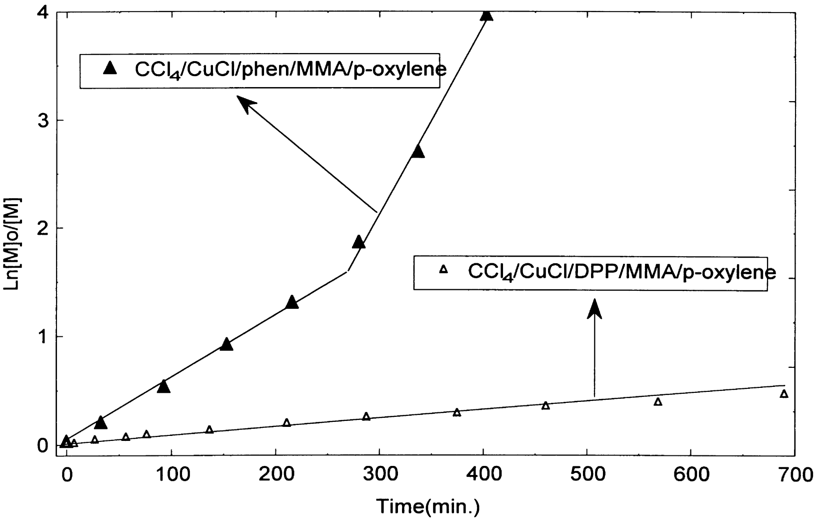

Fig. 1. Ln$[M]_0/[M]$ vs. time for the polymerization of MMA in *p*-xylene in the presence of CCl_4 and CuCl/phen or CuCl/DPP complex at 95°C. Polymerization conditions: $[MMA] = 4.70$ M, $[CCl_4] = 0.016$ M, $[CCl_4]$:[CuCl]:[phen or DPP] = 2:1:2.3.

procedure [17]. Phen was recrystallized twice from acetone and dried under argon. Other laboratory reagents were used as received.

2.2. Polymerization procedure

To a previously dried round-bottomed flask, the solid reagents such as CuX and phen were added. After the flask was degassed three times, the liquid reagents — i.e., solvent, monomer and initiator — were introduced with a syringe. The flask was then immersed in an oil bath thermostatted at 95°C and the heterogeneous system was magnetically stirred under an argon atmosphere. As soon as the reaction system reached the desired temperature, a certain amount of sample was taken out of the flask and recorded as the starting point of polymerization. At predetermined times, the same amount of sample was withdrawn from the flask and injected directly into a gel permeation chromatograph to measure the molecular weight and polydispersity index of the polymers produced. The sample used in the kinetics experiments was evaporated to dryness under vacuum to calculate the monomer conversion.

2.3. Measurements

Gel permeation chromotography (g.p.c.) of polymers was performed at a flow rate of 1.0 ml min^{-1} in tetrahydrofuran (THF) at 25°C by using a Waters 150 component system (refractive index detectors) equipped with Ultra-μ-Stragel columns (100 Å and 10 000 Å). Calibration was performed with polystyrene standards. ^{13}C nuclear magnetic resonance (n.m.r.) spectra of PMMA were recorded at 20°C in $CDCl_3$ with a Bruker AM-400 spectrometer operating at 300 Hz using an inverse-gated proton decoupling technique. The

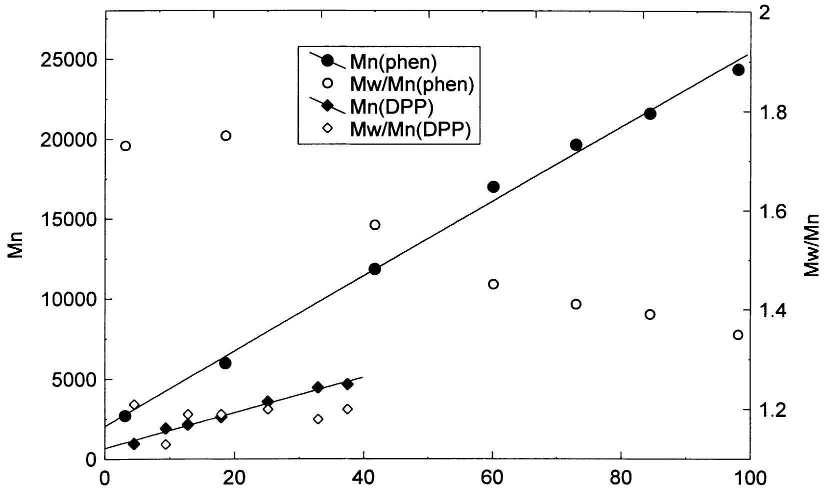

Fig. 2. Dependence of M_n (as determined by g.p.c.) and MWD on monomer conversion for the polymerization of MMA in *p*-xylene in the presence of CCl_4 and CuCl complexed with phen or DPP. Polymerization conditons as indicated in Fig. 1.

Table 1
Composition of the stereoisomers of PMMA prepared through ATRP by using various complexing ligands

Ligand	*mmmm*	*mrrm*	*mrrr*	*rrrr*	*rmrm* + *mmrm*	*rmrr* + *mmrr*	*mmmr*	*rmmr*	*mm*	*mr*	*rr*	*m*	*r*	ρ[a]
DPP[b]	0	0.046	0.223	0.325	0.105	0.226	0.033	0.042	0.416	0.416	0.538	0.254	0.746	0.911
bpy[c]	0.010	0.060	0.220	0.270	0.110	0.260	0.030	0.040	0.050	0.360	0.590	0.230	0.770	1.040
AIBN[d]	0.020	0.040	0.210	0.280	0.110	0.270	0.030	0.040	0.060	0.340	0.600	0.230	0.770	1.04

[a] The persistence ratio, $\rho = 2(m)(r)/(mr)$.
[b] Polymerization conditions as indicated in Fig. 1.
[c] Data from [9].
[d] AIBN = azobisisobutyronitrile. Data from [20].

stereoisomers of PMMA were determined by analysis of ^{13}C-n.m.r. spectra according to the assignment of Peat and Reynolds [18].

3. Results and discussion

Fig. 1 shows the pseudo first-order kinetic plot for the polymerization of MMA in *p*-xylene initiated with CCl_4 in the presence of CuCl/phen complex at 95°C. The linearity of $\ln[M]_0/[M]$ vs. time indicates that the number of active species in this system remains constant throughout the reaction, except when the slope of the linear line changes at the later stage of polymerization (conversion $> 80\%$). Fig. 2 reveals that the M_n of PMMA increases linearly with increasing MMA conversion and the molecular weight distribution (MWD) is quite narrow for the final products. All of these experimental data demonstrate the ‘living’ nature of the CCl_4/CuCl/phen/MMA/*p*-xylene system. However, it is of interest to find that the MWD of PMMA at the early stage of polymerization is broader than that at the later stage. A similar phenomenon has also been observed in the polymerization of styrene with the same initiator and catalyst [15,16] and in the MeOPh-SO_2Cl/CuCl/bpy9/MMA [19] and $CCl_4/RuCl_2(PPh_3)$/MeAl $(ODBP)_2$/MMA systems [6]. This unusual experimental behaviour is quite interesting and will be studied further.

When phen is replaced by DPP the polymerization system becomes more homogeneous, achieving complete homogeniety after about 3 h. However, Fig. 1 shows that the polymerization rate of this system is much slower than that in the heterogeneous CCl_4/CuCl/phen/MMA/*p*-xylene system. This indicates that the activity and/or the concentration of the active species existing in these two systems may be different. The M_n of PMMA synthesized in the homogeneous system also increases linearly with increasing MMA conversion and its MWD is quite narrow (at around 1.20), as shown in Fig. 2. Furthermore, the stereoisomers of PMMA synthesized in the homogeneous system were measured and are listed in Table 1. Table 1 shows that the stereoisomerism of such PMMA is similar to that of PMMA synthesized with a conventional free-radical polymerization initiator [20] and in the RX/CuX/bpy [9] system. This indicates that the MMA monomer added to the living polymer chain end in an atactic fashion.

In conclusion, we have demonstrated for the first time that RX/CuX/phen and RX/CuX/DPP are also effective systems for the controlled polymerization of MMA. Details of MMA polymerization performed by using different kinds of phen as ligands are being investigated.

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