Controlled radical polymerization of methyl methacrylate in the presence of carbon tetrachloride, metallic copper and 2,2′-bipyridine or 1,10-phenanthroline [1]

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Abstract

The polymerization behaviors of methyl methacrylate (MMA) in the presence of carbon tetrachloride (CCl_4), metallic copper powder (Cu^0) and 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) in *p*-xylene at 95°C was examined. In both systems of Cu^0/bpy/CCl_4/MMA/*p*-xylene and Cu^0/phen/CCl_4/MMA/*p*-xylene, the 'living' nature of these two systems was demonstrated by the linear relationship between the MMA conversion and the number-average molecular weight (M_n) of the produced poly(methyl methacrylate) (PMMA) as well as reaction time and $\ln[M]o/[M]$. Furthermore, the polydispersity index of the PMMA obtained in the former case was smaller than that in the latter case. In the Cu^0/bpy/CCl_4/MMA/*p*-xylene system, with decreasing the amount of Cu^0, the polymerization rate decreased and the polydispersity of the obtained PMMA increased, while the M_n of PMMA was still close to the calculated one by assuming that one molecule of CCl_4 initiates only one polymer chain. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Controlled radical polymerization; Methyl methacrylate; Metallic copper; Carbon tetrachloride; 2,2′-Bipyridine; 1,10-Phenanthroline

1. Introduction

Over the past few years controlled/'living' radical polymerization has been studied extensively [1–10]. One of the approaches to the controlled radical polymerization of styrene or acrylates was atom transfer radical polymerization (ATRP), based on RX/CuX/2,2′-bipyridine (bpy) [5–9] or RX/CuX/1,10-phenanthroline (phen) [11–14] system. However, one of the main drawbacks of this method was that it required a large amount of catalyst (the molar ratio of the catalyst to the initiator was from 0.5 to 1.0) which had to be removed after the polymerization for preparing polymer materials. Recently, Matyjaszewski et al. [15] have used toluene sulfonylchloride/Cu^0/4,4′-di-(5-nonyl)-2,2′-bipyridine (dNbpy) in a molar ratio of 1:2:1 at 70°C to synthesize a sample of poly(methyl methacrylate) (PMMA) with an M_n of 8360 g mol^{-1} and a polydispersity of 1.45.

The Cu^0/dNbpy catalyst efficiency was calculated and found to be at 290 g PMMA g^{-1} Cu h^{-1}. Nearly at the same time, we reported that a small amount of copper powder (the molar ratio of the catalyst to the initiator was only from 0.02 to 0.05) was enough to well control the polymerization of methyl methacrylate (MMA) or styrene [16,17]. In this paper, some detailed behaviors of MMA polymerization by using heterogeneous Cu^0/phen/CCl_4 or Cu^0/bpy/CCl_4 system was investigated. This catalyst could yield PMMA with an M_n of 12,000 g mol^{-1} and a polydispersity of 1.33. The catalyst efficiency was higher at 375 g PMMA g^{-1} Cu h^{-1}.

2. Experimental

2.1. Materials

MMA (99.0%, Shanghai No. 1 Chemicals Factory) was vacuum distilled two times from CaH_2 just before use. CCl_4 (99.5%, Shanghai No. 1 Chemicals Factory) and *p*-xylene (98.5%, Shanghai No. 1 Chemicals Factory) were distilled under argon just before use. Copper powder (99.5%, Shanghai No. 3 Chemicals Factory, particle size 200-mesh) was purified by reduction with hydrogen gas at 150°C just before use. Phen (99.5%, Beijing Chemicals Factory) and bpy (99.5%, Beijing Chemicals Factory) were recrystallized two times from acetone and dried under argon.

2.2. Polymerization

To a previously dried round bottom flask, the solid reagents such as Cu^0 and phen or bpy were added. After the flask was degassed three times, the liquid reagents, i.e., *p*-xylene, MMA and CCl_4 were introduced via a syringe. The flask was then immersed in an oil bath thermostated at 95°C and the heterogeneous system was magnetically stirred under argon atmo-

sphere. As soon as the reaction system reached the desired temperature, a certain amount of sample was taken out from the flask and recorded as the starting point of polymerization. At timed schedule, the same amount of sample was withdrawn from the flask and was injected directly into gel permeation chrotomography (GPC) to measure the M_n and the PDI of the produced polymer. The sample corresponding to kinetic experiment was evaporated to dryness under vacuum to calculate the monomer conversion.

2.3. Measurements

GPC analysis of polymers was performed at a flow-rate of 1.0 ml min^{-1} in THF at 25°C by using a Waters150 component system (RI detectors) equipped with ultra-*u*-stragel columns (10^2, 10^3 and 10^4 Å) after calibrated with standard polystyrene. The reported value of the M_n of PMMA was deduced from GPC value by the method of universal calibration [18,19]. The ^{1}H-NMR spectra of polymers were recorded in $CDCl_3$ at 20°C with a Brucker DPX-300 spectrometer operating at 300.13 Hz. Characteristic peaks on ^{1}H-NMR plot were assigned according to known literature [4].

3. Results and discussion

When a solution of MMA and CCl_4 (molar ratio = 150:1) in *p*-xylene containing Cu^0 (0.1 equiv per CCl_4) and phen or bpy (2.5 equiv per copper) is heated at 95°C for 30 min, the red insoluble copper powder disappears completely and the system becomes heterogeneous green, which is different from the ATRA of chloroform to styrene at 140°C [20]. This indicates that in this system the initiation may result from a reaction of CCl_4 with Cu^0 and phen or bpy to generate a new insoluble cupric complex at the early stage of polymerization. Furthermore, the polymerization of MMA proceeds smoothly without an induction period and the conversion
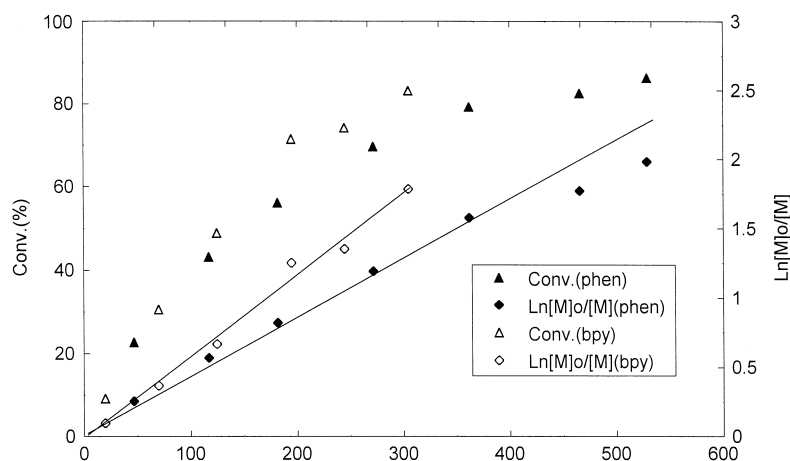
Fig. 1. Monomer conversion and ln[M]o/[M] vs. time for the polymerization of MMA initiated with CCl$_4$ in the presence of Cu^0/bpy or Cu^0/phen in *p*-xylene at 95°C. Polymerization conditions: [MMA] = 4.70 M, [CCl$_4$] = 3.17 × 10^{-2} M, [CCl$_4$]:[Cu^0]:[phen or bpy] = 10:1:2.5.

of MMA reaches over 80% after ca. 5 h and the catalyst efficiency is calculated and found to be at 375 g PMMA g^{-1} Cu h^{-1}, which is higher than that of 290 g PMMA g^{-1} Cu h^{-1} in Cu^0/dNbpy system [15], although such a kind of catalyst is less soluble in the system. Fig. 1 shows the pseudo-first-order kinetic plot for the polymerization of MMA initiated and catalyzed with Cu^0/phen/CCl$_4$ or Cu^0/bpy/CCl$_4$ in

p-xylene at 95°C, respectively. In both cases, the linearity of ln[M]o/[M] vs. time indicates that the number of active species remains constant and the chain-break reaction is insignificant, i.e., K_p[P*] = constant, where K_p stands for rate constant and [P*] stands for concentration of active propagation chain.

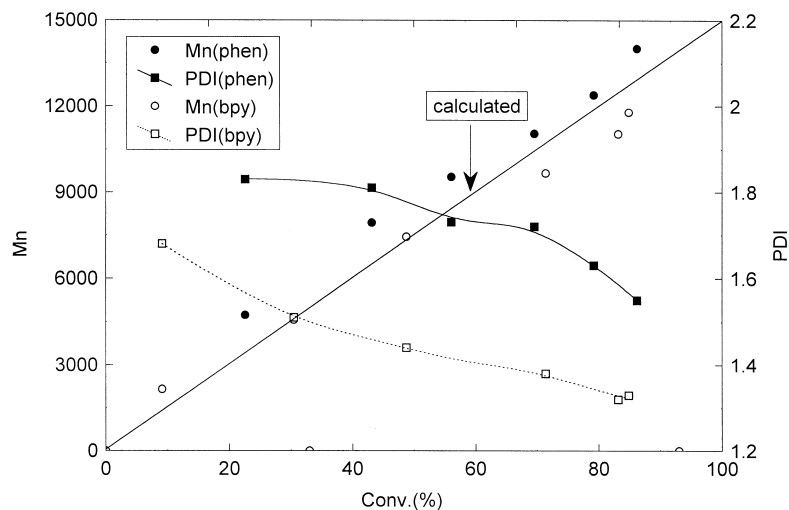Fig. 2 demonstrates the 'living' nature of these two systems. In both cases, the number-

Fig. 2. Dependence of M_n and PDI of the obtained PMMA on monomer conversion for the polymerization of MMA initiated with CCl$_4$ in the presence of Cu^0/bpy or Cu^0/phen in *p*-xylene at 95°C. Polymerization conditions as indicated in Fig. 1.
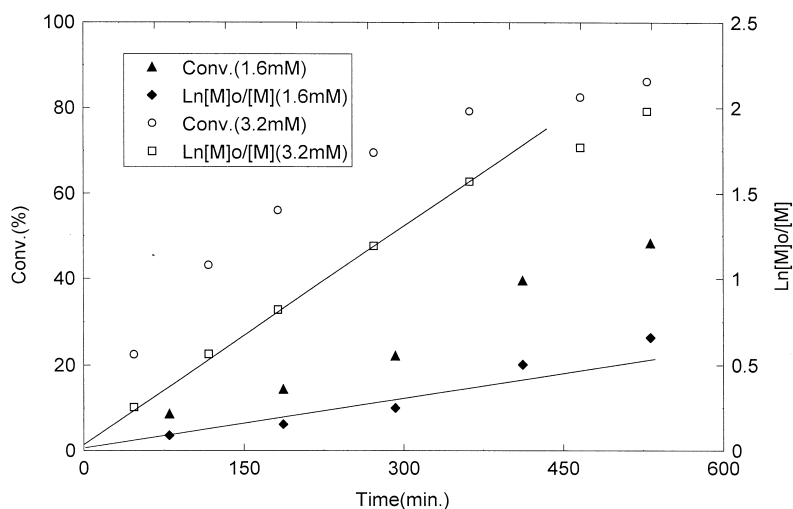
Fig. 3. Monomer conversion and $\ln[M]o/[M]$ vs. time for the polymerization of MMA initiated with CCl_4 at the varying concentration of copper powder in *p*-xylene at 95°C. Polymerization conditions: $[MMA] = 4.70$ M, $[CCl_4] = 3.17 \times 10^{-2}$ M, $[Cu^0] = 3.2$ mM or 1.6 mM, $[CCl_4]:[Cu^0]:[bpy] = 10:1:2.5$ or $10:0.5:1.25$.

average molecular weight (M_n) of the produced PMMA increases linearly with increasing the monomer conversion and matches the calculated value based on the assumption that one molecule of CCl_4 initiates only one polymer chain ($M_n = 100 \times \Delta[MMA]/[CCl_4]_0$). It is noteworthy to point out that the polydispersity index (PDI = M_w/M_n) of the produced PMMA in the phen

system is higher than that in the bpy system and in both cases, the PDI of PMMA decreases over the range from 1.83 to 1.55 and from 1.68 to 1.33, respectively, during the course of polymerization. This indicates that the complexing ability of these two ligands is different and that the addition of MMA monomer to 'living' PMMA chain end at the early stage of poly-
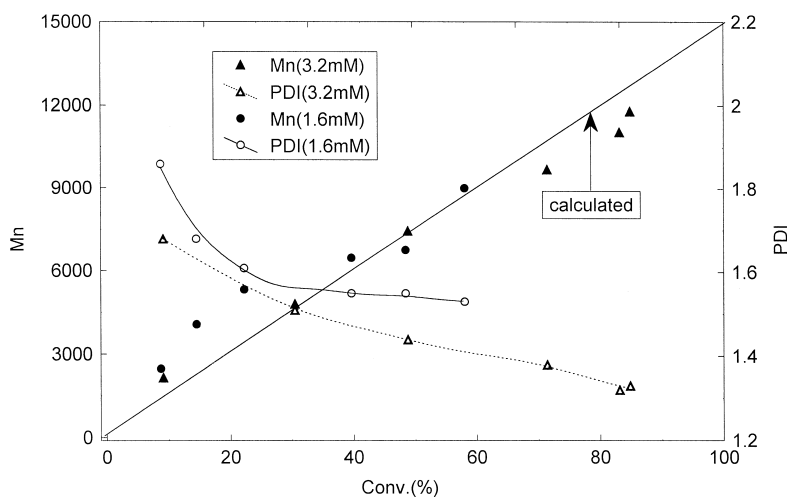

Fig. 4. Dependence of M_n and PDI of obtained PMMA on monomer conversion for the polymerization of MMA initiated with CCl_4 at the varying concentration of copper powder in *p*-xylene at 95°C. Polymerization conditions as indicated in Fig. 3.

merization is more nonuniform than that at the later stage of polymerization.

As the bpy system is better than the phen system for controlling the polymerization of MMA, the polymerization of MMA with Cu^0/bpy/CCl_4 was then examined further. Figs. 3 and 4 show the experimental results of MMA polymerization at the different concentrations of copper powder. In both cases, the polymerization behavior is similar except the lower rate of polymerization for using the smaller amount of Cu^0 due to the lower concentration of initiating system. It can also be seen from Fig. 4 that, with decreasing the amount of Cu^0, the molecular weight distribution of PMMA only slightly broadens while the M_n of PMMA is still close to the calculated one by assuming that one molecule of CCl_4 initiates only one polymer chain. These phenomena suggest that Cu^0 and/or cupric complexes may act as catalysts while CCl_4 may act as an initiator.

Fig. 5 presents the ^{1}H-NMR spectrum of PMMA formed when the monomer conversion reaches 9.1% after 20 min by using Cu^0/bpy/

CCl_4 in p-xylene at 95°C. The large peak c at 3.58 ppm is assigned to the methyl ester protons existing in the repeat units of main-chain while the small peak c' at 3.79 ppm originates from the methyl ester protons which are adjacent to the terminal chlorine atom at the w-end. The peak intensity ratio of c to c' is 11.9 which is close to the half of the number-average degree of polymerization (DP_n) of 22.0 measured by GPC method. This suggests that CCl_4 might act as a bifunctional initiator. Moreover, the two shoulders of peak c at 3.58 ppm may be ascribed to the methyl ester protons which are not adjacent to the chlorine atom existing in some oligomers such as trimers or tetramers etc. [21] because of the low M_n ($M_n = 2,200$) and the high polydispersity (PDI = 1.68) of the measured sample. In addition, the stereochemistry of the produced PMMA is 60.8% rr (from ^{1}H-NMR) which is similar to that synthesized by free radical polymerization with AIBN as an initiator [22], indicating that the MMA monomer added to the 'living' macromolecular chain end should be in an atactic fashion.
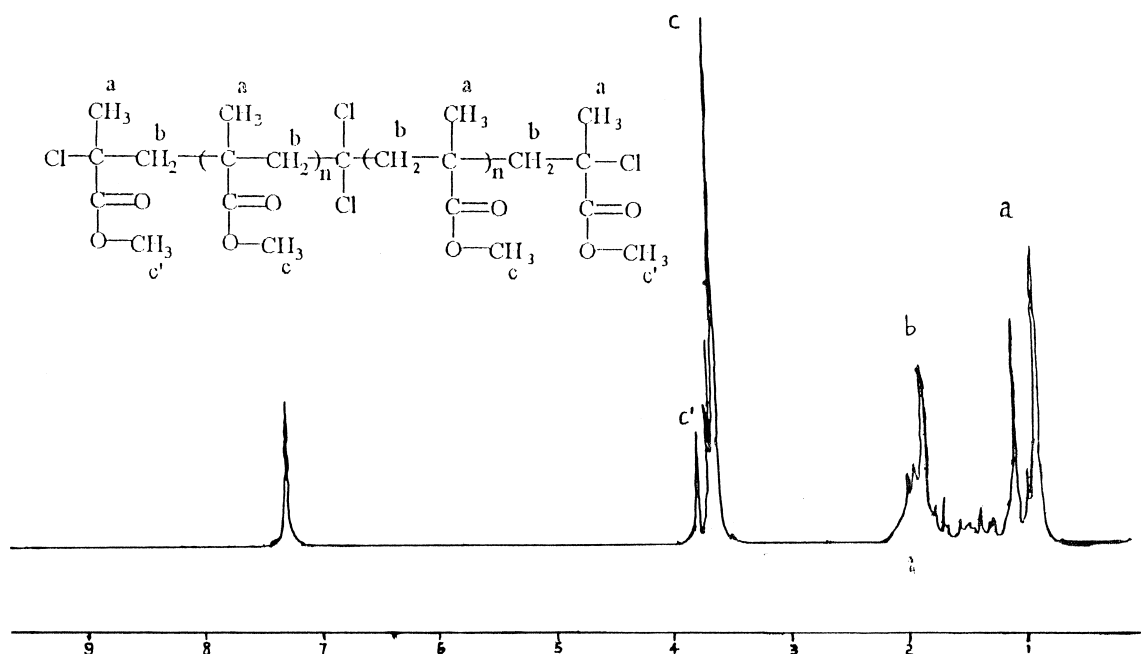

Fig. 5. ^{1}H-NMR spectrum of PMMA synthesized by using [CCl_4]/[Cu^0]/[bpy] in p-xylene at 95°C. Polymerization conditions as indicated in Fig. 1. DP_n(NMR) = 11.9, DP_n(GPC) = 22.0, PDI = 1.68.

In conclusion, controlled/'living' radical polymerization of MMA has been achieved by using Cu^0/phen/CCl_4 or Cu^0/bpy/CCl_4 system respectively. Compared to the Cu^0/dNbpy system [15], the catalyst efficiency is higher and the polydispersity of the yielded PMMA is lower. Details concerning the mechanism of these systems are being studied.

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