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Synthesis of Well-Defined Poly(methyl methacrylate) by Radical Polymerization with a New Initiation System TPED[†]/$FeCl_3$/PPh_3

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ABSTRACT: Well-defined poly(methyl methacrylate) (PMMA) with an α-hydrogen atom and an ω-chlorine atom as the end groups has been synthesized by bulk polymerization of MMA at 95 °C using a new initiation system, 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)/$FeCl_3$/PPh_3. The conversion of polymerization reached to ~100%. The molecular weight of PMMA obtained was high and the polydispersity index was quite narrow (e.g., $M_n = 171\,800$; $M_w/M_n = 1.13$). The polymerization of MMA exhibited some "living"/controlled radical polymerization characteristics. The mechanism of polymerization was proposed as a reverse atom transfer radical polymerization (ATRP). The presence of the hydrogen and the chlorine atoms as end groups of the PMMA obtained was determined by ^1H NMR spectroscopy.

Introduction

The "living"/controlled radical polymerization, atom transfer radical polymerization (ATRP), gives an efficient way to synthesize well-defined polymers.[1] In conventional ATRP, organic halides (RX) are used as initiators; transition metal compounds in their lower oxidation state (Mt^n, where n is the oxidation state), such as Cu(I),[2] Fe(II),[3] Ru(II),[4] Ni(II),[5] Rh(I),[6] and Pa(II),[7] are used as catalysts; electron-donating compounds, such as 2,2′-bipyridine and triphenylphosphine (PPh_3) are used as ligands (L). Styrene (St), methyl methacrylate (MMA), methyl acrylate (MA), acrylonitrile, 2-hydroxyethyl acrylate, etc. have been polymerized successfully via the ATRP.[2,8]

The ATRP process, however, has two major problems in the initiation system: the halide species RX is usually toxic and the catalyst complex Mt^nL_m (where m is the number of ligands) is easily oxidized by the oxygen in air.[9] To overcome these drawbacks, a so-called reverse ATRP has recently been explored. In this process, a conventional radical initiator and a higher oxidation state transition-metal catalyst complex $Mt^{n+1}XL_m$ are used instead of the organic halide initiator RX and the lower oxidation state catalyst complex Mt^nL_m.

So far, two types of efficient reverse initiating systems, AIBN/$CuCl_2$ (or $CuBr_2$)/2,2′-bipyridine[10] and AIBN/$FeCl_3$/PPh_3,[9] have been reported. "Living"/controlled radical polymerizations of MMA, MA, or St were performed with the two systems.

Braun[11] et al. reported that TPED can be used as an initiator for conventional radical polymerization and copolymerization of vinyl monomers. In the initiation step, the activated monomer radicals were produced via a hydrogen transfer addition reaction of the diphenylhydroxymethyl primary radical, which was formed from the homolytic cleavage of TPED. Polymers with α-hydrogen atom end groups were obtained. However, the polydispersity of the polymer is broad, because of the presence of the facile coupling and disproportion reactions between the propagating radicals. Therefore, the radical polymerization is not well-controlled.

In this article, we report the synthesis of well-defined PMMA, with α-hydrogen and ω-chlorine atom end groups, and with high molecular weight and narrow polydispersity, using a new initiation system TPED/$FeCl_3$/PPh_3.

Experimental Section

Materials. $FeCl_3$ (anhydrous) was prepared from $FeCl_3\cdot 6H_2O$ according to reference method.[12] TPED was prepared from benzophenone and 2-propanol[13] and was recrystallized from 95% ethanol; mp 187 °C. MMA was dried over CaH_2 and distilled under reduced pressure. Triphenylphosphine (Aldrich) was recrystallized from ethanol to eliminate triphenylphosphine oxide.

Polymerization. As a general procedure, the monomer was added into a dry glass tube containing the solid mixture of TPED, $FeCl_3$, and PPh_3. Three freeze−pump−thaw cycles were performed. The tube was sealed under vacuum and was then placed in an oil bath held at the desired temperature by a thermostat. At a specific time, the polymerization was stopped by cooling the tube in an ice−water bath. The resultant polymer was dissolved in THF, followed by precipitation in heptane. Upon filtration, the polymer was dried in an oven at 50 °C for 24 h. The conversion of polymerization was determined gravimetrically.

Characterizations. Molecular weights and molecular weight distributions of polymer samples were measured using a Waters 150-C GPC with Ultrastyragel columns (500, 10^3, and 10^4Å), with THF as eluent(1.0 mL/min). Calibration was made with monodispersed polystyrenes as the standards. ^1H NMR spectra were taken on a Brucker ARX400 (400 MHz) spectrometer in $CDCl_3$ at 25 °C, using tetramethylsilane as the internal reference.

Results and Discussion

Polymerization of MMA. The polymerization of MMA was carried out in bulk with the TPED/$FeCl_3$/PPh_3 initiation system at 95 °C. For $[MMA]_0:[TPED]_0:[FeCl_3]_0:[PPh_3]_0 \approx 2500{:}1{:}4{:}12$, the results are shown in Figure 1. It shows that the $M_{n\,(GPC)}$, the number-average molecular weight measured by GPC, increases linearly with conversion from 6.0×10^4 to 1.8×10^5, and the polydispersity index slightly decreases from 1.31 to 1.26 as the monomer conversion is increased from 27 to 78%, respectively. The increase of molecular weight of PMMA with conversion is demonstrated by GPC curves as

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[†] TPED: 1,1,2,2-tetraphenyl-1,2-ethanediol.

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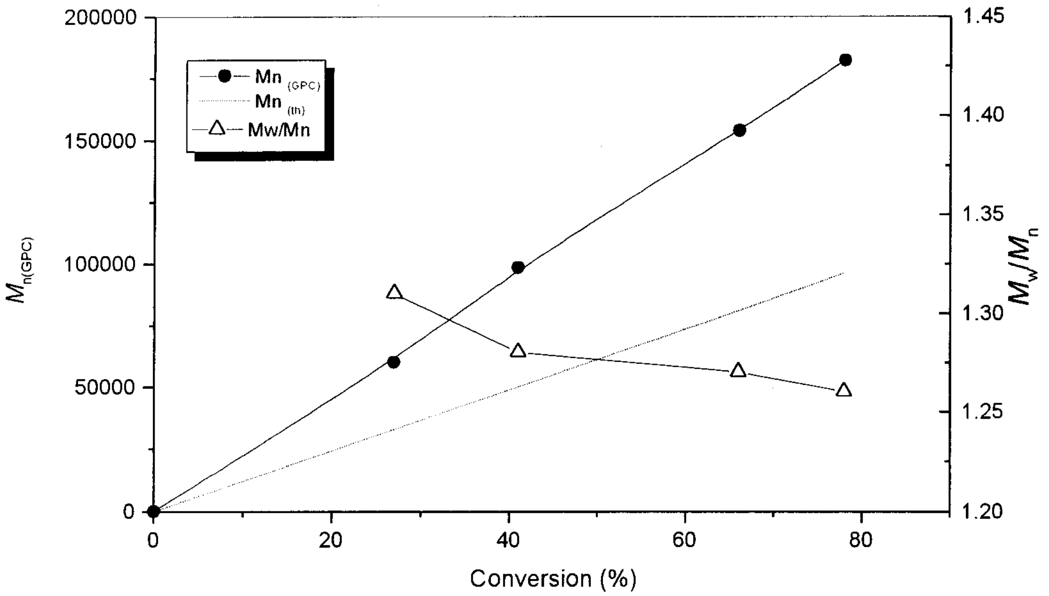


Figure 1. Dependence of the molecular weight and polydispersity of PMMA on the monomer conversion at 95 °C. Conditions: $[MMA]_0 = 9.43$ mol/L, $[TPED]_0 = 3.82 \times 10^{-3}$ mol/L, $[FeCl_3]_0 = 1.55 \times 10^{-2}$ mol/L, and $[PPh_3]_0 = 4.65 \times 10^{-2}$mol/L. $M_{n(th)} = ([MMA]_0/2[TPED]_0) \times MW_{MMA} \times$ conversion.

Table 1. Results of Polymerization of MMA with TPED/FeCl$_3$/PPh$_3$ System with Various Initial Concentrations of TPED at 95 °C[a]

entry no.	$[I^b]_0 \times 10^2$ (mol/L)	$[M^c]_0/[I]_0$	time (h)	convn (%)	$M_{n(th)}{}^d$	$M_{n(GPC)}{}^e$	M_w/M_n
control[f]	0.38	2482:1	6	96	11 800	47 900	2.62
1	1.53	616:1	8	98.6	30 600	57 800	1.24
2	1.15	820:1	10	99.2	40 700	104 600	1.15
3	0.76	1240:1	12	99.1	61 500	171 800	1.13

[a] Conditions: $[MMA]_0 = 9.43$ mol/L; $[TPED]_0/[FeCl_3]_0/[PPh_3]_0 = 1:4:12$. [b] I = TPED. [c] M = monomer. [d] $M_{n\,(th)} = ([MMA]_0/2[TPED]_0) \times MW_{MMA} \times$ conversion. [e] GPC calibrated with PS standards. [f] Control: the polymerization initiated by TPED alone, without FeCl$_3$ and PPh$_3$.

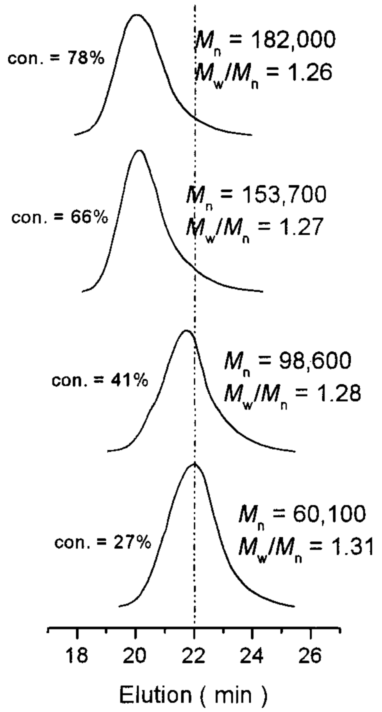


Figure 2. GPC curves of PMMAs obtained from bulk polymerization at 95 °C. Conditions: $[MMA]_0 = 9.43$ mol/L, $[TPED]_0 = 3.82 \times 10^{-3}$ mol/L, $[FeCl_3]_0 = 1.55 \times 10^{-2}$ mol/L, and $[PPh_3]_3 = 4.65 \times 10^{-2}$ mol/L.

shown in Figure 2. When the conversion is at 27%, narrower polydispersity index ($M_w/M_n = 1.31$) of the polymer is observed. It indicates that the polymerization has proceeded following an conventional ATRP. However, the efficiencies of initiator f as calculated from $f = M_{n(th)}/M_{n(GPC)}$ are generally low, around 0.5; $M_{n(th)}$ is the theoretical number-average molecular weight, computed from $M_{n(th)} = ([MMA]_0/2[TPED]_0) \times MW_{MMA} \times$ conversion.

In a plot of $\ln([M]_0/[M])$ vs time as shown in Figure 3, a straight line is observed, indicating that the kinetics is first order in monomer. This means that the concentration of propagating radicals is constant during the polymerization.

From the results mentioned above, it can be revealed that MMA polymerization with the TPED/FeCl$_3$/PPh$_3$ initiation system at 95 °C exhibits some “living”/controlled radical polymerization characteristics.

The polymerization of MMA with various initial initiator concentrations were investigated. The data are compiled in Table 1. When $[TPED]_0 = 1.53 \times 10^{-2}$ mol/L, $M_n = 57\,800$ and $M_w/M_n = 1.24$ (see entry no. 1 in Table 1) are obtained, while when $[TPED]_0$ is decreased to 7.6×10^{-3} mol/L, a higher molecular weight and a narrower polydispersity index are observed, i.e., $M_n = 171\,800$ and $M_w/M_n = 1.13$ (see entry no. 3 in Table 1). It shows that a lower initial concentration of TPED, a higher number-average molecular weight, and a narrower polydispersity of PMMA are produced.

Therefore, PMMA with high molecular weight and narrow polydispersity can be synthesized using the new initiation system.

In comparison with the TPED/FeCl$_3$/PPh$_3$ initiation system, the polymerization of MMA was carried out

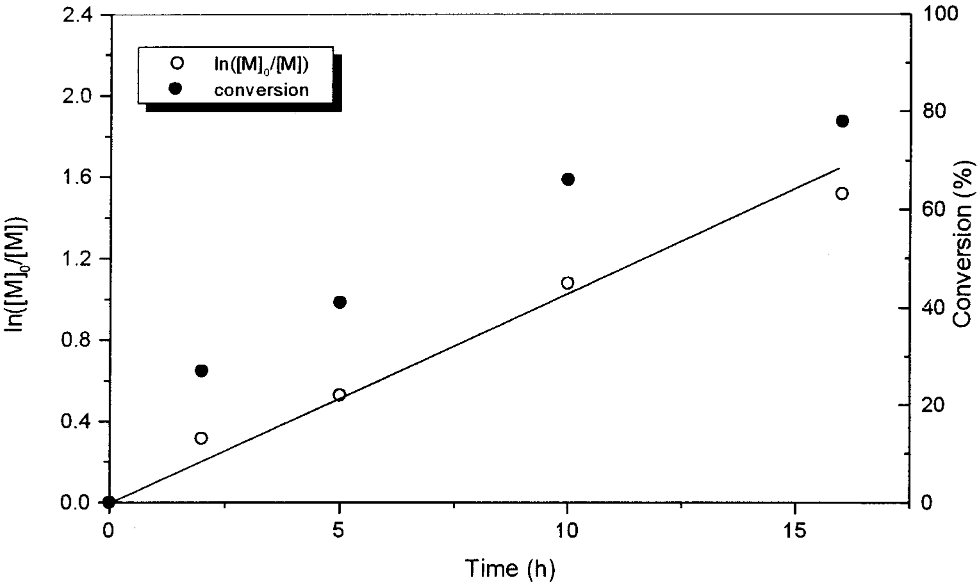


Figure 3. Time dependence of ln[M]$_0$/[M] and conversion at 95 °C, where [M]$_0$ and [M] are the MMA concentration at times 0 and *t*, respectively. Conditions: $[MMA]_0 = 9.43$ mol/L, $[TPED]_0 = 3.82 \times 10^{-3}$ mol/L, $[FeCl_3]_0 = 1.55 \times 10^{-2}$ mol/L, and $[PPh_3]_3 = 4.65 \times 10^{-2}$ mol/L.

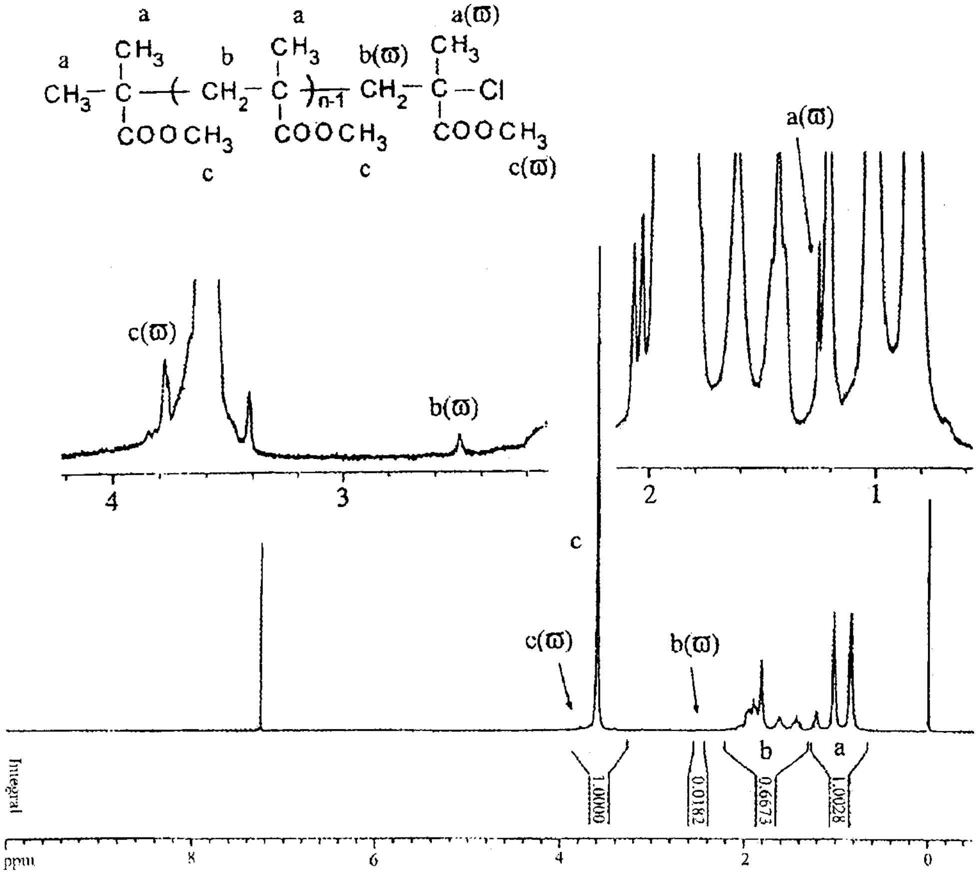


Figure 4. ^{1}H NMR (in $CDCl_3$, 400 MHz) of PMMA ($M_n = 3800$ and $M_w/M_n = 1.19$) synthesized with the TPED/$FeCl_3$/PPh_3 system ($[MMA]_0$:$[TPED]_0$:$[FeCl_3]_0$:$[PPh_3]_0$ = 200:1:4:12) in bulk at 95 °C.

with TPED alone at 95 °C, the polydispersity of PMMA was rather broad, 2.62, at a conversion of 96%, with $M_{n(GPC)} = 47\,900$ and $M_{n(th)} = 11\,800$ (see "control" in Table 1). The radical polymerization initiated with TPED alone cannot be well-controlled due to the presence of the terminations between the propagating active species.

End Group Characterization. Figure 4 shows a representative ^{1}H NMR spectrum of the well-defined PMMA. The spectrum is the same as that reported by Sawamoto.[14] First, there is no signal corresponding to the protons on the benzene ring, indicating that the diphenylhydroxymethyl radicals, formed from the initiator TPED, cannot directly initiate MMA polymerization. The result is identical with the initiation reaction of polymerization of MMA initiated with TPED alone proposed by Braun.[11] Second, the signals at 0.84–1.21, 1.43–2.07, and 3.41–3.60 ppm are assigned to the

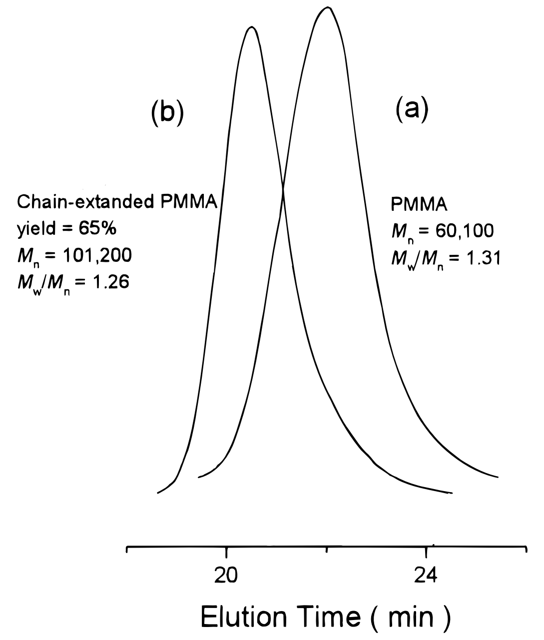


Figure 5. GPC curves of PMMA (a) before and (b) after the chain extension.

protons of methyl groups [peak *a*] of $-C(C\boldsymbol{H}_3)(COOCH_3)$, methylene groups [peak *b*] of $-C\boldsymbol{H}_2$-, and methoxy groups [peak *c*] of $-C(CH_3)(COOC\boldsymbol{H}_3)$, respectively. These results suggest that the chains of the PMMA only have methyl groups and methylene groups. It indicates that one end group of the PMMA chain is a hydrogen atom. In particular, the signal at 3.79 ppm [peak *c(ϖ)*] is for the protons of the methoxy group, that at 2.50 ppm [peak *b(ϖ)*] is for the methylene protons, and that at 1.26 ppm [peak *a(ϖ)*] exhibits the characteristic chemical shifts of the terminal MMA unit capped with an ω-end chlorine. Thus, an ω-chlorine atom end group is just another end group.

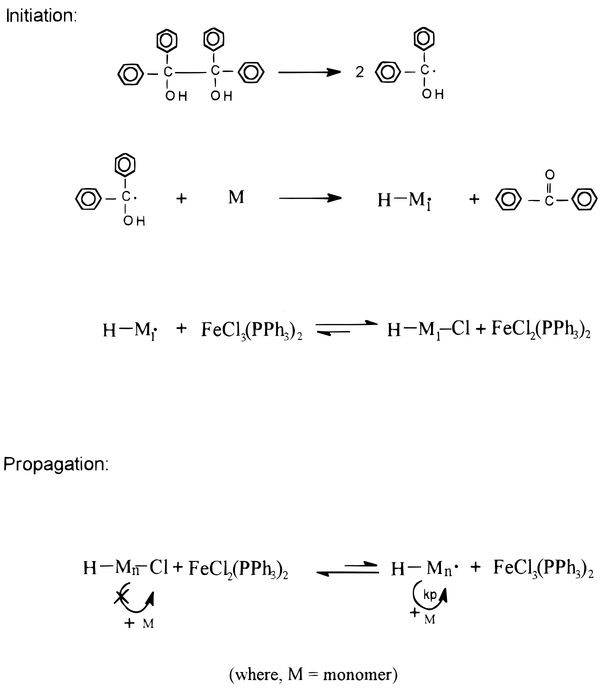
Additionally, as determined from the signal intensity ratio of the terminal methylene [*b(ϖ)*] to the ester methyl protons [*c*] of the main chain, $M_{n(NMR)}$ (3700) is close to $M_{n(GPC)}$ (3800), indicating that all the polymer chains have chlorine ends.

Therefore, the polymers produced by using the initiation system are well-defined, not only with high molecular weight and quite narrow polydispersity but also with precise end groups, i.e., α-hydrogen atom and ω-chlorine atom groups.

Chain Extension of PMMA. The PMMA with an ω-chlorine atom end group can be used as a macroinitiator for chain extension polymerization using a conventional ATRP initiation system, i.e., CuBr/2,2′-bipyridine.[15] A chain extension polymerization of MMA with PMMA (M_n = 60 100; M_w/M_n = 1.31) as the initiator was carried out in toluene at 85 °C. When $[MMA]_0 = 4.99$ mol/L, $[PMMA]_0 = 5.0 \times 10^{-3}$ mol/L, $[CuBr]_0 = 5.0 \times 10^{-3}$ mol/L, and $[2,2'\text{-bipyridine}]_0 = 1.5 \times 10^{-2}$ mol/L, a conversion of 65% was achieved after polymerization for 24 h. The M_n of the chain-extended PMMA was increased to 101 200 with essentially the same polydispersity of 1.26. The increase in the molecular weight is clearly demonstrated in the GPC curves as shown in Figure 5.

Polymerization Mechanism. The mechanism of polymerization for MMA with the TPED/$FeCl_3$/PPh_3 initiation system is proposed to be as depicted in Scheme 1.

Scheme 1



The initiation step includes the decomposition of the initiator TPED and the formation of monomer radicals ($H-M_1^{\bullet}$, M = monomer) via a hydrogen transfer reaction.[11] The monomer radicals can react with the monomers to create propagating chains. They may also directly abstract the halogen atom Cl from the oxidized transition-metal species $FeCl_3(PPh_3)_2$, which results in a reduction of the oxidized transition-metal species to $FeCl_2(PPh_3)_2$ and an organic chloro compound ($H-M_1-Cl$). The subsequent propagation is the same as in conventional ATRP.

Conclusions

Well-defined PMMA with an α-hydrogen atom and an ω-chlorine atom as end groups, a high number-average molecular weight, and a narrow polydispersity can be synthesized using a new initiation system consisting of TPED, $FeCl_3$, and PPh_3. The mechanism of polymerization is proposed to be similar to the reverse ATRP. Since the polymer chain is end-functionalized by a chlorine atom, it can then be used as a macroinitiator to undergo chain extension polymerization via conventional ATRP process.

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