The *in situ* atom transfer radical polymerization of MMA using the TD–$FeCl_3$–PPh_3 initiating system

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Well-defined poly(methyl methacrylate) (PMMA) with very low polydispersity and with α-Et_2NCS_2 and ω-Cl end groups was synthesized *via in situ* atom transfer radical polymerization (ATRP), using a tetraethylthiuram disulfide (TD)–$FeCl_3$–PPh_3 initiating system. The *in situ* ATRP of methyl methacrylate (MMA) was a "living"/controlled polymerization and the polydispersity indices of PMMA were very narrow ($M_n = 7100$ and $M_w/M_n = 1.04$). The presence of the Et_2NCS_2 and the chlorine atoms as end groups in PMMA was determined by ^1H NMR, FT-IR and UV spectroscopies. The presence of an ω-chlorine end group on the polymer chain was used to chain extend the PMMA using a conventional ATRP initiation system.

Well-defined polymers with low polydispersities and complex architectures can be achieved by living polymerization processes in which there is neither chain transfer nor termination. Since Szwarc *et al.*[1] first reported the concept of living polymerization in 1956, a number of living polymerization systems have been reported for anionic,[1] cationic[2] or group transfer polymerization.[3] Generally, free radical polymerizations often yield polymers with a large variety of monomers under relatively mild experimental conditions; but they are ill-controlled because of the facile coupling and disproportionation reactions between the propagating species. In recent years, some effective controlled/"living" radical polymerizations[4] or living radical polymerizations[5] have been reported, such as the polymerization of styrene in the presence of the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) stable free radical,[6] atom transfer radical polymerization (ATRP) using chloro compounds and transition metal complex catalysts,[7,8] and living radical polymerization by the reversible addition-fragmentation chain transfer (RAFT) process in the presence of dithioesters.[9]

ATRP is one of the most widely investigated systems for living polymerization of vinyl monomers. Sawamoto *et al.*[10] and Matyjaszewski *et al.*[11] have reported that PMMA with well-controlled molecular weights and narrow polydispersity indices could be obtained with iron-based catalyst systems such as RX–$FeCl_2$–PPh_3,[10] RX–$FeBr_2$–dNbipy[4,4′-bis(5-nonyl)-2,2′-bipyridine] or $N(Bu^n)_3$.[11] PMMA with a polydispersity of about 1.05 was obtained using benzhydryl chloride–CuCl–4,4′-di(5-nonyl)-2,2′-bipyridine as the ATRP initiating system, but the rate of polymerization was very slow (*ca.* 10% conversion after 18 h) at 90 °C.[12] In RAFT systems, the polydispersities of PMMA obtained were very narrow with reasonable rates of polymerization at 60 °C, for example, $M_w/M_n = 1.04$, *ca.* 78% conversion after 16 h using benzoyl peroxide (BPO) as the initiator in the presence of $PhC(S)SC(CH_3)_2Ph$; $M_w/M_n = 1.05$, *ca.* 92% conversion after 16 h using 2,2′-azo-bisisobutyronitrile (AIBN) as the initiator in the presence of $PhC(S)SC(CH_3)(CN)CH_2CH_2CH_2OH$.[9]

Controlled/"living" radical polymerization *via* ATRP is an efficient way to synthesize well-defined polymers.[5,6] So far, there are two kinds of ATRP: (conventional) ATRP and reverse ATRP. In ATRP, organic halides (RX) are used as initiators, transition metal compounds in their lower oxidation state (M^n, where *n* is the oxidation state) are used as catalysts, and electron-donating compounds, such as 2,2′-bipyridine and triphenylphosphine (PPh_3) are used as ligands (L). In a reverse ATRP system,[13–20] a radical initiator and a higher oxidation state transition metal catalyst complex $M^{n+1}XL_m$ are used instead of the organic halide initiator RX (usually toxic) and the lower oxidation state catalyst complex M^nL_m(easily oxidized by the oxygen in air). Common free radical initiators are often used for reverse ATRP, such as AIBN[13–15] or BPO.[16] Very recently, we reported the controlled/"living" radical polymerization of MMA or styrene (St) with a new reverse ATRP system based on 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)–$FeCl_3$–PPh_3, in which TPED is a C–C bond type initiator.[17,18] In our laboratories, other initiators such as diethyl 2,3-dicyano-2,3-diphenylsuccinate have been used in conjunction with $FeCl_3$–PPh_3 catalyst for MMA reverse ATRP.[19,20]

Tetraethylthiuram disulfide (TD) is a S–S bond type initiator for radical polymerizations that proceeded in a "living" manner but the molecular weight and molecular weight dispersities of the obtained polymers were not well-controlled.[21] More recently, in a rapid communication we reported a third kind of ATRP process, *in situ* ATRP.[22] In this case, an organic halogen compound, (diethylthiocarbamoyl)sulfur chloride (Et_2NCS_2Cl), and a transition metal compound in its lower oxidation state, Fe^{2+}, were both created *in situ* from a TD–$FeCl_3$–PPh_3 initiating system. The polymerization proceeded *via* conventional ATRP and the polymerization mechanism was proposed to be an *in situ* ATRP process. In this article, we wish to report further details of this MMA polymerization.

Experimental

Materials

$FeCl_3$ (anhydrous) was prepared from $FeCl_3 \cdot 6H_2O$ according to a literature method.[23] TD was prepared by oxidation of sodium diethyldithiocarbamate with sodium hypochlorite at 4–7 °C[24] and was recrystallized[21] from ethanol; mp 73–74 °C. MMA was dried over CaH_2 and distilled under reduced pressure. Triphenylphosphine (Aldrich) was recrystallized from ethanol to eliminate triphenylphosphine oxide.

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Polymerization

As a general procedure, the monomer was added to a dry glass tube containing the solid mixture of TD, $FeCl_3$, and PPh_3. Three freeze-pump-thaw cycles were performed. The tube was sealed under vacuum and then allowed to stand overnight with stirring with a magnetic bar at room temperature. As the ingredients of the initiating system are not soluble in MMA, this allows the inorganic reaction to proceed completely. The tube was then placed in an oil bath held at the desired temperature by a thermostat. After a certain time, the tube was cooled in a liquid nitrogen bath to quench the polymerization. The polymer product was dissolved in tetrahydrofuran (THF), followed by precipitation in n-heptane. Upon filtration, the polymer was dried. Conversions were determined gravimetrically.

Characterization

Molecular weights and molecular weight distributions of polymers were measured using a Waters 515 GPC instrument equipped with Styragel columns (HT2 + HT3 + HT4) operating at 35 °C, using THF as eluent (1.0 ml min^{-1}), polystyrene (PSt) calibration standards, and Waters Millennium 32 as data processing software. ^1H NMR spectra were recorded using a Brucker ARX400 (400 MHz) spectrometer in $CDCl_3$ at 25 °C, using tetramethylsilane as internal reference. Fourier transform infrared (FT-IR) spectra were measured using a Nicolet Magna-IR 750 spectrometer with KBr pellets. UV spectra were recorded on a Shimadzu UV-250 model spectrophotometer at room temperature.

Results and discussion

Polymerization of MMA

The bulk polymerization of MMA was carried out using the $TD–FeCl_3–PPh_3$ initiation system at 100 °C. When $[MMA]_0 : [TD]_0 : [FeCl_3]_0 : [PPh_3]_0 \approx 200 : 1 : 10 : 30$, the results shown in Fig. 1 were obtained. It can be seen that $M_{n(GPC)}$, the number-average molecular weight measured by GPC, increased linearly from 2200 to 7100 while the polydispersity index remained very narrow, 1.04–1.07, as the monomer conversion increased from 21.5 to 85% within 8 min. $M_{n(GPC)}$ was nearly equal to $M_{n(th)}$, suggesting that the initiator efficiencies $f(f = M_{n(th)}/M_{n(GPC)})$ were about 1.0; $M_{n(th)}$ is the theoretical number-average molecular weight, calculated from $M_{n(th)} = ([MMA]_0/2[TD]_0) \times MW_{MMA} \times$ conversion. The GPC curves Fig. 2) also demonstrate the increase of molecular weight of PMMA with conversion. A straight line is obtained from a plot of $\ln([MMA]_0/[MMA])$ *vs.* time, as shown in Fig. 3, showing that the concentration of propagating radicals was constant during the polymerization and that the kinetics was first order in the monomer.

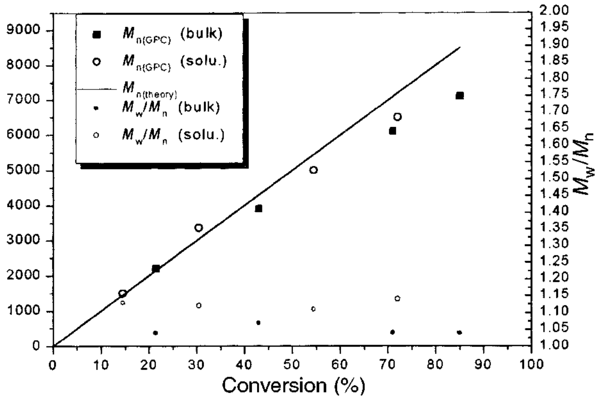


Fig. 1 Dependence of the PMMA molecular weight and polydispersity on the monomer conversion at 100 °C. Conditions: in bulk, $[MMA]_0 = 9.38$ mol l^{-1}, $[TD]_0 = 4.69 \times 10^{-2}$ mol l^{-1}, $[FeCl_3]_0 = 4.69 \times 10^{-1}$ mol l^{-1}, $[PPh_3]_0 = 1.41$ mol l^{-1}; in anisole, $[MMA]_0 = 4.69$ mol l^{-1}, $[TD]_0 = 2.35 \times 10^{-2}$ mol l^{-1}, $[FeCl_3]_0 = 2.35 \times 10^{-1}$ mol l^{-1}, $[PPh_3]_0 = 7.05 \times 10^{-1}$ mol l^{-1}. $M_{n(th)} = ([MMA]_0/2[TD]_0) \times MW_{MMA} \times$ conversion.

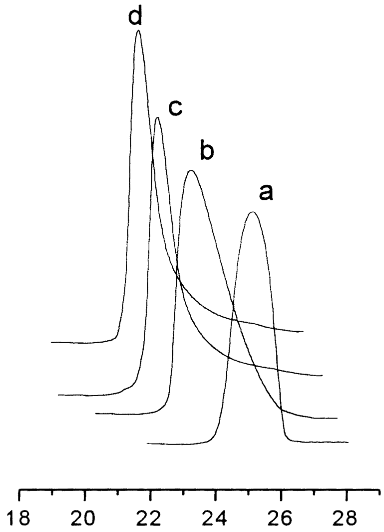


Fig. 2 GPC curves of PMMA obtained from bulk polymerization at 100 °C. Conditions in bulk as in Fig. 1. (peak a) $t = 1$ min, conversion = 21.5%, $M_n = 2200$, $M_w/M_n = 1.04$; (peak b) $t = 2$ min, conversion = 43%, $M_n = 3900$, $M_w/M_n = 1.07$; (peak c) $t = 5$ min, conversion = 71%, $M_n = 6100$, $M_w/M_n = 1.05$; (peak d) $t = 8$ min, conversion = 85%, $M_n = 7100$, $M_w/M_n = 1.04$.

When $[MMA]_0 : [TD]_0 : [FeCl_3]_0 : [PPh_3]_0 \approx 200 : 1 : 10 : 30$, similar results for the solution polymerization of MMA in anisole were obtained, with a lower rate of polymerization, and the polydispersities of PMMA were about 1.1 (See Fig. 1 and 3).

From the results mentioned above, it is clear that the MMA polymerization in bulk or in anisole with the $TD–FeCl_3–PPh_3$ initiation system at 100 °C proceeds *via* a controlled/"living" polymerization. However, in the case of styrene (St) polymerization in bulk using this initiating system, the conversion was low and the polydispersity index of PSt ($M_w/M_n = 1.8–1.9$) was higher than that of PMMA ($M_w/M_n = 1.1$).

The effect of varying the initiator concentration on the polymerization of MMA was investigated. The data are compiled in Table 1. When $[TD]_0 = 3.13 \times 10^{-2}$ mol l^{-1}, $M_n =$

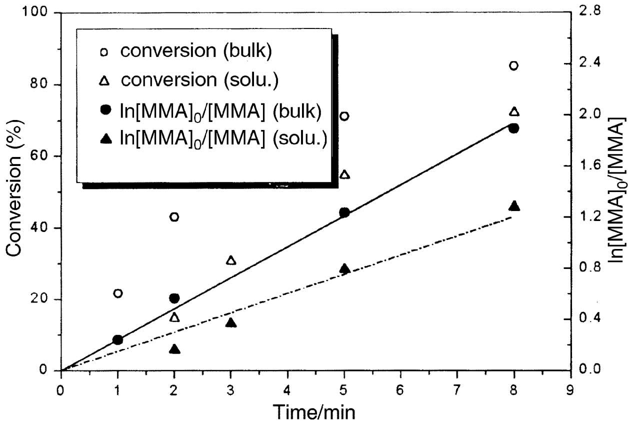


Fig. 3 Time dependence of $\ln[MMA]_0/[MMA]$ and conversion at 100 °C, where $[MMA]_0$ and $[MMA]$ are the MMA concentrations at times 0 and t, respectively. Conditions in bulk as in Fig. 1. Solid lines are $M_{n(th)}$.

Table 1 The results of polymerization of MMA with the TD–$FeCl_3$–PPh_3 system with various initial concentrations of TD at 100 °C[a]

Entry	$[TD]_0/10^{-2}$ mol l^{-1}	$[MMA]_0/[TD]_0$	Time/h	Conv. (%)	$M_{n(th)}$[b]	$M_{n(GPC)}$[c]	M_w/M_n	f[d]
Control 1[e]	4.69	200 : 1	2	38.7	3900	13000	1.63	—
Control 2[e]	4.69	200 : 1	6	92.8	9300	18900	1.55	—
1	3.13	300 : 1	0.67	*ca.* 100	15000	18400	1.11	0.82
2	1.88	500 : 1	1.0	*ca.* 100	25000	28400	1.15	0.88
3	0.94	1000 : 1	1.5	*ca.* 100	50000	43500	1.19	1.15

[a] Conditions: $[MMA]_0 = 9.38$ mol l^{-1}, $[TD]_0 : [FeCl_3]_0 : [PPh_3]_0 = 1 : 10 : 30$. [b] $M_{n(th)} = ([MMA]_0/2[TD]_0) \times MW_{MMA} \times$ conversion. [c] GPC calibrated with PSt standards. [d] $f = M_{n(th)}/M_{n(GPC)}$. [e] Control: polymerization initiated by TD alone, without $FeCl_3$ and PPh_3.

18 400 and $M_w/M_n = 1.11$ (see entry in Table 1), whereas if $[TD]_0$ is decreased to 9.4×10^{-3} mol l^{-1}, a higher molecular weight with a broader polydispersity index is observed: $M_n = 43\,500$, $M_w/M_n = 1.19$ (see entry in Table 1). This shows that for a lower concentration of TD, a higher number-average molecular weight of PMMA is obtained, whereas the polydispersity index is almost the same. Therefore, PMMA with a high molecular weight and narrow polydispersity can be synthesized using the new initiation system.

In comparison with the TD–$FeCl_3$–PPh_3 initiation system, the polydispersity of PMMA synthesized with TD alone at 100 °C was rather broad, with $M_w/M_n = 1.63$ or 1.55, at conversions of 38.7% or 92.8%, respectively (see Control 1 and Control 2 in Table 1). The radical polymerization initiated with TD alone was not well-controlled; $M_{n(GPC)}$ deviated from $M_{n(th)}$ and the M_w/M_n values were high, due to the presence of termination between the propagating active species.

End group characterization

The FTIR, UV and NMR spectra reveal that the Et_2NCS_2– group is one of the end groups of the polymer. The signals at 1267 and *ca.* 3450 cm^{-1} in the FTIR spectra of PMMA obtained either by the TD–$FeCl_3$–PPh_3 initiating system or by TD alone are ascribed to the characteristic absorption bands of the Et_2NCS_2– group. The band at *ca.* 283 nm in the UV spectrum of the PMMA powder also identifies Et_2NCS_2– as an end group. The number of Et_2NCS_2– groups per molecular chain was determined by UV spectroscopy in $CHCl_3$ to be about 1. Fig. 4 shows the ^1H NMR spectrum of PMMA. The chemical shift at 3.07 ppm of the methylene protons f in $Et_2NCS_2CH_2$– suggests the possible presence of the Et_2NCS_2– group. The signal at 3.79 ppm is due to the protons d of the methoxy group, while that at 2.50 ppm shows the characteristic chemical shift of the methylene protons e of the terminal MMA unit capped with an ω-end chlorine, similar to that reported by Ando *et al.*[25] The presence of an ω-end chlorine demonstrates that the polymerization proceeds *via* an ATRP process. The $M_{n(NMR)}$ (6,600) is close to $M_{n(GPC)}$ (6,500), indicating that almost every polymer chain has a chlorine end group. Thus, the polymers produced by the initiation system are well-defined, not only with very narrow polydispersity but also with precise α-Et_2NCS_2– and ω-chlorine atom end groups.

In order to clarify the nature of the polymerization, some control experiments were carried out under the following fixed conditions: $[MMA]_0 = 9.38$ mol l^{-1}, $[TD]_0 = 4.69 \times 10^{-2}$ mol l^{-1}, $[FeCl_3]_0 = 4.69 \times 10^{-1}$ mol l^{-1}, $[PPh_3]_0 = 1.41$ mol l^{-1}, 100 °C. In this case, the conversion was 85% within 8 min, as shown in entry 1 in Table 2. However, the conversion decreased to 75 and 45% after 20 min in the presence of TEMPO, $[TEMPO]_0 = 12.57 \times 10^{-2}$ mol l^{-1} and 15.79×10^{-2} mol l^{-1}, respectively, as shown in Entries 3 and 4 in Table 2. When 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) ($[DMPO]_0 = 19.39 \times 10^{-2}$ mol l^{-1}) was used as the additive (entry 2 in Table 2), the conversion reached 85% after 20 min; the reaction time is longer compared to entry 1 in Table 2. This suggests that the activated species are possibly radicals. When H_2O was added ($[H_2O]_0 = 281.4 \times 10^{-2}$ mol l^{-1}), the polymerization still proceeded at a moderate

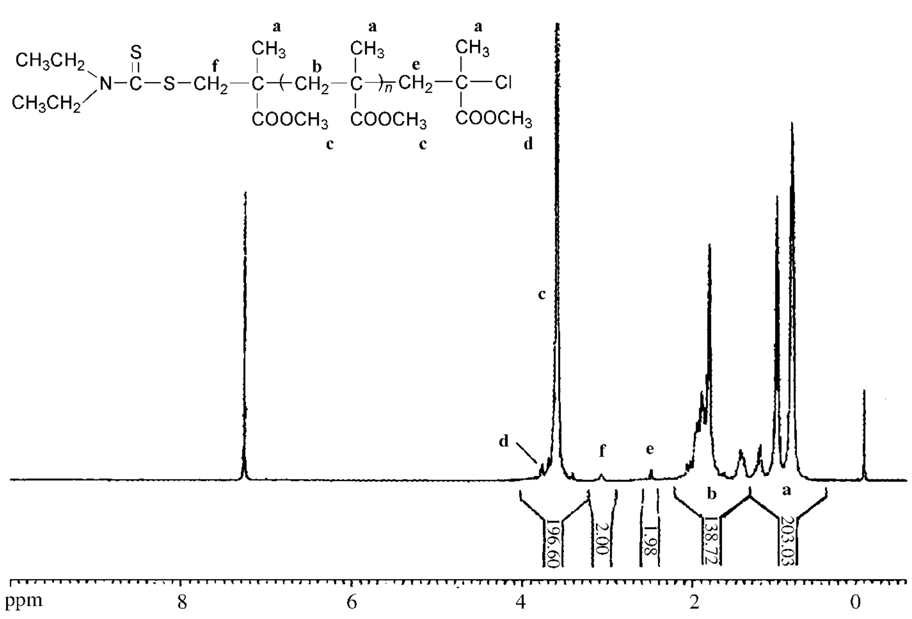


Fig. 4 ^1H-NMR (in $CDCl_3$, 400 MHz) of PMMA ($M_n = 6500$ and $M_w/M_n = 1.19$) synthesized with the TD–$FeCl_3$–PPh_3 system ($[MMA]_0 : [TD]_0 : [FeCl_3]_0 : [PPh_3]_0 = 200 : 1 : 4 : 12$) in bulk at 95 °C.

Table 2 The results of control polymerization of MMA at 100 °C[a]

Entry	System	Additive	$[\text{Additive}]_0$/ 10^{-2} mol l^{-1}	Time/ min	Conv. (%)
1	TD–$FeCl_3$–PPh_3	—	—	8	85
2	TD–$FeCl_3$–PPh_3	DMPO	19.39	20	85
3	TD–$FeCl_3$–PPh_3	TEMPO	12.57	20	75
4	TD–$FeCl_3$–PPh_3	TEMPO	15.79	20	45
5	TD–$FeCl_3$–PPh_3	H_2O	281.4	20	49.3
6	TD–$FeCl_3$	—	—	16 h	*ca.* 0 ($FeCl_2\downarrow$)

[a] Conditions: $[\text{MMA}]_0 = 9.38$ mol l^{-1}, $[\text{TD}]_0 = 4.69 \times 10^{-2}$ mol l^{-1}, $[FeCl_3]_0 = 4.69 \times 10^{-1}$ mol l^{-1}, $[PPh_3]_0 = 1.41$ mol l^{-1}.

rate, with 49.3% conversion at 20 min. Generally speaking, MMA is an electron-poor monomer and the polymerization of MMA cannot be carried out *via* cationic initiation. It is impossible to perform ionic polymerizations in the presence of water, $[H_2O]_0 : [\text{TD}]_0 = ca.\ 60$. Therefore, the polymerization with the TD–$FeCl_3$–PPh_3 system is probably radical in nature. When the polymerization was carried without the PPh_3 ligand, that is, with TD–$FeCl_3$, no polymer was obtained after 16 h but $FeCl_2$ was produced as a precipitate. Therefore, the three components, TD, $FeCl_3$ and PPh_3, are indispensable for the polymerization of MMA.

Sawamoto *et al.*[26,27] have reported that in MMA polymerization with the $PhCOCHCl_2$–$RuCl_2(PPh_3)$–$Al(OPr^i)_3$ initiating system, TEMPO will terminate radical polymerization whereas water had no effect. However, polystyrene capped with TEMPO can be used as a macroinitiator for the block copolymerization of MMA and other alkyl methacrylate monomers.[28,29]

The results of various MMA polymerizations, under the following fixed conditions: $[\text{MMA}]_0 = 9.38$ mol l^{-1}, $[\text{TD}]_0 = 4.69 \times 10^{-2}$ mol l^{-1} at 100 °C, with different ratios of $[\text{TD}]_0 : [FeCl_3]_0 : [PPh_3]_0$ are summarized in Table 3. From these results, it can be seen that when $[\text{TD}]_0 : [FeCl_3]_0 : [PPh_3]_0 = 1 : 4 : 12$ (entry 2 in Table 3) in the bulk, the rate of polymerization dramatically decreased, with 85% conversion now taking 2 h and the polydispersity index of PMMA being relatively high, $M_w/M_n = 1.27$, while for $[\text{TD}]_0 : [FeCl_3]_0 : [PPh_3]_0 = 1 : 10 : 30$ (entry 1 in Table 3), the same conversion took only 8 min and the polydispersity index was very low, $M_w/M_n = 1.04$. Similar results were observed for solution polymerization in anisole (entries 3 and 4 in Table 3). Thus a very narrow polydispersity of the PMMA and a fast rate of polymerization are obtained at a higher initial concentration of $FeCl_3$ when $[\text{MMA}]_0 : [\text{TD}]_0 = 200 : 1$.

Mechanism of the polymerization

When TD was added to the mixture of $FeCl_3$, MMA and PPh_3 at room temperature, the color of the system instantly became dark green.[24] This indicates that TD rapidly reacts with $FeCl_3$ and two complex halide products, such as $Et_2NCS_2Cl\cdot FeCl_3$ (**A**) and $Fe(S_2CNEt_2)_2Cl$ {**B** ≡ $[Fe(dtc)_2Cl]$}, are produced as depicted in eqn. (1), and as reported by Tamminen and Hjelt in 1950.[30]

Table 3 The results of polymerization of MMA in different concentrations at 100 °C

Entry	Conditions[a]	Time/min	Conv. (%)	M_w/M_n
1	200 : 1 : 10 : 30; in bulk	8	85	1.04
2	200 : 1 : 4 : 12; in bulk	120	85	1.27
3	200 : 1 : 10 : 30; in anisole	8	72	1.14
4	200 : 1 : 4 : 12; in anisole	120	65	1.33

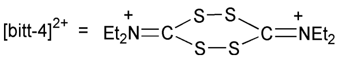
[a] Ratio of $[\text{MMA}]_0 : [\text{TD}]_0 : [FeCl_3]_0 : [PPh_3]_0$.

$$2(Et_2NCS_2)_2(\text{TD}) + 3FeCl_3 \rightarrow 2Et_2NCS_2Cl\cdot FeCl_3(\mathbf{A}) + Fe(S_2CNEt_2)_2Cl(\mathbf{B}) \qquad (1)$$

In 1969, however, Willemse and Steggerda[31] suggested that **A** is present in the form of a dimeric dipositive ion with an *S*-tetrathian ring, *i.e.* bis(dialkylimonium)tetrathiolane (bitt-4), as shown below:

$$2\text{TD} + 3FeCl_3 \rightarrow \underset{\mathbf{C}}{[\text{bitt-4}]^{2+}[FeCl_4]_2^-} + \underset{\mathbf{B}}{Fe(dtc)_2Cl} \qquad (2)$$

$$\mathbf{C} \rightarrow 2Et_2NCS(S)Cl + 2FeCl_3 \qquad (3)$$



$[\text{bitt-4}]^{2+}$ was possibly formed instead of bis(dialkylimonium)trithiolane (bitt-3)[32] from the reaction of **B** with $FeCl_3$ in the presence of MMA and PPh_3:

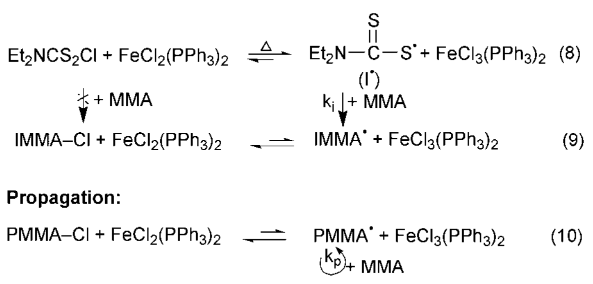
$$3\mathbf{B} + 3FeCl_3 \rightarrow 2[Fe(dtc)_3]^+[FeCl_4]^- + 2FeCl_2 \qquad (4)$$

$$2[Fe(dtc)_3]^+[FeCl_4]^- + 9FeCl_3 \rightarrow 3[\text{bitt-4}]^{2+}[FeCl_5]^{2-} + 10FeCl_2 \qquad (5)$$

At high temperatures, such as 100 °C, $[\text{bitt-4}]^{2+}$ thermally decomposes into (diethylthiocarbamoyl)sulfur chloride (Et_2NCS_2Cl):

$$[\text{bitt-4}]^{2+}[FeCl_5]^{2-} \rightarrow 2Et_2NC(S)SCl + FeCl_3 \qquad (6)$$

According to the results mentioned above, we propose an *in situ* ATRP mechanism as briefly depicted in Scheme 1. The Et_2NCS_2Cl initiator and the transition metal catalyst in its lower oxidation state $FeCl_2$ for an ATRP system were created *in situ* from the reaction of TD with $FeCl_3$ [eqn. (7), which is simplified from the overall reactions in eqns. (2)–(6)]. The primary radical $Et_2NCS_2^{\bullet}$, formed from the reaction of Et_2NCS_2Cl with $FeCl_2(PPh_3)_2$, can initiate MMA poly-



Scheme 1

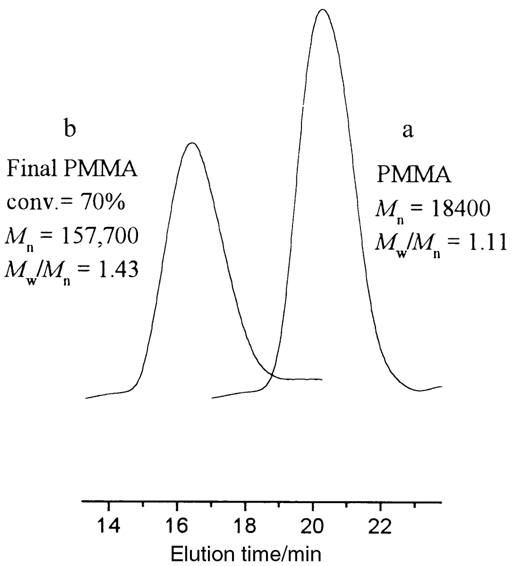


Fig. 5 GPC curves of PMMA (*a*) before and (*b*) after the chain extension.

merization. The subsequent reactions follow conventional ATRP.

Chain extension polymerization

Due to the presence of an ω-chlorine end group on the polymer chain, chain extension of PMMA can be carried out using a conventional ATRP initiation system. The results are as follows: in bulk at 100 °C, M_n of PMMA = 18 400, $M_w/M_n = 1.11$, $[\mathrm{PMMA}]_0 = 5.33 \times 10^{-3}$ mol l^{-1}, $[\mathrm{MMA}]_0 = 8.23$ mol l^{-1}, $[\mathrm{FeCl_2}]_0 = 5.33 \times 10^{-3}$ mol l^{-1}, $[\mathrm{PPh_3}]_0 = 1.6 \times 10^{-2}$ mol l^{-1}; a conversion of 70% was achieved after 36 h, M_n of the chain-extended PMMA = 157 700, $M_w/M_n = 1.43$ as shown in Fig. 5.

A control chain extension polymerization of MMA with PMMA ($M_n = 4700$, $M_w/M_n = 1.19$), synthesized with the TD–$FeCl_3$–PPh_3 initiating system, was performed in bulk at 85 °C. With initial weights of MMA and PMMA of 1.3223 g and 0.3703 g, respectively, the weight of the PMMA remained almost unchanged after reacting for 10 h. This indicated that chain extension did not occur without a transition metal catalyst. It can be inferred that the PMMA chains obtained from the TD–$FeCl_3$–PPh_3 initiation system contain ω-Cl end groups. If the PMMA had an ω-Et_2NCS_2 end group, chain extension of MMA would proceed with the PMMA under heating.[33] So, the initial radical should be $Et_2NCS_2^{\cdot}$, which initiates MMA polymerization and forms an α-Et_2NCS_2 end group on PMMA.

The results of the chain extension mentioned above also suggest that the PMMA synthesized with the novel initiating system is well-defined with an α-Et_2NCS_2 end group and an ω-Cl end group.

Conclusion

The *in situ* ATRP of MMA with the TD–$FeCl_3$–PPh_3 initiation system in bulk and in anisole is well-controlled, with a fast polymerization rate at 100 °C. Well-defined PMMA is obtained, with a very narrow polydispersity and having α-Et_2NCS_2 and ω-Cl end groups, as determined by ^{1}H NMR, FT-IR and UV spectroscopy. Due to the presence of an ω-chlorine end group on the polymer chain, chain extension of PMMA was possible using a conventional ATRP initiation system.

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