

A novel ATRP initiating system $\text{Fe}(\text{dtc})_3/\text{FeCl}_3/\text{PPh}_3$ for MMA polymerization

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Received (in Cambridge, UK) 5th June 2000, Accepted 14th June 2000

Published on the Web 7th July 2000

A 'living'/controlled radical polymerization of MMA was carried out with a novel ATRP initiation system: iron(III) tri(diethylthiocarbamate) $[\text{Fe}(\text{dtc})_3]/\text{FeCl}_3/\text{PPh}_3$, where neither an organic halide nor a radical initiator was used.

As we know, atom transfer radical polymerization (ATRP) is one of the effective controlled/'living' radical polymerization systems to synthesize well-defined polymers with low polydispersities and complex architectures;^{1,2} and up to now, two types of ATRP, *i.e.* (conventional) ATRP and reverse ATRP,³⁻⁵ have been known.

In ATRP, organic halides (RX) are used as initiators, transition-metal compounds in their lower oxidation state (M^n) are used as catalysts and electron-donating compounds are used as ligands (L). In reverse ATRP, a radical initiator and a higher oxidation state transition-metal catalyst complex $M^{n+1}XL_m$ are used instead of an organic halide initiator RX and lower oxidation state catalyst complex M^nL_m . As in ATRP, a controlled/'living' radical polymerization can also be carried out in a reverse ATRP system, under which a dynamic equilibrium is established, where the dormant polymer chains are reversibly activated *via* a halogen atom transfer reaction.

More recently, we have first reported a third ATRP process, *i.e.* *in situ* ATRP of MMA polymerization using the tetraethylthiuram disulfide (TD)/ $\text{FeCl}_3/\text{PPh}_3$ system.⁶ In the *in situ* ATRP process, RX and M^{n+1} are both created *in situ* from the reaction between a radical initiator TD and FeCl_3 at a given polymerization temperature. The polymerization proceeds following a conventional ATRP and is well-controlled.

So far, from the reported literature, one of components in an ATRP initiating system must be either an organic halide^{1,2} (in ATRP) or a radical initiator³⁻⁵ (in reverse ATRP or *in situ* ATRP). Recently, however, a paper concerning a living radical polymerization of styrene with $\text{Fe}(\text{dtc})_3/\text{AIBN}$ system in a halogen-free living process was published.⁷

Here we report a novel initiating system $\text{Fe}(\text{dtc})_3/\text{FeCl}_3/\text{PPh}_3$, in which neither an organic halide nor a radical initiator as the initiator for ATRP was used. The polymerization of MMA with this initiating system proceeded *via* an ATRP process.

The bulk polymerization of MMA was carried out using the $\text{Fe}(\text{dtc})_3/\text{FeCl}_3/\text{PPh}_3$ initiation system at 80 °C. With $[\text{MMA}]_0: [\text{Fe}(\text{dtc})_3]_0: [\text{FeCl}_3]_0: [\text{PPh}_3]_0 \approx 300: 1: 30: 90$, a plot of $\ln([\text{M}]_0/[\text{M}])$ vs. time as shown in Fig. 1, showed a straight line, indicating that the kinetics was first order in monomer and that the concentration of propagating radicals was unchanged during the polymerization. It can be seen in Fig. 2 that the M_n (GPC), number-average molecular weight measured by GPC, increased linearly with conversion from 1300 to 7200. A quite narrow polydispersity index (1.10–1.16) was obtained as the monomer conversion increased from 11 to 79% in 40 min. The value of M_n (GPC) was almost equal to M_n (th), a theoretical number-average molecular weight calculated from M_n (th) = $([\text{MMA}]_0/3[\text{Fe}(\text{dtc})_3]_0) \times \text{MW}_{\text{MMA}} \times \text{conversion}$. The efficiencies (*f*) of initiator as computed from $f = M_n$ (th)/ M_n (GPC) were ≈ 1.0 .

When the ratio of feeds in a separate experiment was the same as in bulk, similar results of solution polymerization of MMA in anisole were obtained although with a lower rate of polymeriza-

tion, *e.g.* the conversion was 52% at 40 min, M_n (GPC) was 4700 and M_w/M_n was 1.19.

Accordingly, the above results clearly suggested that the MMA polymerization with the $\text{Fe}(\text{dtc})_3/\text{FeCl}_3/\text{PPh}_3$ initiation system at 80 °C exhibited some 'living'/controlled radical polymerization characteristics.

We investigated the effects of initial initiator concentration on the polymerization of MMA under fixed conditions: $[\text{MMA}]_0 = 9.38 \text{ mol l}^{-1}$, $[\text{Fe}(\text{dtc})_3]_0: [\text{FeCl}_3]_0: [\text{PPh}_3]_0 = 1: 30: 90$, at 80 °C. When $[\text{Fe}(\text{dtc})_3]_0$ is $3.13 \times 10^{-3} \text{ mol l}^{-1}$, the conversion was 62%, $M_n = 55\,800$, $M_w/M_n = 1.23$, while when $[\text{Fe}(\text{dtc})_3]_0$ was increased to $6.25 \times 10^{-3} \text{ mol l}^{-1}$, the conversion was 68.7%, $M_n = 28\,100$, $M_w/M_n = 1.32$ after the same polymerization time of 5 h. This indicated that PMMA with higher number-average molecular weight and narrow polydispersity can be obtained using a lower initial concentration of $\text{Fe}(\text{dtc})_3$.

The polymers obtained are well-defined PMMA with α - Et_2NCS_2 - and ω -chlorine groups according to FTIR, UV and

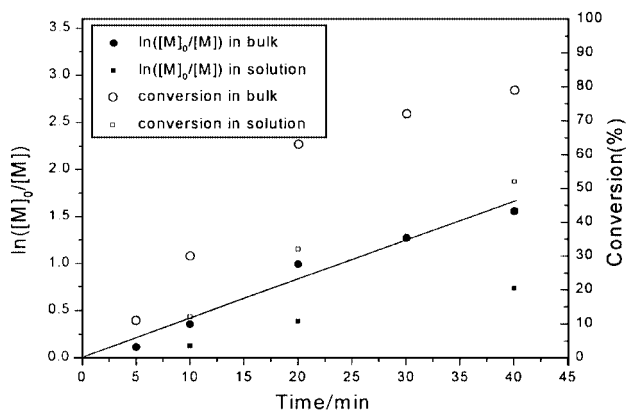


Fig. 1 Time dependence of $\ln([\text{M}]_0/[\text{M}])$ and conversion at 80 °C, where $[\text{M}]_0$ and $[\text{M}]$ are the MMA concentration at times 0 and *t*, respectively. Conditions: in bulk, $[\text{MMA}]_0 = 9.38 \text{ mol l}^{-1}$, $[\text{Fe}(\text{dtc})_3]_0 = 3.13 \times 10^{-2} \text{ mol l}^{-1}$, $[\text{FeCl}_3]_0 = 9.38 \times 10^{-1} \text{ mol l}^{-1}$, $[\text{PPh}_3]_0 = 2.81 \text{ mol l}^{-1}$; in anisole, $[\text{MMA}]_0 = 5.25 \text{ mol l}^{-1}$, $[\text{Fe}(\text{dtc})_3]_0 = 1.75 \times 10^{-2} \text{ mol l}^{-1}$, $[\text{FeCl}_3]_0 = 5.25 \times 10^{-1} \text{ mol l}^{-1}$, $[\text{PPh}_3]_0 = 1.57 \text{ mol l}^{-1}$.

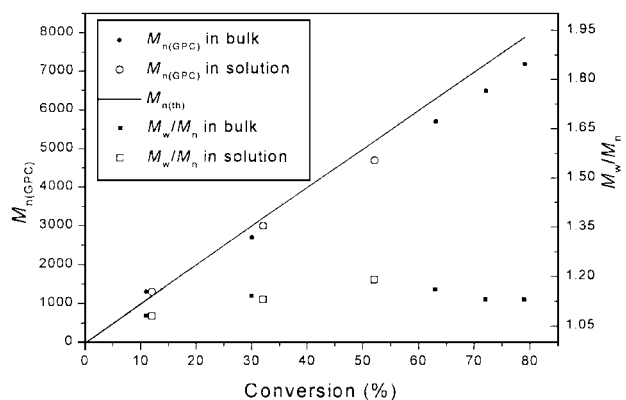
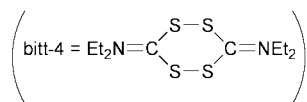
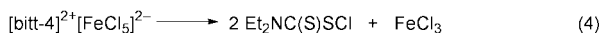
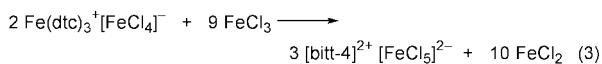
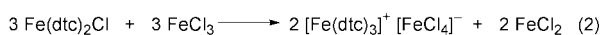
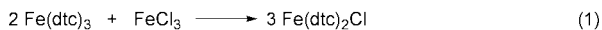


Fig. 2 Dependence of the molecular weight and polydispersity of PMMA on the monomer conversion at 80 °C (conditions as in Fig. 1).



Scheme 1

NMR spectra. In the FTIR spectrum of the PMMA, signals at 1272 and *ca.* 3440 cm^{-1} are characteristic absorption bands of the Et_2NCS_2- group while the UV spectrum of the PMMA powder identifies Et_2NCS_2- (*ca.* 276.8 nm) as an end group. In the ^1H NMR spectrum, the chemical shift at δ 3.07 corresponds to the methylene protons $\text{Et}_2\text{NCS}_2\text{CH}_2$, whilst that at δ 3.70 is due to $(\text{CH}_3\text{CH}_2)_2\text{NCS}_2-$. A signal at δ 3.79 arises from protons of the methoxy group, whilst that at δ 2.50 arises from the methylene protons of the terminal MMA unit capped with an ω -end chlorine, similar to that reported by Sawamoto and coworkers⁸ and by us.⁶ The $M_{n(\text{NMR})}$ value (5100) is close to $M_{n(\text{GPC})}$ (4700), indicating that all the polymer chains have chlorine ends. The presence of an ω -chlorine end group at the polymer chains suggests the polymerization proceeds in an ATRP process.

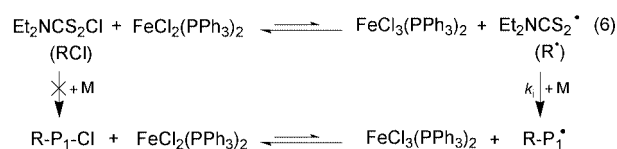
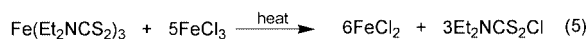
Some control experiments were carried out to clarify the polymerization mechanism. The polymerization of MMA with $\text{Fe}(\text{dtc})_3$ alone did not take place after 160 minutes at 80 °C or after 60 min at 100 °C indicating that $\text{Fe}(\text{dtc})_3$ was not a thermal radical initiator. Addition of PPh_3 did not modify the observed behavior, and polymerization only occurred in the presence of all three components $\text{Fe}(\text{dtc})_3$, FeCl_3 and PPh_3 , *e.g.* the conversion was 11% after 5 min at 80 °C. Using $\text{Fe}(\text{dtc})_3$ and FeCl_3 in the absence of PPh_3 at 80 °C, led to precipitation of FeCl_2 after *ca.* 10 min whilst no polymer was obtained even after 15.5 h.

According to the above results and the reaction of $\text{Fe}(\text{dtc})_3$ with FeCl_3 reported in the literature⁹ and our previous work,⁶ we propose the reaction of $\text{Fe}(\text{dtc})_3$ with FeCl_3 as shown in Scheme 1.

Reactions (1) and (2) are the same as the results reported by Victoriano *et al.*,⁹ whilst in the step (3), bis(dialkylimonium)tetra-thiolane (bitt-4) is possibly formed instead of bis(dialkylimonium)trithiolane (bitt-3)⁹ in the presence of the monomer MMA and PPh_3 . Bitt-4 may decompose into (diethylthiocarbamoyl)sulfur chloride ($\text{Et}_2\text{NCS}_2\text{Cl}$) as shown in step (4).

Therefore, the mechanism of polymerization proposed is as depicted in Scheme 2.

Initiation:



Propagation:



Scheme 2

At the temperature of polymerization, $\text{Fe}(\text{dtc})_3$ reacts with FeCl_3 *via* a redox process to form an organic halide, ($\text{Et}_2\text{NCS}_2\text{Cl}$) and FeCl_2 [eqn. (5) in Scheme 2; simplified from the combination of the reactions in Scheme 1]. Thus, the initiator ($\text{Et}_2\text{NCS}_2\text{Cl}$) and the transition-metal catalyst in the lower oxidation state (FeCl_2) for an ATRP system are created *in situ*. The primary radical $\text{Et}_2\text{NCS}_2^\bullet$, formed from the reaction of $\text{Et}_2\text{NCS}_2\text{Cl}$ with $\text{FeCl}_2(\text{PPh}_3)_2$, probably initiates MMA polymerization [eqn. (6) in Scheme 2], with subsequent reactions following a conventional ATRP.

Chain extension polymerization of PMMA with an ω -chlorine end group can be carried out using the ATRP catalyst system. For a bulk process at 100 °C, using PMMA with $M_n = 2500$, $M_w/M_n = 1.14$, $[\text{PMMA}]_0 = 2.73 \times 10^{-2} \text{ mol l}^{-1}$ and $[\text{MMA}]_0 = 8.32 \text{ mol l}^{-1}$, $[\text{CuCl}]_0 = 2.73 \times 10^{-2} \text{ mol l}^{-1}$, $[\text{2,2'-bipyridine}]_0 = 8.19 \times 10^{-2} \text{ mol l}^{-1}$; a conversion of 96.4% was achieved after 12 h, with M_n of the chain-extended PMMA = 41900, $M_w/M_n = 1.12$.

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