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Controlled/'living' radical polymerization of MMA *via in situ* ATRP process

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Well-defined PMMA with very low polydispersity and α-Et_2NCS_2 and ω-Cl end groups was synthesized *via* a novel controlled/'living' radical polymerization (*in situ* ATRP process) using a tetraethylthiuram disulfide (TD)/$FeCl_3$/PPh_3 initiating system.

Recently, some effective controlled/'living' radical polymerization systems have been reported, such as stable free radical polymerization with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO),[1] atom transfer radical polymerization (ATRP) systems,[2,3] and reversible addition–fragmentation chain transfer (RAFT) systems.[4] Thus, the controlled/'living' radical polymerization has become a reality.

So far, there are two kinds of ATRP, *i.e.* conventional ATRP and reverse ATRP. In conventional 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 are used as ligands (L). In this process, a dynamic equilibrium is established where the dormant polymer chains are reversibly activated *via* a halogen atom transfer reaction.

In reverse ATRP,[5–9] a radical initiator and a higher oxidation state transition-metal catalyst complex $M^{n+1}XL_m$ (where m is the number of ligands) are used. Reverse ATRP differs from conventional ATRP in the initiation step, where the initiating active species or the propagating active species can abstract a halogen atom from the oxidized transition-metal complex to form the dormant species and the reduced transition-metal species.

Here we report a novel ATRP (*in situ* ATRP), using TD/$FeCl_3$/PPh_3 as the initiating system. In the *in situ* ATRP process, the essential initiator [halide species (Et_2NCS_2Cl)], and the catalyst [transition-metal compound in its lower oxidation state ($FeCl_2$)] were both produced *in situ* from the reactions of TD and $FeCl_3$. The subsequent polymerization proceeded *via* a conventional ATRP process. The PMMAs synthesized using the TD/$FeCl_3$/PPh_3 system have very narrow polydispersities (1.04–1.07) and a very fast rate of polymerization.

The polymerization of MMA was carried out in bulk with the TD/$FeCl_3$/PPh_3 initiation system at 100 °C. Results for the system with the initial ratio of $[MMA]_0:[TD]_0:[FeCl_3]_0:[PPh_3]_0 \approx 200:1:10:30$ are shown in Fig. 1. It shows that the $M_{n\,(GPC)}$ (number-average molecular weight measured by GPC), increases linearly with conversion from 2200 to 7100, and the polydispersity index is very narrow (1.04–1.07) as the monomer conversion is increased from 21.5 to 85% in 8 min. The $M_{n\,(GPC)}$ is close to the $M_{n(th)}$, a theoretical number-average molecular weight computed from $M_{n(th)} = ([MMA]_0/2[TD]_0) \times MW_{MMA} \times$ conversion. The efficiencies of initiator f as calculated from $f = M_{n(th)}/M_{n(GPC)}$ are around 1.0. In a plot of $\ln([M]_0/[M])$ *vs.* time as shown in Fig. 2, 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.

When $[MMA]_0:[TD]_0:[FeCl_3]_0:[PPh_3]_0 \approx 200:1:10:30$, the results of solution polymerization of MMA in anisole are similar to those of bulk polymerization, while a lower rate of polymerization and slightly broader polydispersities (about 1.1) were obtained.

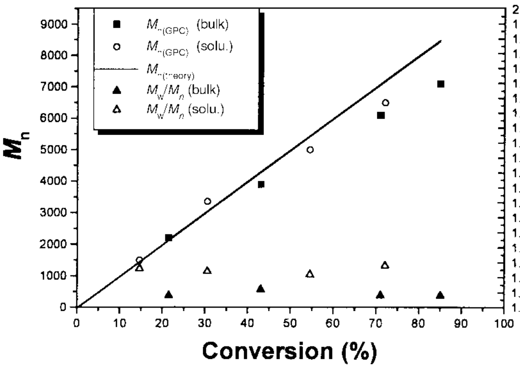


Fig. 1 Dependence of the PMMA molecular weight and polydispersity on the monomer conversion at 100 °C. Conditions: in bulk, $[MMA]_0 = 9.38$ mol l^{-1}, $[TD]_0 = 4.69 \times 10^{-2}$ mol l^{-1}, $[FeCl_3]_0 = 4.69 \times 10^{-1}$ mol l^{-1}, $[PPh_3]_0 = 1.41$ mol l^{-1}; in anisole, $[MMA]_0 = 4.69$ 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. Molecular weights and molecular weight distributions of polymer samples were measured using a Waters 515 GPC with polystyrene calibration standards.

From the results mentioned above, it can be observed that the MMA polymerization with the TD/$FeCl_3$/PPh_3 initiation system at 100 °C proceeds in a controlled/'living' manner.

From the FTIR, UV and NMR spectra, it can be seen that the Et_2NCS_2– group is one of the end groups of the polymer. The signals at 1267 and ~3450 cm^{-1} in the FTIR spectrum are characteristic absorption bands of the Et_2NCS_2– group. The UV spectrum of the PMMA powder identifies Et_2NCS_2– (~283 nm) is an end group. The number of Et_2NCS_2– groups was determined by UV spectroscopy in $CHCl_3$ to be *ca.* 1. In the ^1H NMR spectrum of the PMMA, the signal at δ_H 3.07 is that of the methylene of $Et_2NCS_2CH_2$–, and that at δ_H 3.70 is from the methylene of $(CH_3CH_2)_2NCS_2$–. The signal at δ_H 3.79 is that of the protons of the methoxy group, and that at δ_H 2.50 is from the methylene protons of the terminal MMA unit capped with an ω-chlorine, similar with that reported by Ando *et al.*[10] The $M_{n(NMR)}$ (6600) is close to $M_{n(GPC)}$ (6500), indicating that all the polymer chains have chlorine end groups. So, the polymers

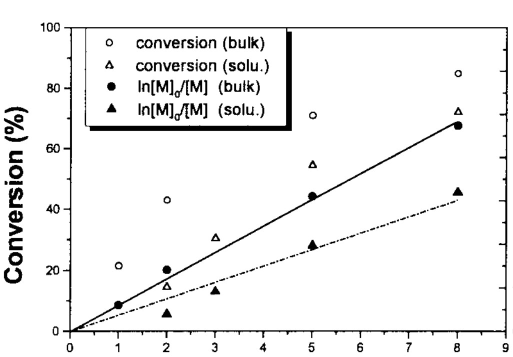
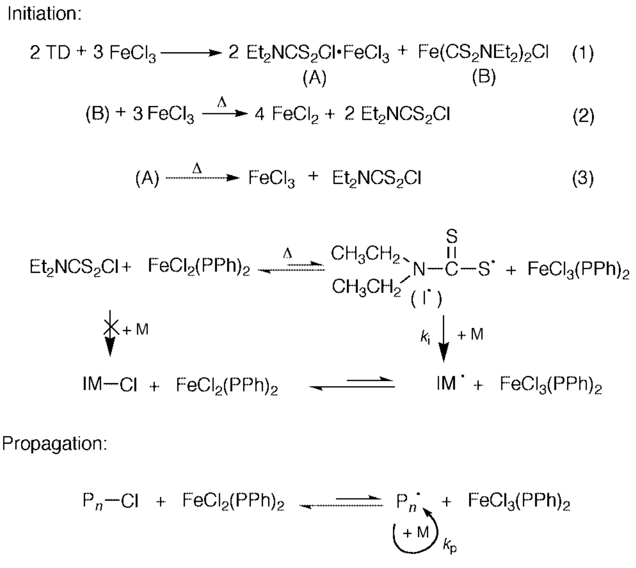


Fig. 2 Time dependence of $\ln[M]_0/[M]$ and conversion at 100 °C, where $[M]_0$ and $[M]$ are the MMA concentration at times 0 and t, respectively. Under the same conditions as in Fig. 1.



Scheme 1

produced using the initiation system are well-defined, not only with very narrow polydispersity but also with precise end groups, *i.e.* α-Et$_2$NCS$_2$– and ω-chlorine groups. The presence of an ω-chlorine end group in the obtained PMMA suggests the polymerization proceeds *via* an ATRP process.

In order to clarify the nature of the polymerization, we carried out some control experiments under fixed conditions: $[\mathrm{MMA}]_0 = 9.38$ mol l^{-1}, $[\mathrm{TD}]_0 = 4.69 \times 10^{-2}$ mol l^{-1}, $[\mathrm{FeCl_3}]_0 = 4.69 \times 10^{-1}$ mol l^{-1}, $[\mathrm{PPh_3}]_0 = 1.41$ mol l^{-1}, 100 °C. In this case, the conversion was 85% (8 min). However, the conversion decreased to 75% after 20 min in the presence of TEMPO ($[\mathrm{TEMPO}]_0 = 12.57 \times 10^{-2}$ mol l^{-1}). This suggests that the activate species are possibly radicals. When H$_2$O was added ($[\mathrm{H_2O}]_0 = 281.4 \times 10^{-2}$ mol l^{-1}), the polymerization still proceeded at a moderate rate with 49.3% conversion after 20 min. Generally speaking, MMA is an electron poor monomer and cannot be polymerized *via* a cationic process. It is impossible to perform an ionic polymerization in the presence of water ($[\mathrm{H_2O}]_0/[\mathrm{TD}]_0 = {\sim}60$). Therefore, the polymerization with the TD/FeCl$_3$/PPh$_3$ system is a radical polymerization. When the polymerization was carried without the PPh$_3$ ligand, no polymer was obtained after 16 h but precipitated FeCl$_2$ was produced.

According to the results mentioned above, we propose a mechanism for the *in situ* ATRP as depicted in Scheme 1.

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.[11] This indicated that TD rapidly reacted with FeCl$_3$ and two complex products of halide, Et$_2$NCS$_2$Cl·FeCl$_3$ (A) and Fe(Et$_2$NCS$_2$)$_2$Cl (B) were produced,[12] as depicted in eqn. (1) in Scheme 1. At high temperature, such as 100 °C, (B) reacted with FeCl$_3$ to form Et$_2$NCS$_2$Cl and FeCl$_2$ [eqn. (2) in Scheme 1)]. (A) thermally decomposed into Et$_2$NCS$_2$Cl and FeCl$_3$ [eqn. (3) in Scheme 1]. Thus, the initiator (Et$_2$NCS$_2$Cl) and the transition-metal catalyst in its lower oxidation state (FeCl$_2$) for an ATRP system were *in situ* created. The primary radical Et$_2$NCS$_2^{\cdot}$, formed from the reaction of Et$_2$NCS$_2$Cl with FeCl$_2$(PPh$_3$)$_2$, can initiate MMA polymerization. The subsequent reactions proceeded following a conventional ATRP.

Due to the presence of an ω-chlorine end group on the polymer chain, chain extension polymerization of the 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, $M_\mathrm{w}/M_\mathrm{n} = 1.11$, $[\mathrm{PMMA}]_0 = 5.33 \times 10^{-3}$ 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, $M_\mathrm{w}/M_\mathrm{n} = 1.43$.

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