A novel photo atom transfer radical polymerization of methyl methacrylate

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Photo atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) was realized with a novel photo initiating system, 2,2-dimethoxy-2-phenylacetophenone (DMPA)/ferric tri(N,N-diethyldithiocarbamate) [Fe(dtc)$_3$], which proceeds with DPMA as the photo initiator, Fe(dtc)$_3$ as the catalyst and dtc as a reversible transfer group, and is halogen and ligand free; well-defined polyMMA was prepared and the polymerization was found to involve a reverse ATRP mechanism.

Living polymerization is one of the most useful methods for the synthesis of well-defined polymers and copolymers (block and graft copolymers). Recent progress in the field of living radical polymerization has made it possible to modify polymer architectures using this mechanism and many initiating systems have been developed.[1–7] These systems are all based on dynamic equilibria between the active growing radicals and the dormant species to keep the concentration of the active growing radicals low. In general, the dormant species is activated photochemically,[1,6,7] thermally,[2,5] or chemically (with a catalyst).[3,4]

Atom transfer radical polymerization (ATRP) is a robust method for the synthesis of polymers with designed architectures and low polydispersities. In the known ATRP systems, including conventional and reverse ATRP, the dormant species is activated thermally with a transition metal complex as catalyst. Photoinduced radical polymerization is a useful technique due to its low cost of operation, mild reaction conditions and the accurate control of reaction time which can be exerted an important factor for dynamic studies. In the area of photoinduced living radical polymerization, besides the living graft polymerization system using benzophenone developed recently,[6,7] the most extensively studied system is the photoiniferter technique reported by Otsu and co-workers,[1,8] in which the diethyldithiocarbamyl (dtc) group is the end-trapping group. However, as reported by Otsu and others, the bulk polymerization of MMA using photoiniferter is a pseudo-living process, while the solution polymerization is a conventional free radical polymerization.[9,10]

Recently, it was reported that the ATRP of MMA or styrene can be carried out with Fe(dtc)$_3$ in conjunction with FeCl$_3$[11] or AIBN[12] as the initiating system. Here, we report for the first time on a novel photo ATRP initiating system, DMPA/Fe(dtc)$_3$, for the living radical polymerization of MMA in toluene.

MMA was polymerized with a combination of Fe(dtc)$_3$ and DMPA in toluene under UV light irradiation at ambient temperature. Results for the polymerization with fixed concentrations of MMA and DMPA in conjunction with various Fe(dtc)$_3$ concentrations are illustrated in Fig. 1 and 2. Fig. 1 shows the kinetic results which reveal that the polymerization proceeds without an induction period in the presence of various concentrations of Fe(dtc)$_3$, the straight lines for

ln([M]$_0$/[M]) *vs.* time indicate that the kinetics are first order in monomer, *i.e.* the concentration of propagating radicals is constant during the polymerization period. It can also be seen from Fig. 1 that when the concentration of Fe(dtc)$_3$ is increased, the polymerization rate decreases, this means that the iron(III) does not act as an initiator, but as a radical trapping agent or a deactivator. The number-average molecular weights of the resulting polymers increase proportionally to
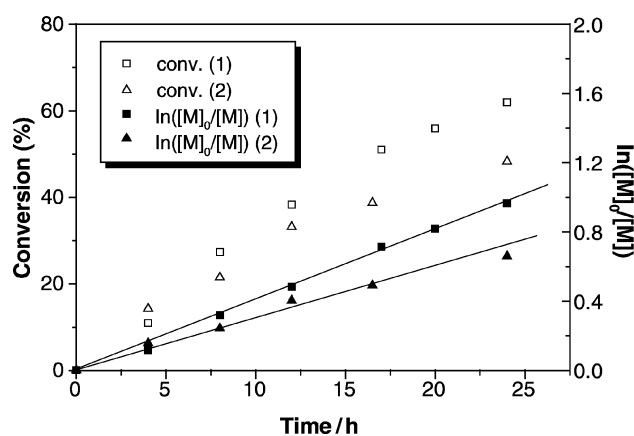

Fig. 1 Dependence of conversion and ln([M]$_0$/[M]) on time for MMA polymerization in toluene at ambient temperature with UV light irradiation. *Conditions*: [MMA] = 4.0 mol l^{-1}, [DMPA] = 2.0 × 10^{-3} mol l^{-1}. (1) [Fe(dtc)$_3$] = 4.0 × 10^{-3} mol l^{-1}; (2) [Fe(dtc)$_3$] = 8.0 × 10^{-3} mol l^{-1}.
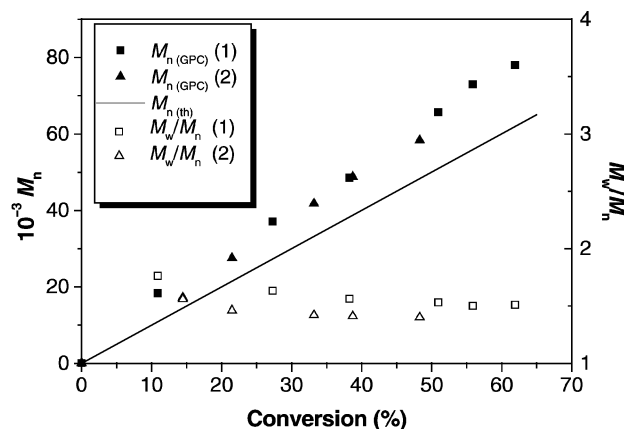

Fig. 2 Dependence of the molecular weight and molecular weight distributions of polyMMA on the monomer conversion under the same conditions as in Fig. 1. $M_{n(th)}$ = ([MMA]$_0$/[2DMPA]$_0$) × M_W(MMA) × Conv.

the monomer conversion, as shown in Fig. 2, and the values are in agreement with the calculated values based on the DMPA concentration. The initiation efficiency (f) was evaluated to be about 0.79 in the presence of various concentrations of Fe(dtc)$_3$. This result indicates the molecular weight does not depend on the concentration of the iron(III), while the molecular weight distribution does, a high iron salt concentration leads to a lower polymerization rate and also to a lower molecular weight distribution, as shown in Fig. 1 and 2. This demonstrates that a high concentration of iron(III) salt can trap the growing radical more efficiently.

From the results discussed above, it can be concluded that the solution polymerization of MMA with the novel photo ATRP initiating system, DMPA/Fe(dtc)$_3$, proceeds in the manner of a living polymerization. Since the polymerization was carried out at ambient temperature, the formation of thermally initiated PMMA should be negligible.

The end groups of the resulting polymer were characterized by FT-IR, UV and ^{1}H NMR spectroscopic analyses. In the FT-IR spectrum, the absorption at 1271 cm^{-1} is characteristic of the dtc group. The UV spectrum also shows the presence of dtc end groups (ca. 282 nm in THF), and the number of dtc groups was determined by UV spectroscopy in THF to be about 1. In the ^{1}H NMR spectrum, the signal at δ_H 7.5–7.9 results from the benzene rings of the DMPA fragments, and the peak at δ_H 3.8–4.1 arises from the methylene protons of dtc. The resonance at δ_H 3.7 is due to the methoxy protons in the polyMMA unit adjacent to the terminal dtc group, which is resolved from other methoxy proton signals of the repeating polyMMA units (δ_H 3.4–3.6). Although the methyl peak derived from the other fragments of DMPA is interfered with by the signals due to polyMMA, it can be ascertained from the M_n values. The $M_{n(NMR)}$ value (10 600) calculated with the signal of dtc as standard is close to $M_{n(GPC)}$ (11 200), while the $M_{n(NMR)}$ (18 400) value calculated with the benzene ring resonance as standard is larger than $M_{n(GPC)}$, indicating that the polyMMA bears another α-end group. Therefore, the resulting polyMMA should carry a fragment of DMPA at the α-end and a dtc group from Fe(dtc)$_3$ at the ω-end.

Various control experiments were carried out in toluene under similar experimental conditions in order to further understand the mechanism. The photopolymerization with DMPA alone was a conventional radical polymerization yielding uncontrolled polymer. Fe(dtc)$_3$ alone gave a trace of polyMMA, though the diethyldithiocarbamyl radical (dtc˙) can be produced by irradiation of Fe(dtc)$_3$,[13,14] which mainly participates in the termination reaction. In contrast, the polymerization with benzyl N,N-diethyldithiocarbamate as a photoiniferter, gave polyMMA with a molecular weight higher than the theoretical value and a broader molecular weight distribution; the process is a conventional radical polymerization as reported by Otsu.[9] Thus, in our novel initiating system, the dtc group does not act as an iniferter. Both the DMPA and the Fe(dtc)$_3$ are necessary to induce the living radical polymerization.

According to the results discussed above, we proposed the mechanism for this novel photo ATRP depicted in Scheme 1, proceeding with DMPA as the photo initiator, Fe(dtc)$_3$ as the catalyst, dtc as a reversible transfer group, while the halogen and ligand are free. Under UV light irradiation, DMPA generates an active benzoyl radical (R˙) and an inert α,α-dimethoxybenzyl radical, the latter rapidly decomposes further to methyl benzoate and an active methyl radical (R˙).[15,16] R˙ (both benzoyl and methyl radicals) can be trapped by Fe(dtc)$_3$ to form R–S$_2$CNEt$_2$ and the lower oxidation state metal salt Fe(dtc)$_2$. In addition, it can react with monomer to form the activated monomer radical, then the activated monomer radical is trapped by Fe(dtc)$_3$ to form the dormant species (P$_n$–S$_2$CNEt$_2$) and Fe(dtc)$_2$. Under UV light irradiation and catalyzed by Fe(dtc)$_2$, both R–S$_2$CNEt$_2$ and P$_n$–S$_2$CNEt$_2$ can

Initiation:
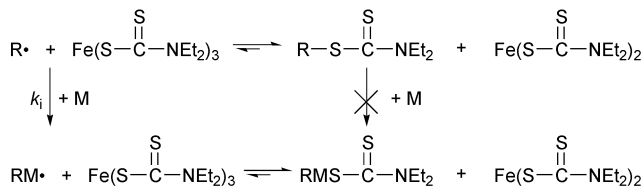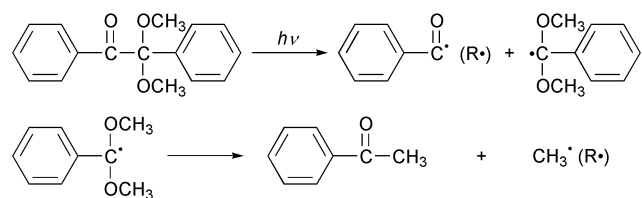
Propagation:
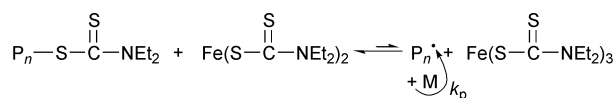
Scheme 1

be activated, then the polymerization proceeds in a manner similar to the ATRP process,[3,4] although the transfer group is a dtc moiety not a halogen atom. The low initiation efficiency and rather broad molecular weight distribution could be a result of the different initiation activity of the two primary radicals, as shown in Scheme 1.

As described above, the polyMMA prepared with the DMPA/Fe(dtc)$_3$ initiating system has an ω-dtc end group, it is expected to act as a macro photoinitiator for block copolymerization in conjunction with Fe(dtc)$_2$ catalyst via a conventional photo ATRP mechanism. The dtc-terminated polyMMA is also a macro photoiniferter which can be used alone for block copolymerization. Thus, block copolymerizations of styrene initiated with the polyMMA ($M_n = 27\,500$, $M_w/M_n = 1.46$) obtained were carried out under UV light irradiation under different conditions: (a) [polyMMA] = 3.4×10^{-3} mol l^{-1}, [Fe(dtc)$_2$] = 3.4×10^{-3} mol l^{-1}, [styrene] = 8.7 mol l^{-1}; (b) [polyMMA] = 3.4×10^{-3} mol l^{-1}, [styrene] = 8.7 mol l^{-1}. Under condition (a), a conversion of 31% was achieved after 23 h, and a polyMMA-b-polystyrene copolymer with $M_n = 45\,800$ and $M_w/M_n = 1.50$ was obtained. While under condition b, the styrene conversion reached 56% after only 7 h; the resulting block copolymer possessed high molecular weight ($M_n = 162\,700$) and a rather broad molecular weight distribution ($M_w/M_n = 2.26$). These results demonstrate that the two processes obviously proceed via different polymerization mechanisms. It also confirms that the mechanism of MMA polymerization with the DMPA/Fe(dtc)$_3$ initiating system is a photo ATRP process, as shown in Scheme 1.

Experimental

Polymerization

In a typical run, MMA (1.88 g, 18.8 mmol) was added to a dried glass tube containing DMPA (2.4 mg, 9.4×10^{-3} mmol), Fe(dtc)$_3$ (9.4 mg, 18.8×10^{-3} mmol) and toluene 2.7 ml. The mixture was immediately degassed by the three freeze–pump–thaw cycles and sealed under vacuum. The homogenous reaction mixture was irradiated with a 250 W UV lamp at a distance of 20 cm at ambient temperature. After 4 h, the UV lamp was removed to halt polymerization. Then, the resultant polymer was dissolved in THF and the polyMMA was precipitated with methanol and dried under

vacuum. The conversion (0.21 g of polyMMA, 11.2%) was determined gravmetrically. Other polymerizations and copolymerizations were carried out using the same procedure.

Characterization

Molecular weights and molecular weight distributions of the polymers were determined on a Waters 515 gel permeation chromatograph (GPC). ^{1}H NMR and FT-IR spectra were recorded on Brucker ARX400 (400 MHz) and Nicolet IR 750 spectrometers, respectively. UV spectra were recorded on a Shimadzu UV-2101 PC spectrometer.

References

1 T. Otsu and M. Yoshida, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 127.
2 M. K. Geroges, R. P. N. Veregin, P. M. Kazmaier and G. K. Hamer, *Macromolecules*, 1993, **26**, 2987.
3 J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614.
4 M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1995, **28**, 1721.
5 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559.
6 W. T. Yang and B. Rånby, *Macromolecules*, 1996, **29**, 3308.
7 H. M. Ma, R. H. Davis and C. N. Bowman, *Macromolecules*, 2000, **33**, 331.
8 T. Otsu and A. Matsumoto, *Adv. Polym. Sci.*, 1998, **136**, 75.
9 T. Otsu, T. Matsunaga, T. Doi and A. Matsumoto, *Eur. Polym. J.*, 1995, **31**, 67.
10 S. R. Turner and R. W. Blevins, *Macromolecules*, 1990, **23**, 1856.
11 X. P. Chen and K. Y. Qiu, *Chem. Commun.*, 2000, 1403.
12 M. Nishimura, M. Kamigaito and M. Sawamoto, *Polym. Prepr.*, 1999, **40**, 470.
13 D. P. Schwendiman and J. I. Zink, *J. Am. Chem. Soc.*, 1976, **98**, 4439.
14 B. G. Jeliazkova and N. D. Yordanov, *Inorg. Chim. Acta*, 1993, **203**, 201.
15 M. R. Sandner and C. L. Oshorn, *Tetrahedron. Lett.*, 1974, **5**, 415.
16 C. J. Groenenboom, H. J. Hageman, T. Overeem and A. J. M. Weber, *Makromol. Chem.*, 1982, **183**, 281.