

Rapid Communication

A NOVEL PHOTO-INITIATING SYSTEM FOR ATOM TRANSFER RADICAL POLYMERIZATION OF STYRENE

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Abstract A novel photo-induced initiating system, 2,2-dimethoxy-2-phenylacetophenone (DMPA)/ferric tri(*N,N*-diethyldithiocarbamate) $[\text{Fe}(\text{DC})_3]$, was developed and used for the atom transfer radical polymerization (ATRP) of styrene in toluene. The polymerization proceeds with DMPA as photo-initiator, $\text{Fe}(\text{DC})_3$ as catalyst and DC as a reversible transfer group, while the halogen and ligands are free. Well-defined PSt was prepared and the polymerization mechanism revealed by end group analysis belongs to a reverse ATRP. Block copolymer was prepared by using thus obtained PSt as macroinitiator and $\text{Fe}(\text{DC})_2$ as catalyst under UV light irradiation via a conventional ATRP process.

Keywords Photo atom transfer radical polymerization, Living radical polymerization, Well-defined polystyrene, Block copolymer

INTRODUCTION

Living radical polymerization is a major theme of contemporary research by polymer chemists because it can provide good control of molecular weight and molecular weight distribution of the resulting polymers, and also good control of the polymer architecture. So far, living radical polymerization can be achieved by using iniferter^[1], nitroxides or alternative stable free radicals polymerization^[2-4], atom transfer radical polymerization (ATRP)^[5, 6], and reversible addition fragmentation chain transfer (RAFT) polymerization^[7], all of which rely on the dynamic equilibrium between the active growing radicals and the dormant species to maintain low concentration of the active growing radicals. Among them, ATRP is one of the most versatile methods as it is applicable to many type of monomers in the presence of various transition metal complexes within a wide range of temperatures. It proceeds by a reversible redox process between an initiator, alkyl halide ($\text{R}-\text{X}$) and transition metal halides based on Cu, Fe, Ni, Re, Ru, Rh and Pd complexed with phosphine or nitrogen based ligands as catalyst. Instead of halides, pseudohalide such as thiocyanate (SCN) and diethyldithiocarbamyl (DC) groups can also be used as reversible transfer groups in ATRP^[8-11].

In the realized ATRP systems including both conventional and reverse ATRP, the dormant species is the fully activated and thermally catalyzed with transition metal complex. It was found recently that the ATRP of MMA or St can be carried out with $\text{Fe}(\text{DC})_3$ in conjunction with DCDPS^[9] or AIBN^[10] as thermal initiating system, in which DC serves as the reversible transfer group. However, very little work on the photo ATRP of vinyl monomers has been published, only one paper reported a remarkable visible light effect on ATRP of MMA^[12]. In this communication, we would like to report a novel photo ATRP initiating system, DMPA/ $\text{Fe}(\text{DC})_3$, developed for St living polymerization, in which DMPA was used as a photo-initiator, and $\text{Fe}(\text{DC})_3$ as a catalyst. The living radical polymerization of St was realized in toluene and the polymerization mechanism was summarized based on end group analysis.

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EXPERIMENTAL

Materials

$\text{Fe}(\text{DC})_3$ was prepared by the reaction of FeCl_3 with NaSSCNET_2 in water, and recrystallized twice in chloroform^[13]. $\text{Fe}(\text{DC})_2$ was prepared by the reaction of FeCl_2 with NaSSCNET_2 in water and used immediately. Styrene and methyl methacrylate were distilled under vacuum; solvents and other reagents were purified by usual methods.

Polymerization

In a typical run, St (1.35 g, 12.98 mmol) was added into a dried glass tube containing DMPA (6.6 mg, 2.6×10^{-2} mmol), $\text{Fe}(\text{DC})_3$ (6.5 mg, 1.3×10^{-2} mmol) and toluene 2.0 mL. The mixture was immediately degassed by the three freeze-pump-thaw cycles and sealed under vacuum. The homogeneous reaction mixture was irradiated with a 250 W UV lamp at a distance of 20 cm at ambient temperature. After 10.5 h, the tube was removed from the UV lamp to stop the polymerization. Then the resulting polymer was dissolved in THF, the PSt was precipitated with methanol and dried in vacuum. The conversion (0.17 g of PSt, 12.6%) was determined gravimetrically. Other polymerization and copolymerization steps were carried out in the same way.

Characterization

Molecular weights and molecular weight distributions of the polymers were determined on a Waters gel permeation chromatograph (GPC) equipped with a 515 HPLC pump, 2410 refractive index detector, and three μ -Styragel columns (HT2 + HT3 + HT4) in series. All samples were eluted with THF at 35°C at an eluting rate of 1.0 mL/min. Linear polystyrene standards were used for calibration. The data were analyzed on a Waters Millennium 32 system. ^1H -NMR and FT-IR spectra were recorded on a Bruker ARX400 (400MHz) spectrometer and a Nicolet IR 750 spectrometer, respectively. UV spectra were recorded on a Shimadzu UV-2101 PC spectrometer.

RESULTS AND DISCUSSION

The polymerization of St was carried out by UV irradiation in toluene with DMPA/ $\text{Fe}(\text{DC})_3$ as the initiating system ($[\text{St}]_0:[\text{DMPA}]_0:[\text{Fe}(\text{DC})_3]_0 = 1000:2:1$) at ambient temperature; the results are illustrated in Figs. 1 and 2. Figure 1 represents the kinetics results. It shows that the polymerization proceeded without induction periods. The straight line in the plot of $\ln([\text{M}]_0/[\text{M}])$ versus time indicates that the kinetics is first order in monomer, *i.e.*, the concentration of propagating radicals is constant during the polymerization period. The M_n of the resulting PSt increased linearly with increasing monomer conversion from 6,000 to 19,500 as shown in Fig. 2 and the values were in good agreement with the calculated values based on the DMPA concentration. The initiation efficiency (f) was evaluated to be about 0.89. This result indicates that the solution polymerization of St with DMPA/ $\text{Fe}(\text{DC})_3$ initiating system exhibits some characteristics of living polymerization.

In order to gain a better understanding of the polymerization mechanism, we have studied the effect of various concentrations of $\text{Fe}(\text{DC})_3$ in conjunction with fixed concentrations of St and DMPA on the level of the control of polymerization. As shown in Table 1, when the concentration of $\text{Fe}(\text{DC})_3$ increases, the polymerization rate decreases, indicating that the $\text{Fe}(\text{DC})_3$ does not act as an initiator but as a radical trapping agent or as a deactivator. At different $\text{Fe}(\text{DC})_3$ concentrations, the molecular weight of the resulting PSt agrees well with the calculated values based on the DMPA concentration, which demonstrates that the molecular weight is independent of the $\text{Fe}(\text{DC})_3$ concentration, while the molecular weight distribution depends on the concentration as shown in Table 1. A high $\text{Fe}(\text{DC})_3$ concentration leads to a lower polymerization rate and also to lower molecular weight distributions, revealing the high concentration of $\text{Fe}(\text{DC})_3$ can trap the growing radical more efficiently.

From the results discussed above, it can be concluded that the solution polymerization of St with the novel photo ATRP initiating system, DMPA/ $\text{Fe}(\text{DC})_3$, assumes the form of living polymerization. As the polymerization was carried out at ambient temperature, the formation of thermally initiated PSt is negligible.

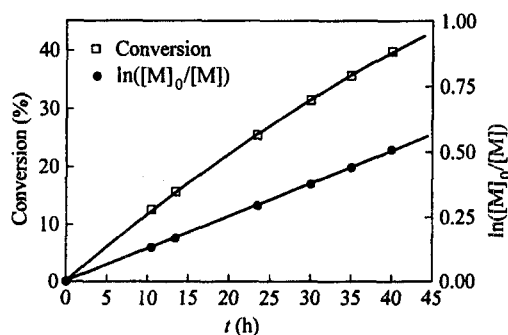


Fig. 1 Dependence of conversion and $\ln([M]_0/[M])$ on time for St polymerization in toluene at ambient temperature with UV light irradiation

Conditions: $[St] = 3.7 \text{ mol L}^{-1}$, $[DMPA] = 7.4 \times 10^{-3} \text{ mol L}^{-1}$, $[Fe(DC)_3] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$

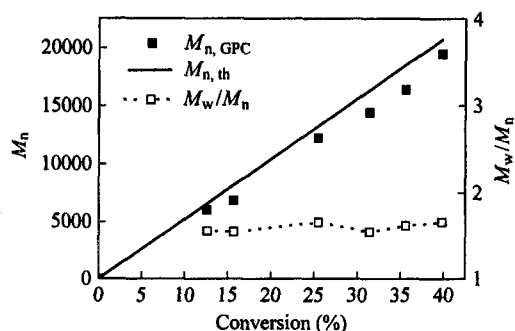


Fig. 2 Dependence of the molecular weight and molecular weight distributions of PSt on the monomer conversion under the same conditions as in Fig. 1

$$M_{n(th)} = \frac{[St]_0}{2[DMPA]_0} \times MW(St) \times \text{Conv}$$

Table 1. Data of PSt obtained by DMPA/ $Fe(DC)_3$ initiating system at various $Fe(DC)_3$ concentrations ^a

Entry	$[Fe(DC)_3]$ (10^3 mol L^{-1})	Conversion (%)	$M_n(\text{GPC})^b$	$M_{n(th)}^c$	M_w/M_n (MWD)
1	8.7	10.1	4 800	5 200	1.48
2	5.4	18.4	8300	9 600	1.55
3	3.7	25.5	12 200	13 200	1.66
4	1.2	31.6	14 500	16 400	1.71

^a Condition: $[St] = 3.7 \text{ mol L}^{-1}$, $[DMPA] = 7.4 \times 10^{-3} \text{ mol L}^{-1}$, $t = 23.5 \text{ h}$

^b GPC calibrated with PSt standards

^c Calculated by the equation $M_{n(th)} = \frac{[St]_0}{2[DMPA]_0} \times MW(St) \times \text{Conv}$

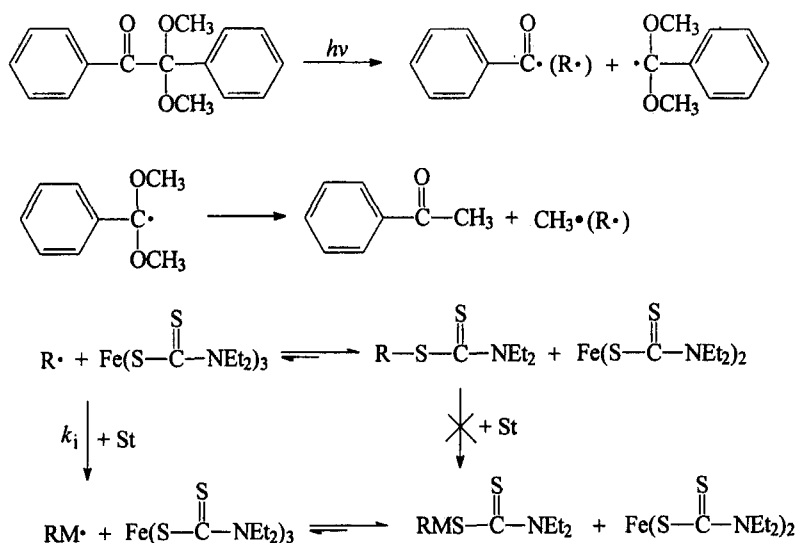
The end groups of the resulting polymer were characterized by FT-IR, UV and $^1\text{H-NMR}$ spectral analyses. In the FT-IR spectrum, the peak at 1271 cm^{-1} is characteristic for the DC group. The UV spectrum also shows the presence of DC end groups ($\sim 282 \text{ nm}$ in THF), and the number of DC groups was estimated by UV spectroscopy in THF to be about 1. In the $^1\text{H-NMR}$ spectrum, the signal at $\delta_H = 7.4\text{--}8.0$ is attributed to the proton of the benzene ring derived from a fragment of DMPA, and the signal at $\delta_H = 4.0\text{--}4.3$ belongs to the methylene protons of DC. The signal at $\delta_H = 4.7\text{--}4.9$ is that of the methine proton in the PSt unit adjacent to the terminal DC group, which is resolved from other methine protons of the repeated PSt units ($\delta_H = 1.7\text{--}2.3$). Although the signal of methyl derived from the fragmentation of primary radical $\text{C}_6\text{H}_5(\text{CH}_3\text{O})_2\text{C}\cdot$ is overlapped by the signals of PSt, but its presence can be deduced from the M_n . The $M_n(\text{NMR})$ (6100) calculated with the signal of DC as standard is close to $M_n(\text{GPC})$ (6000), while the $M_n(\text{NMR})$ (10300) calculated with the signal of benzene ring as standard is almost twice as that of $M_n(\text{GPC})$, indicating that the PSt should bear another α -end group. Therefore, it is presumed that the resulting PSt would carry a fragment of DMPA at the α -end and a DC group from the $Fe(DC)_3$ at ω -end.

Various control experiments were carried out in toluene under similar experimental conditions for further mechanistic understanding, *i.e.*, $[St] = 3.7 \text{ mol L}^{-1}$, $[DMPA] = 7.4 \times 10^{-3} \text{ mol L}^{-1}$, $[Fe(DC)_3] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$, under UV light irradiation at ambient temperature for 10.5 h. The photopolymerization with DMPA alone was a conventional radical polymerization giving uncontrolled polymer with $M_n = 116\,500$ and $M_w/M_n = 2.25$. $Fe(DC)_3$ alone gave a trace of PSt, though diethyldithiocarbamyl radical ($DC\cdot$) can be produced by $Fe(DC)_3$ under irradiation^[14, 15], which mainly participates in the terminating reaction. On the contrary, the polymerization of St with benzyl *N,N*-diethyldithiocarbamate as a photoiniferter, gave a PSt with molecular weight much higher than the theoretical value and a quite broader molecular weight distribution ($M_n = 147,600,500$ and $M_w/M_n = 2.54$), indicating which is not well controlled the polymerization. Thus, in our novel initiating system, the DC group

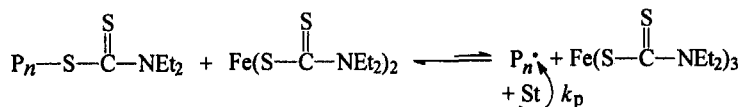
does not act as an iniferter. Both the DMPA and the $\text{Fe}(\text{DC})_3$ are necessary to induce the living radical polymerization.

According to the results discussed above, we proposed the mechanism for this novel photo ATRP as depicted in Scheme 1, which is realized with DMPA as photo-initiator, $\text{Fe}(\text{DC})_3$ as catalyst, DC as a reversible transfer group, while the halogen and ligands are free. Under UV light irradiation, DMPA generates an active benzoyl radical ($\text{R}^\bullet$) and an inert α,α -dimethoxybenzyl radical; the latter quickly decomposes again to methyl benzoate and an active methyl radical ($\text{R}^\bullet$) [16, 17]. $\text{R}^\bullet$ (both benzoyl and methyl radicals) can be trapped by $\text{Fe}(\text{DC})_3$ to form $\text{R}-\text{DC}$ and lower oxidation state metal salt $\text{Fe}(\text{DC})_2$. Also, it can react with monomer to form the activated monomer radical; then the activated monomer radical is trapped by $\text{Fe}(\text{DC})_3$ to form the dormant species (P_n-DC) and $\text{Fe}(\text{DC})_2$. Under UV light irradiation and on catalysis with $\text{Fe}(\text{DC})_2$, both $\text{R}-\text{DC}$ and P_n-DC can be activated; then the polymerization proceeds similarly to the ATRP process^[5, 6], the transfer group being a DC group but not a halogen atom.

Initiation:



Propagation:



Scheme 1

As mentioned above, the PSt prepared with the DMPA/ $\text{Fe}(\text{DC})_3$ initiating system has an ω -DC end group. It is expected to act as a macro photo-initiator for block copolymerization in conjunction with $\text{Fe}(\text{DC})_2$ as catalyst via a conventional photo ATRP mechanism. The DC-terminated PSt is also a macro photoiniferter which can be used alone for block copolymerization. Thus, block copolymerizations of MMA initiated with above obtained PSt ($M_n = 6000$, $M_w/M_n = 1.56$) were carried out under UV light irradiation via an ATRP and an iniferter mechanism, respectively. In the ATRP mechanism using $[\text{PSt}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{Fe}(\text{DC})_2] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{MMA}] = 9.4 \text{ mol L}^{-1}$, a conversion of 34% was achieved after 21 h, and a PSt-*b*-PMMA copolymer with $M_n = 38\,500$ and $M_w/M_n = 1.59$ was obtained. On the other hand, in the iniferter mechanism using $[\text{PSt}] = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{MMA}] = 9.4 \text{ mol L}^{-1}$, the MMA conversion reached 64% after only 6 h, and the resulting block copolymer possessed high molecular weight ($M_n = 146,400$) and rather broad molecular weight distribution

($M_w/M_n = 2.05$). These results obviously demonstrate that the two processes proceeded via different polymerization mechanisms. They also confirm that the mechanism of St polymerization with the DMPA/Fe(DC)₃ initiating system is a photo ATRP process as shown in Scheme 1.

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