Supporting information for

A novel radical polymerization system initiated by a redox reaction with NHPI and xanthone

Materials.

Tetrahydrofuran (THF) (Beijing No. 2 Reagent Co., Ltd., 99%), N, N-Dimethylformamide (DMF) (Beijing No. 2 Reagent Co., Ltd., 99%), toluene (Beijing No. 2 Reagent Co., Ltd., 99%) and acetonitrile (Tianjin Fuchen Chemical Reagents Factory) were distilled and stored in a refrigerator before use.

Methyl methacrylate (MMA) (Sinopharm Chemical Reagent Beijing Co., Ltd.), butyl acrylate (BA) (Sinopharm Chemical Reagent Beijing Co., Ltd.) and Styrene (St) (Beijing No. 2 Reagent Co., Ltd., 99%) were distilled under vacuum and stored in a refrigerator before use.

Xanthone (XT) (Alfa Aesar, 99%), N-hydroxyphthalimide (NHPI) (Alfa Aesar, 99%), Benzophenone (BP) (Alfa Aesar, 99%), 9-Fluorenone (FL) (Alfa Aesar, 99%) and methanol (Beijing No. 2 Reagent Co., Ltd., 99%) were used as received.

Characterizations.

Conversion of monomer was determined by gravimetry at RT. Number and weight average molecular weight (Mn and Mw, respectively) and polydispersity (PDI=Mw/Mn) were determined by gel permeation chromatography (GPC). The GPC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 105,103,102 A) in THF as an eluent at 30°C at a flow rate of 1 mL/min. The column system was calibrated with linear PST standards. An NMR (Bruker AC-600) spectrum was recorded in CDCl₃ as solvent and was reported in parts million (δ) from internal TMS (for proton). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were acquired with a Bruker Autoflex-II mass spectrometer (Bruker Daltonics) with a nitrogen laser (k5337 nm) operated in the positive linear mode. The solution for MALDI-TOF MS analysis was obtained by mixing 2, 5-dihydroxybenzoic acid matrix (10 mg mL⁻¹), and solution in a 1/1 volumetric ratio. Then, 1μL portion of the mixture was analyzed on MALDI-TOF MS in the positive-ion mode.

Polymerization of MMA by NHPI/ketone redox polymerization system in Fig.1

The concentration of the MMA in THF was set to be 25wt%. Specifically, the ratios of reagents [NHPI/ketones] were 1/0 for pure NHPI; 1:1 for NHPI/BP; NHPI/FL and NHPI/XT, respectively. The concentration of NHPI was 2.50×10⁻²mol/L. In a typical run, all the reagents were introduced into a dry one-necked round-bottom flask (50mL) and then the reactant was deoxygenated by three freeze-evacuate-
thaw cycles and backfilled with nitrogen (N2). Subsequently, the solution was stirred at 70°C under nitrogen atmosphere. Then aliquots were withdrawn from the reaction mixture via a N2-purged syringe at different time intervals. The resulting mixture was poured into a vigorously stirred methanol and then the precipitates were dried at 35°C in vacuum and analyzed by GPC.

Polymerization of MMA by NHPI/XT redox polymerization system with the different monomer concentrations (Fig.S1 and Fig.S2)

The concentrations of NHPI and XT were both set to be 2.50×10⁻²mol/L in toluene and DMF mixed solvent (toluene: DMF (wt) is 49:1); while the concentrations of MMA were set to be 12.5wt%, 25.0wt% and 50.0wt% respectively. In a typical run, all the reagents were introduced into a dry one-necked round-bottom flask (50mL) and then the reactant was deoxygenated by three freeze-evacuate-thaw cycles and backfilled with nitrogen (N2). Subsequently, the solution was stirred at 70°C under nitrogen atmosphere. The other steps are similar to of the NHPI/XT polymerization with MMA as the monomer.

Polymerization of MMA by NHPI/XT redox polymerization system with the different temperatures (Fig.S3 and Fig.S4)

The concentrations of NHPI and XT were both set to be 2.50×10⁻²mol/L in toluene and DMF mixed solvent (toluene: DMF (wt) is 49:1); while the concentrations of MMA were set to be 25.0wt%. The temperatures were set to be 60°C, 70°C and 80°C, respectively. In a typical run, all the reagents were introduced into a dry one-necked round-bottom flask (50mL) and then the reactant was deoxygenated by three freeze-evacuate-thaw cycles and backfilled with nitrogen (N2). Subsequently, the solution was stirred at certain temperature under nitrogen atmosphere. The other steps are similar to of the NHPI/XT polymerization with MMA as the monomer.

Polymerization of MMA by NHPI/XT redox polymerization system with the different ratios of NHPI/XT (Fig.S5 and Fig.S6)

The concentration of the MMA in THF was set to be 25wt%. Specifically, the ratios of reagents [NHPI/XT] were 1/0 for pure NHPI; 1:1 and 1:2, respectively. The concentration of NHPI was 2.50×10⁻²mol/L. In a typical run, all the reagents were introduced into a dry one-necked round-bottom flask (50mL) and then the reactant was deoxygenated by three freeze-evacuate-thaw cycles and backfilled with nitrogen (N2). Subsequently, the solution was stirred at 70°C under nitrogen atmosphere. The other steps are similar to of the NHPI/XT polymerization with MMA as the monomer.

Synthesis of the PMMA oligomer:

Toluene and acetonitrile were distilled again before use. NHPI was dissolved in acetonitrile while XT was dissolved in toluene at the same concentrations (1.25×10⁻²mol/L). Then the system is constructed by the NHPI/ acetonitrile and XT/ toluene mixed solvent (1:1) in the test tube. One drop of MMA was then added into the test tube. The solution was heated at 70°C over night. Then the solvent was send to the maldi-tof analysis without further purification.
Synthesis of the PMMA NMR samples:

The concentrations of NHPI and XT in toluene and DMF mixed solvent (toluene: DMF(wt) is 49:1) were set to be $1.25 \times 10^{-2}$ mol/L and $5.00 \times 10^{-2}$ mol/L respectively. All the reagents were introduced into a dry one-necked round-bottom flask (50mL) and then the reactant was deoxygenated by three freeze-evacuate-thaw cycles and backfilled with nitrogen (N2). Subsequently, the solution was stirred at 70°C under nitrogen atmosphere for 5 hours. The resulting mixture was poured into a vigorously stirred methanol (300mL). The precipitated polymer was collected and dissolved in THF again. The precipitate/dissolve process was repeated for 5 times to remove the remnant NHPI and XT.

Polymerization of different monomers by NHPI/XT redox polymerization system (Fig. 4)

The concentrations of NHPI and XT in toluene and DMF mixed solvent (toluene: DMF(wt) is 49:1) were both set to be $2.50 \times 10^{-2}$ mol/L; while the concentration of monomers were set to be 10wt%. The monomer for the NHPI/XT system are MMA, BA and styrene, respectively and stirred at 70°C under nitrogen atmosphere. The other steps are similar to of the NHPI/XT polymerization with MMA as the monomer.

The synthesis of block copolymers with PSt as macroinitiator:

PSt macroinitiator ($M_{n,GPC}=34,300$ g mol$^{-1}$; PDI=1.88) was prepared using the NHPI/XT redox system as described in the procedures for the homopolymerization of PSt in THF/DMF mixed solvent at 70°C under nitrogen atmosphere for 5 hours. The ratio of NHPI/XT is 1:10. The macro initiator was purified by precipitate/dissolve for 5 times to remove the remnant NHPI and XT. The product was dried and protected in dark place. Then we utilized the PSt macroinitiator to initiate the MMA polymerization in THF/DMF (49:1) mixed solvent. The recipe is 1.00 g of PSt macroinitiator, 1.00 g of MMA in 8g solvent at 70°C for 24hours under nitrogen atmosphere. Then aliquots were withdrawn from the reaction mixture via a N$_2$-purged syringe at different time intervals. The other steps are similar to of the NHPI/XT polymerization with MMA as the monomer.
**Fig. S1.** Conversion evolution of MMA vs time with three different monomer concentrations of NHPI/XT as redox initiator concentration at 70°C in toluene/DMF: $C_{\text{NHPI}} = 2.50 \times 10^{-2}$ mol/L, $C_{\text{XT}} = 2.50 \times 10^{-2}$ mol/L, MMA 12.5 wt% (●); $C_{\text{NHPI}} = 2.50 \times 10^{-2}$ mol/L, $C_{\text{XT}} = 2.50 \times 10^{-2}$ mol/L MMA 25.0 wt% (■); $C_{\text{NHPI}} = 2.50 \times 10^{-2}$ mol/L, $C_{\text{XT}} = 2.50 \times 10^{-2}$ mol/L MMA 50.0 wt% (▲).

**Fig. S2.** Evolution of Mn and PDI with time of MMA with three different monomer concentrations of NHPI/XT as redox initiator concentration at 70°C in toluene/DMF: $C_{\text{NHPI}} = 2.50 \times 10^{-2}$ mol/L, $C_{\text{XT}} = 2.50 \times 10^{-2}$ mol/L, MMA 12.5 wt% (●); $C_{\text{NHPI}} = 2.50 \times 10^{-2}$ mol/L, $C_{\text{XT}} = 2.50 \times 10^{-2}$ mol/L MMA 25.0 wt% (■); $C_{\text{NHPI}} = 2.50 \times 10^{-2}$ mol/L, $C_{\text{XT}} = 2.50 \times 10^{-2}$ mol/L MMA 50.0 wt% (▲).
Fig. S3. Conversion evolution of MMA vs time with three different temperature of NHPI/XT as redox initiator concentration and 25% (wt) MMA concentration in toluene/DMF: $C_{\text{NHPI}} = 2.50 \times 10^{-2} \text{ mol/L}$, $C_{\text{XT}} = 2.50 \times 10^{-2} \text{ mol/L}$, in 60°C (●); $C_{\text{NHPI}} = 2.50 \times 10^{-2} \text{ mol/L}$, $C_{\text{XT}} = 2.50 \times 10^{-2} \text{ mol/L}$ in 70°C ( ■ ); $C_{\text{NHPI}} = 2.50 \times 10^{-2} \text{ mol/L}$, $C_{\text{XT}} = 2.50 \times 10^{-2} \text{ mol/L}$ in 80°C (▲).

Fig. S4. Evolution of Mn and PDI with time of MMA with three different temperature of NHPI/XT as redox initiator concentration and 25% (wt) MMA concentration in toluene/DMF: $C_{\text{NHPI}} = 2.50 \times 10^{-2} \text{ mol/L}$, $C_{\text{XT}} = 2.50 \times 10^{-2} \text{ mol/L}$, in 60°C (●); $C_{\text{NHPI}} = 2.50 \times 10^{-2} \text{ mol/L}$, $C_{\text{XT}} = 2.50 \times 10^{-2} \text{ mol/L}$ in 70°C ( ■ ); $C_{\text{NHPI}} = 2.50 \times 10^{-2} \text{ mol/L}$, $C_{\text{XT}} = 2.50 \times 10^{-2} \text{ mol/L}$ in 80°C (▲).
Fig. S5. Conversion evolution of MMA vs time with three ratio of NHPI/XT as redox initiator and 25% (wt) MMA concentration at 70°C in THF: \(C_{\text{NHPI}} = 2.50 \times 10^{-2}\) mol/L (●); \(C_{\text{NHPI}} = 2.50 \times 10^{-2}\) mol/L, \(C_{\text{XT}} = 2.50 \times 10^{-2}\) mol/L (■); \(C_{\text{NHPI}} = 2.50 \times 10^{-2}\) mol/L, \(C_{\text{XT}} = 5.00 \times 10^{-2}\) mol/L (▲).

Fig. S6. Evolution of Mn and PDI with conversion of MMA with three ratios of NHPI/XT as redox initiator and 25% (wt) MMA concentration at 70°C in THF: \(C_{\text{NHPI}} = 2.50 \times 10^{-2}\) mol/L (●); \(C_{\text{NHPI}} = 2.50 \times 10^{-2}\) mol/L, \(C_{\text{XT}} = 2.50 \times 10^{-2}\) mol/L (■); \(C_{\text{NHPI}} = 2.50 \times 10^{-2}\) mol/L, \(C_{\text{XT}} = 5.00 \times 10^{-2}\) mol/L (▲).