Supporting Information:

Novel tetraphenylethylene (TPE) functionalized nitroxide/alkoxyamine for nitroxide mediated homogeneous and heterogeneous polymerization

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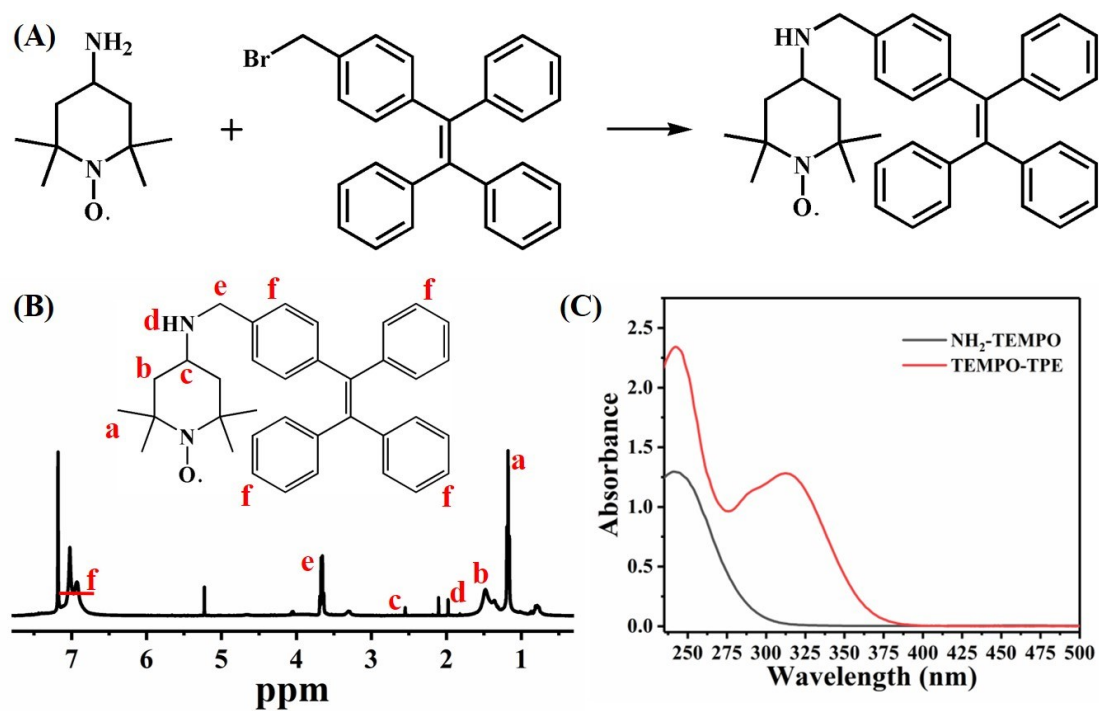***Synthesis of Dispolreg 007-TPE***

The preparation process of Dispolreg 007-TPE was shown in Fig S2.

Step 1: 4 g TPE-Br was dissolved in 100 mL CH_2Cl_2 in a 250mL round-bottomed flask and the solution was cooled in an ice bath. To the stirred solution was added drop wise 3.8 mL cyclohexylamine in ca. 1 h and the resulting mixture was stirred overnight at room temperature. 0.5 mL triethylamine was added to the reaction system and continued reaction for 6 h. The reaction mixture was washed by 150mL 1 M hydrochloric acid solution for 3 times. The organic layers were collected and CH_2Cl_2 was removed by rotary evaporation. This gave 4.3 g (96 %) of product 1 as a light-yellow solid that was sufficiently pure for the next step. ^{1}H NMR δ2.39 (a, 1 H), 3.58-3.71 (b, 2 H), 1.05-1.99 (c, 10 H), 6.86-7.22 (d, 19H).

Step 2: according to the general recipe described in the first example using the product of Step 1 and 3.71 g of sodium bicarbonate in 250 mL each of THF and water, then adding portion wise 6.55 g of Oxone® in aqueous solution gave crude product. THF was removed by rotary evaporation, and then the rotary evaporated product was extracted with CH_2Cl_2, the product is obtained by rotary distillation of the extract. Total yield: 3 g (70 %) of product 2. ^{1}H NMR δ 3.63 (a, 1 H), 6.84-7.28 (b, f, 20 H), 0.71-1.86 (c, 10 H).

Step 3: 3 g product 2 and 1.776 g (1.65 equiv.) of AIBN in 250 mL of toluene were stirred at 92 ℃ (bath temp) for 6 h. Evaporation of the solvent, re-dissolving the product in hot isopropanol and slowly cooling to room temperature, afforded the crop. Total yield: 1.5 g (45 %) of Dispolreg 007-TPE. ^{1}H NMR δ 3.71 (a, 1 H), 4.72 (b, 1 H), 1.20-
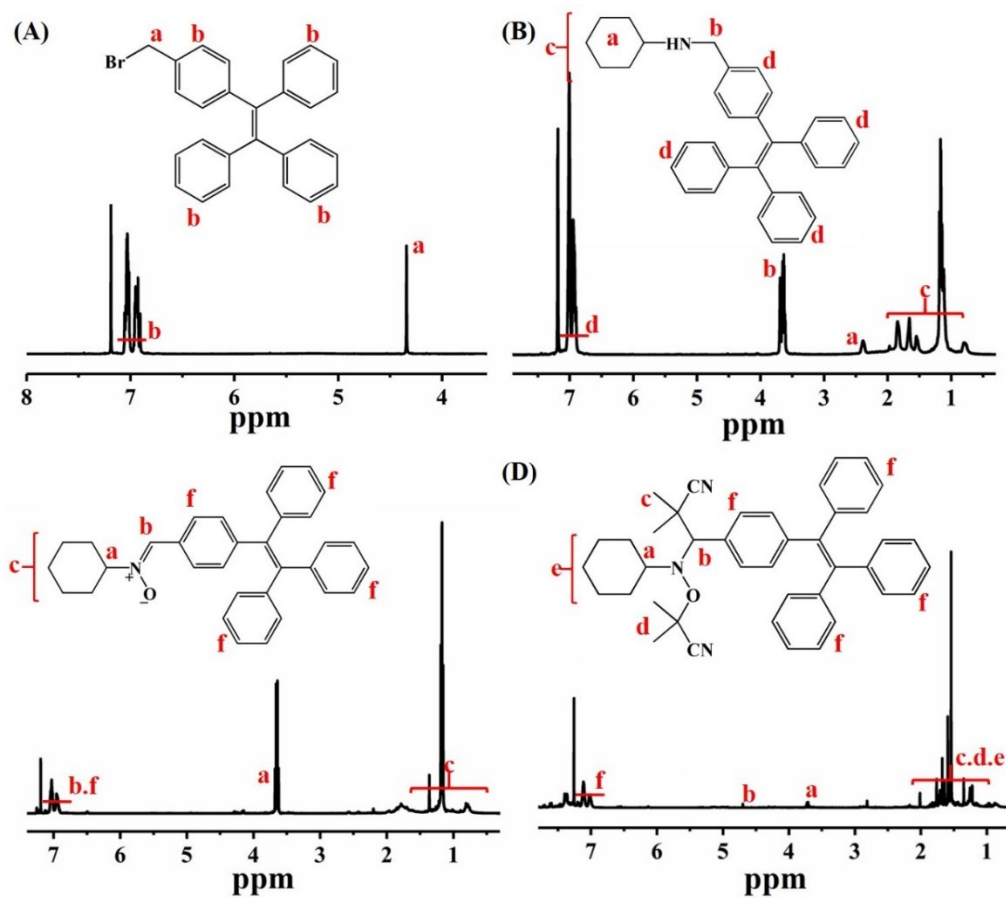
2.03 (c, d, e, 22 H), 6.95-7.45 (f, 19 H).

Fig. S1. (A) Preparation process of TEMPO-TPE nitroxide (B) ^{1}H NMR spectra of TEMPO-TPE nitroxide (C) UV-vis spectra of NH$_2$-TEMPO and TEMPO-TPE nitroxide.
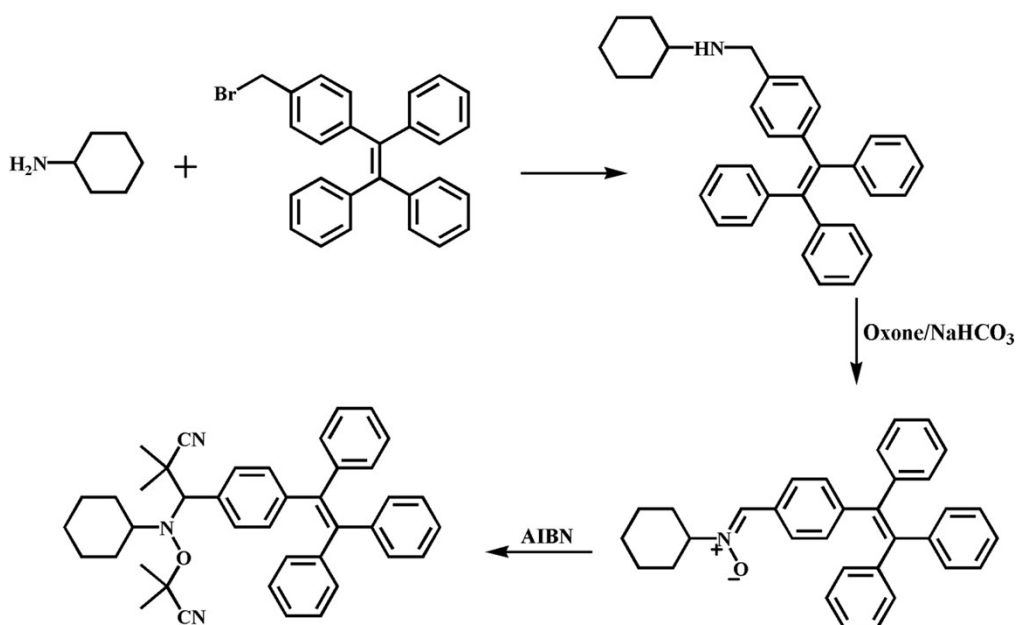
**Fig. S2.** Preparation process of Dispolreg 007-TPE.

Fig. S3. (A) ^{1}H NMR spectra of TPE-Br (B) ^{1}H NMR spectra of product 1 (C) ^{1}H NMR spectra of product 2 (D) ^{1}H NMR spectra of Dispolreg 007-TPE.

Table S1. Amount of experimental feed for Entry 2-3

Entry	Monomer	Nitroxide	[Monomer]/mL	[Nitroxide]/mg	[BPO]/mg
2	St	TEMPO-TPE	2	44.78	10
3	St	TEMPO-TPE	2	44.78	10

Table S2. Amount of experimental feed for Entry 6-7

Entry	Monomer	Nitroxide	[Monomer]/g	[Nitroxide]/mg	[Toluene]/g
4	MMA	Dispolreg 007	1	15.7	4
6	MMA	Dispolreg 007-TPE	1	29.6	1
7	St	Dispolreg 007-TPE	1	28.5	4
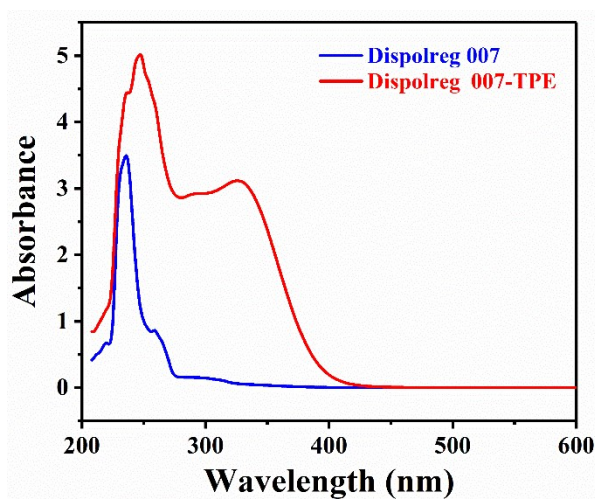
Fig. S4. UV-vis spectra of Dispolreg 007 and Dispolreg 007-TPE.

Quantum chemical calculation

Software：Gaussian16

Modeling software：GaussView

Calculation method: At the required red bond, molecular (f) is broken into two parts (fa and fb), and the Gaussian software is used to calculate the energy of two parts and molecular, respectively.
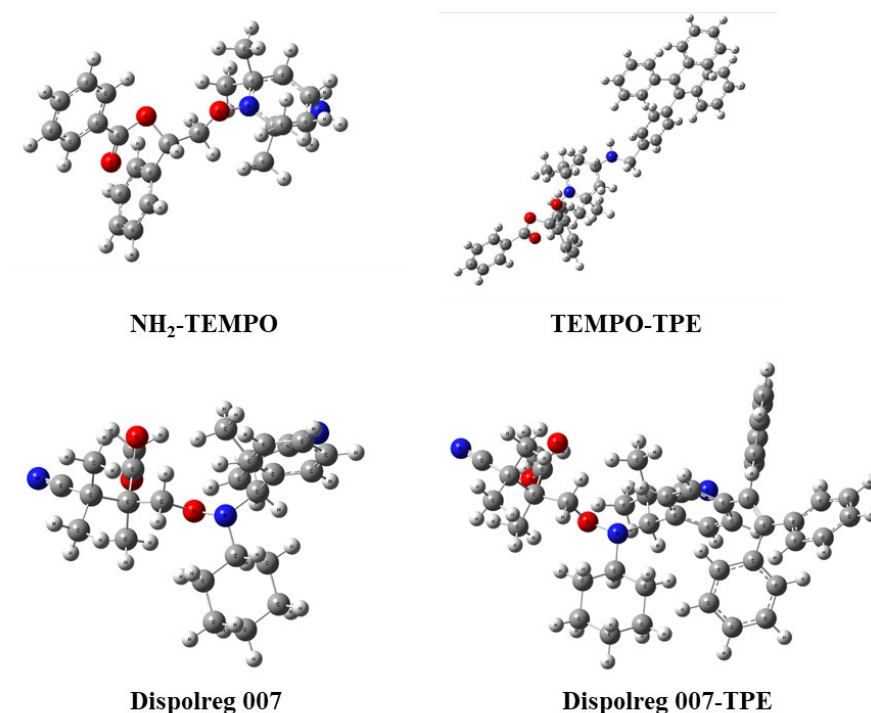
Density functional method: b3lyp
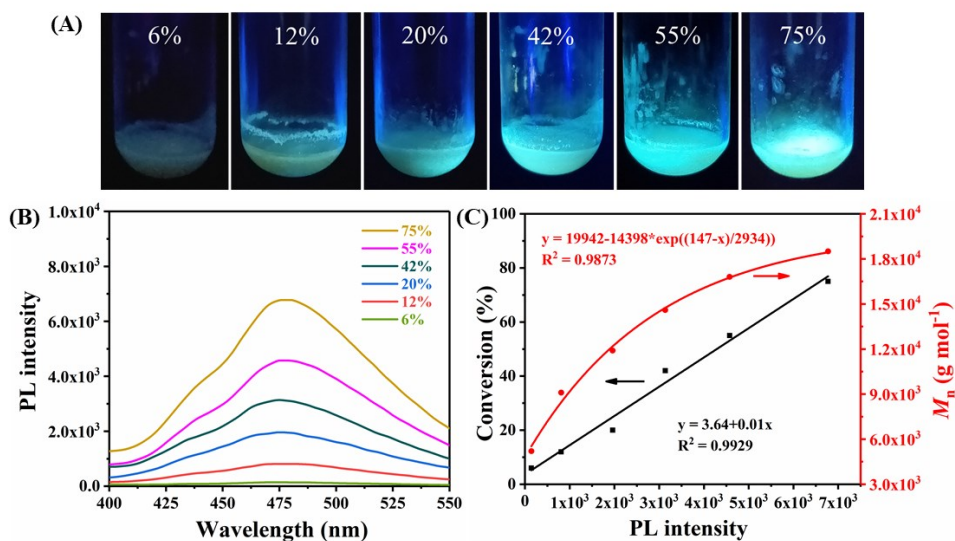
Basic set：6-31+g(d)

Correction factor: scale=0.9829

Bonding energy calculation formula：$\triangle E=(E_{fa}+E_{fb})-E_f$
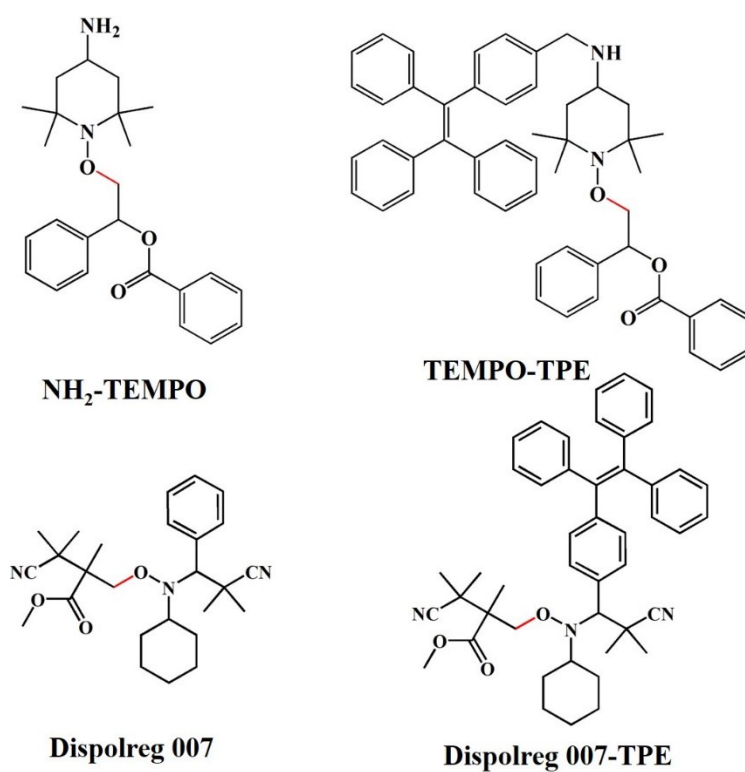
Fig. S5. Molecular formulas and models of NH_2-TEMPO-St, TEMPO-TPE-St, Dispooreg 007-MMA and Dispooreg 007-TPE-MMA used in the quantum chemical simulations.

NH$_2$-TEMPO   TEMPO-TPE

Dispolreg 007   Dispolreg 007-TPE

Fig. S6. Molecular models used in the quantum chemical simulations shown during the transition states of the intermolecular disproportionation reaction.


(A) 6%   12%   20%   42%   55%   75%

(B)
75%
55%
42%
20%
12%
6%

(C)
$y = 19942-14398*exp((147-x)/2934))$
$R^2 = 0.9873$

$y = 3.64+0.01x$
$R^2 = 0.9929$

Fig. S7. Visualization of TEMPO-TPE mediated polymerization of PMS under 130 ℃. (A) Fluorescent photos of the polymer solutions at different conversion taken under 365 nm UV

irradiation from a hand-held UV lamp. (B) PL spectra of the polymerization mixtures at different

conversion. (C) The relationship of conversion and M_n with PL intensity.
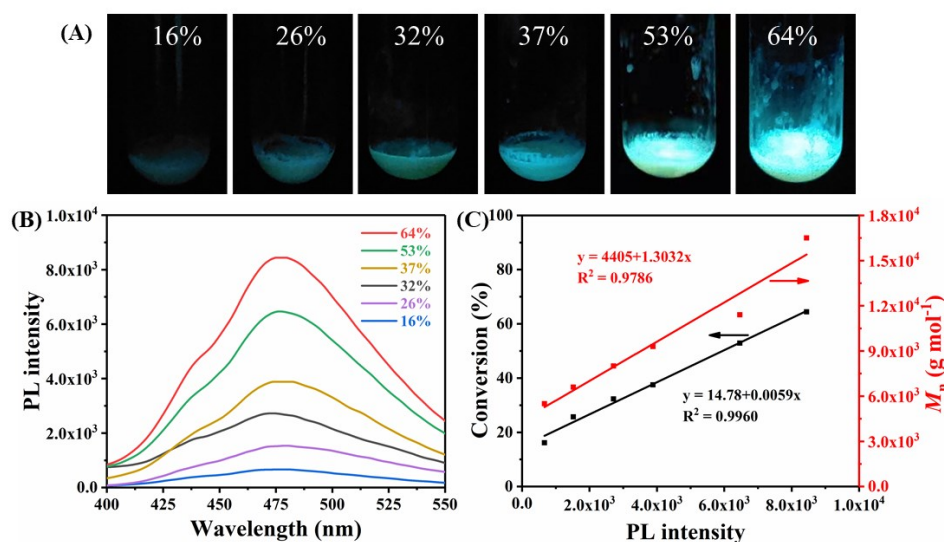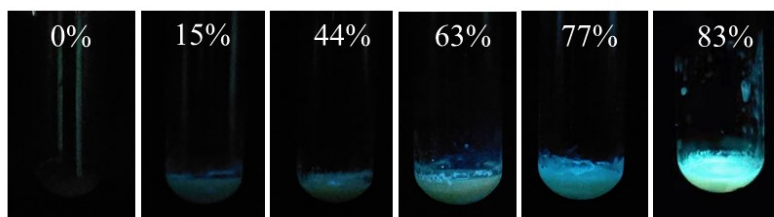

Fig. S8. Visualization of TEMPO-TPE mediated polymerization of St under 120 ℃. (A) Fluorescent

photos of the polymer solutions at different conversion taken under 365 nm UV irradiation from a

hand-held UV lamp. (B) PL spectra of the polymerization mixtures at different conversion. (C) The

relationship of conversion and M_n with PL intensity.
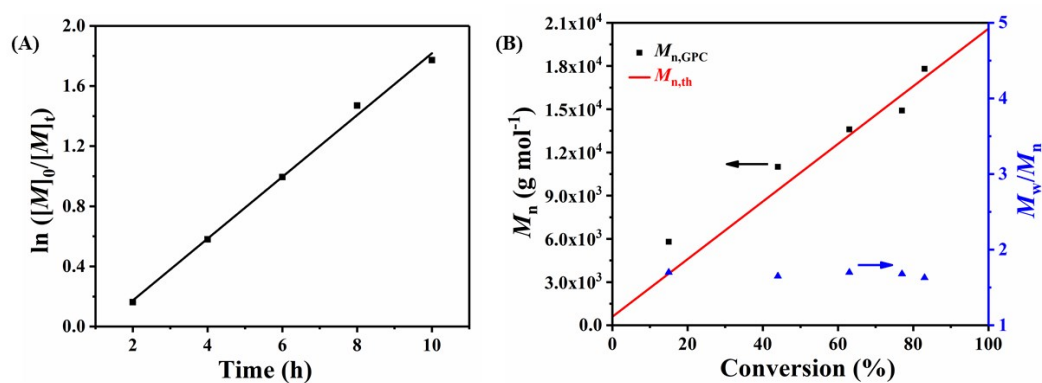
Fig. S9. NMP of MMA mediated by Dispolreg 007-TPE under 96 ℃. (The ratio of monomer to

solvent is 1:1.) (A) Kinetic plot of $\ln([M]_0/[M]_t)$ versus time (B) Evolution of M_n, and dispersity
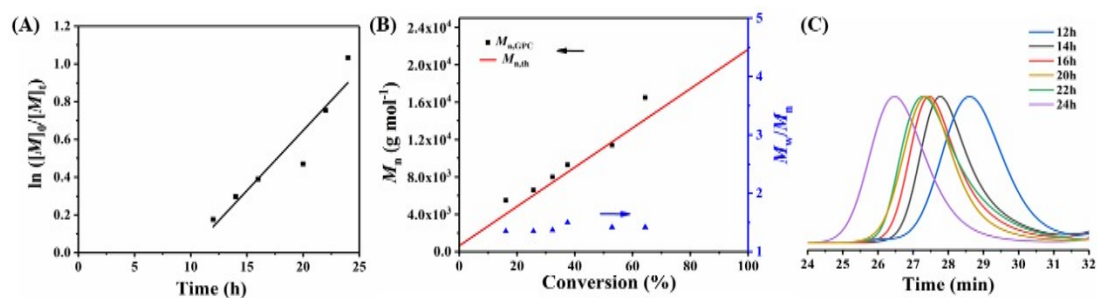
(M_w/M_n) with conversion.

Fig. S10. Visualization of Dispolreg 007-TPE mediated polymerization of MMA. Fluorescent photos of the polymerization system at different conversion taken under 365 nm UV irradiation from a hand-held UV lamp.
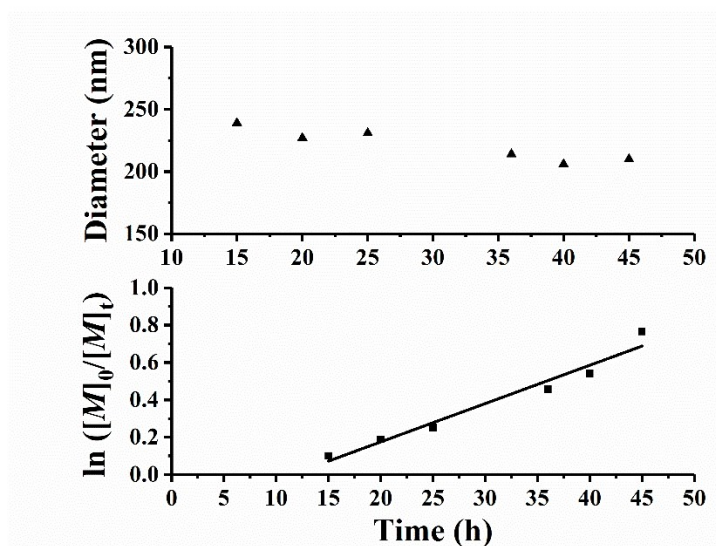
Fig. S11. The evolution of particle size in miniemulsion polymerization of BMA (A) and $\ln([M]_o/[M]_t)$ vs time (B).

Fig. S12. NMP of St mediated by TEMPO-TPE under 120 ℃. (A) Kinetic plot of $\ln([M]_0/[M]_t)$ versus time (B) Evolution of M_n and dispersity (M_w/M_n) with conversion (C) Size exclusion chromatograms of PS with time.