Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for：

Simple and Robust Nitroxide-mediated Polymerization with Oxygen Tolerance

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Experimental Section

Materials

Unless otherwise specified, all chemical reagents were purchased and used through commercial channel. Styrene (St), methyl methacrylate (MMA), *tert*-butyl acrylate (*t*BA), and *n*-butyl methacrylate (BMA) were passed over basic aluminum oxide to remove inhibitors prior to use. Benzyl bromide, cyclohexylamine, 2,2′-azobis(2-methylpropionitrile) (AIBN), isopropanol, n-heptane, ethyl acetate, and the 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl free radical (NH_2-TEMPO) were purchased from Aladdin Chemistry. s-Trioxane was purchased from Macklin Chemistry. potassium peroxymonosulfate (Oxone®) was purchased from Sigma Aldrich. Sodium bicarbonate ($NaHCO_3$), acetone, N,N-dimethylformamide (DMF) and toluene were purchased from Tianjin Kaitong Chemical Reagent Company. 3-(((2-cyanopropan-2-yl)oxy)-(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile (Dispolreg 007) was synthesized according to previously published procedure[1].

Instrumentation

^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer with $CDCl_3$ used as the solvent. Molecular weights were characterized using a gel permeation chromatography (GPC) system equipped with a Waters 1515 HPLC pump and a refractive index detector (RID-0.65 A, 220 V). THF was used as the mobile phase at a flow rate of 1.0 ml min^{-1} at 35 °C. The EPR spectra were recorded on Bruker A300 spectrometer at 90°C. The solid samples were dissolved in toluene and one was deoxygenated by bubbling N_2 for several minutes then sealed before EPR measurements, while the other was not deaerated. GC510 handheld oxygen detector can collect the gas in the schlenk flask through the built-in air pump for detection.

Procedures

General Procedure for the self-deoxygenating NMP of MMA in toluene with targeted DP = 100

A 10ml schlenk flask was charged with MMA (3.300g, 33.00mmol), Dispolreg 007(0.112g, 0.33mmol), toluene (50 vol%) ([MMA]:[Dispolreg 007]=100:1) and 2 cm olive type PTFE magnetic stirrer. The schlenk flask was septum-sealed and the solution was degassed by four freeze-pump-thaw cycles after complete dissolution. The schlenk flask was immersed in oil bath at 90°C with the stir speed of 360 r/min. A small aliquot of the reaction mixture was withdrawn periodically and the samples at timed intervals were analyzed monomer conversion using ^{1}H NMR spectroscopy and M_W using THF eluted GPC.

NMP of MMA in toluene with targeted DP = 100 in the presence of oxygen.

A 10ml schlenk flask was charged with MMA (3.300g, 33.00mmol), Dispolreg 007 (0.112g, 0.33mmol), toluene (50 vol%) ([MMA]:[Dispolreg 007]=100:1) and 2cm olive type PTFE magnetic stirrer. After the solution was completely dissolved, the schlenk flask was septum-sealed and immersed in oil bath pot at 90°C with the speed of 360r/min. A small aliquot of the reaction mixture was withdrawn periodically and the samples at timed intervals were analyzed monomer conversion using ^{1}H NMR spectroscopy and M_W using THF eluted GPC.

Supporting Figures

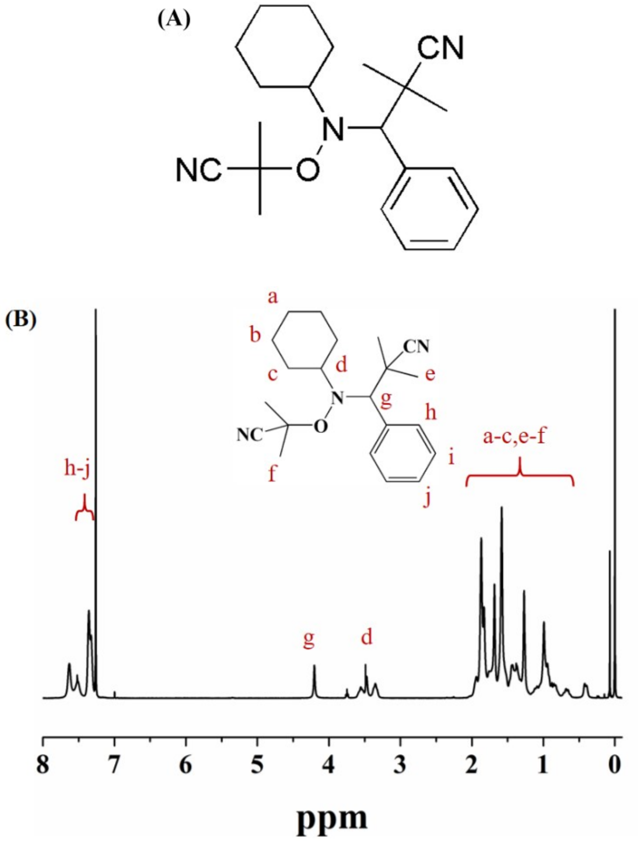

Figure S1. Additional characterization data that were obtained for Dispolreg 007. (A) Chemical structures and (B) ^1H NMR spectrum (400 MHz) as recorded in $CDCl_3$ at 25 °C.

Table S1. NMP polymerization initiated by Dispolreg 007[a].

Entry	Oxygen condition	Solvent	Monomer	Temperature(°C)	Conv.[b]（%）	$M_{n,th}$[c]（g .mol^{-1}）	$M_{n,GPC}$（g . mol^{-1}）	M_w/M_n[d]
1	D[e]	toluene	MMA	90	81.7	8500	8100	1.64
2	WD[f]	toluene	MMA	90	94.2	9800	8800	1.63
3	D	toluene	styrene	120	69.3	7500	6700	1.56
4	WD	toluene	styrene	120	50.9	5500	7600	1.55
5	D	toluene	BMA	90	95.7	13100	11000	1.73
6	WD	toluene	BMA	90	92.5	13600	11000	1.73
7	D	toluene	BzMA	90	89.2	15700	15500	1.74

8	WD	toluene	BzMA	90	66.0	11600	13200	1.73
9	D	DMF	MMA	90	96.1	10000	7100	1.71
10	WD	DMF	MMA	90	97.2	10000	7500	1.71
11[g]	WD	toluene	MMA	90	87.0	9000	11000	1.61

[a] Reactions conditions: the ratio of oxygen to monomer to Dispolreg 007 is 1.01:100:1, reaction time: 20h. [b] Monomer conversions were determined by ^{1}H NMR spectroscopy. [c] Theoretical molecular weight was calculated by the following equation: $M_{n,th} = [M]_0/[I]_0 \times M_W^{Initiator} \times \alpha + M_W^{Monomer}$. [d] Molecular weight and polydispersity were determined by gel permeation chromatography (GPC) using THF as eluent calibrated to poly(methyl methacrylate) standards. [e] "D" means "Degassing". [f] "WD" means "Without Degassing". [g] The reaction was carried out without solvent.

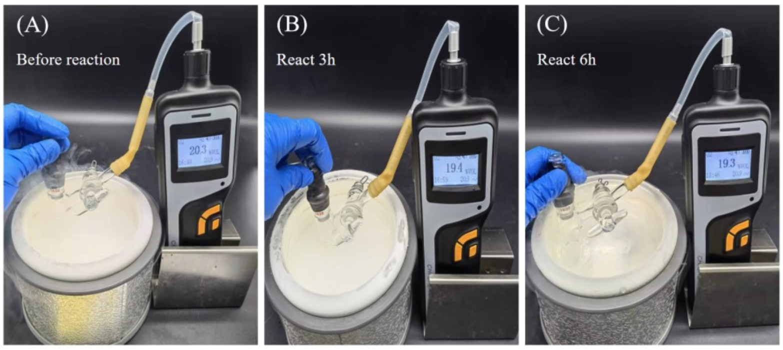

Figure S2. Detection of oxygen content in different stages of polymerization.

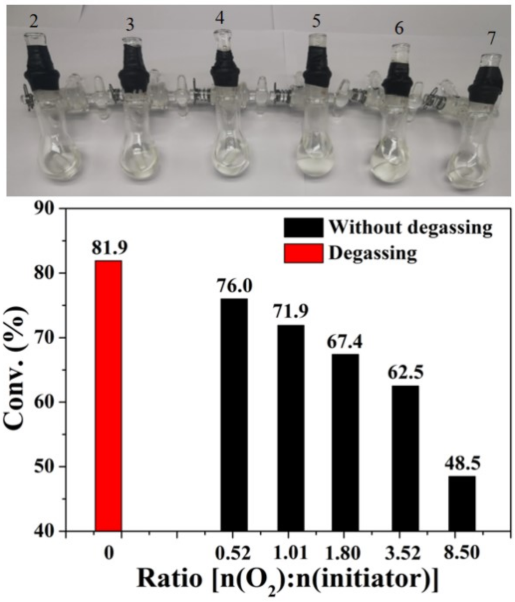

Figure S3. The relationship between conversion and oxygen content to initiator.

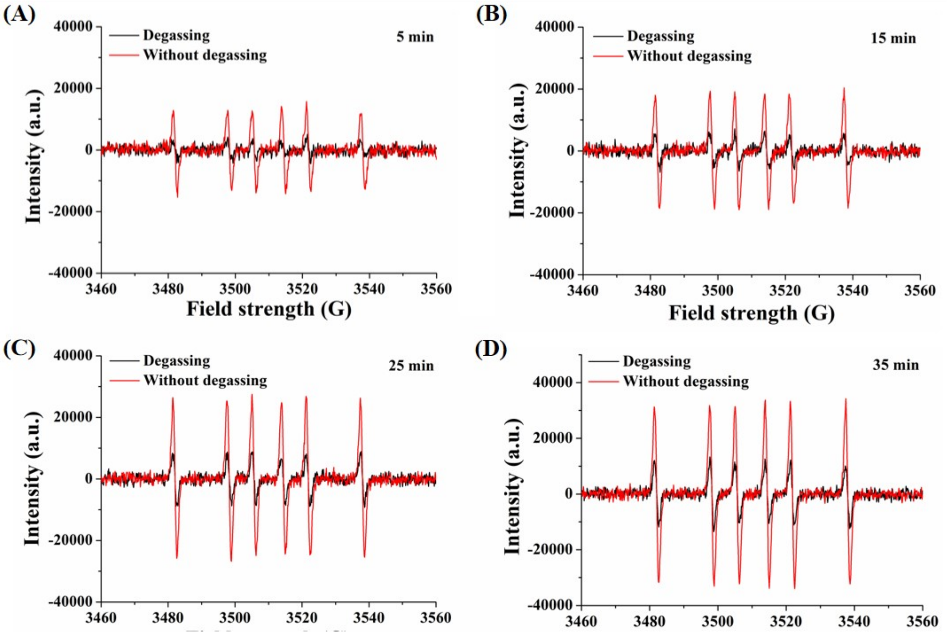

Figure S4. EPR monitoring of the decomposition of Dispolreg 007 in toluene under aerobic and anaerobic conditions at 90°C.

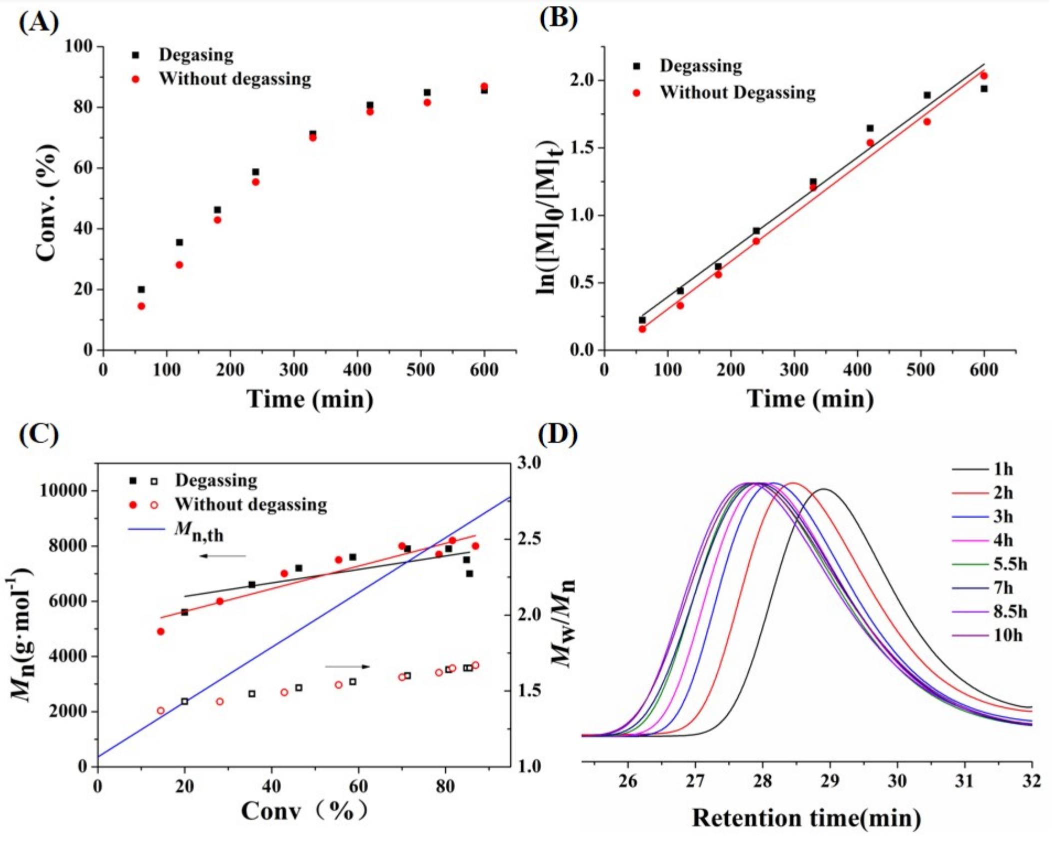

Figure S5. In the absence and presence of oxygen, NMP of MMA mediated by Dispolreg 007 under 90 °C in DMF. (A) The conversion of polymerization with time. (B) Evolution of $\mathrm{M_n}$ and dispersity (M_w/M_n) with conversion. (C) Kinetic plot of monomer conversion. (D) THF-GPC trace of PS with targeted DPs =100 synthesized at the presence of oxygen with time.

References:

1 Ballard, N.; Aguirre, M.; Simula, A.; Agirre, A.; Leiza, J. R.; Asua, J. M.; van Es, S. *ACS Macro Lett.* 2016, ***5***, 1019-1022.