

SUPPORTING INFORMATION

RATE ENHANCEMENT IN CONTROLLED RADICAL POLYMERIZATION OF ACRYLATES USING RECYCLABLE HETEROGENEOUS LEWIS ACID

Rong Luo and Ayusman Sen*

**Department of Chemistry,
The Pennsylvania State University,
University Park, PA 16802**

***E-mail: asen@psu.edu**

Experiment section

Materials. All chemicals and reagents were obtained from Aldrich unless otherwise stated. Methyl acrylate (MA, 99%), n-butyl acrylate (BA, 99%), and 1-hexene were vacuum distilled from CaH_2 and stored under N_2 . 2, 2'-Azobis(isobutyronitrile) (AIBN, 98%), aluminum oxide (activated, acidic, Brockmann I, standard grade, ~ 150 mesh, pH = 4.5 ± 0.5 in aqueous solution), and scandium triflate ($\text{Sc}(\text{OTf})_3$, 98%) was used as received.

The NMP initiator, 2, 2, 5- trimethyl- 3- (1-phenylethoxy)-4-phenyl-3-azahexane, and the NMP control agent, 2, 2, 5- trimethyl-4-phenyl-3-azahexane-3-nitroxide, were synthesized and purified following literature procedure [Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904-3920]. The RAFT agent, benzyl 1-pyrrolcarbodithioate was synthesized and purified following literature procedure [Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273-2283].

Instrumentation. ^1H - and ^{13}C -NMR spectra were recorded using a Bruker 300-DPX spectrometer at ambient temperature (^1H -NMR, 300MHz; ^{13}C -NMR, 75 MHz). Chemical shifts are referenced to CDCl_3 . Molecular weights and polydispersities were determined on a Shimadzu gel permeation chromatography (GPC) chromatograph containing a three-column bed (styragel HR 7.8×300 mm columns with $5 \mu\text{m}$ beads size; 100-5000, 500-30,000, and $2,000-4 \times 10^6$ Da), a Shimadzu RDI-10A differential refractometer, and a Shimadzu SPD-10A tunable absorbance detector (254 nm). GPC samples were run in tetrahydrofuran at a flow rate of 1 ml/min at 35°C and calibrated against polystyrene standards. Analysis was done using EZSTART 7.2 software.

Kinetic study of nitroxide mediated polymerization of BA in the presence and absence of acidic alumina. In a N_2 -filled dry box, a round bottom flask equipped with a magnetic stir bar was charged with NMP initiator (195 mg, 1.0 equiv.), NMP control agent (6 mg, 0.05 equiv.), BA (9.6 g, 125 equiv.), internal standard tetrachloroethane (TCE, 0.5 g), acidic alumina (0.765 g, 1:10 to monomer) and chlorobenzene (20 ml). The flask was then placed in an oil bath at 125°C . Samples were taken at specific time intervals using a syringe and analyzed by GC. The conversion of BA was calculated from the integration of BA peak with respect to TCE peak. The molecular weight was measured by GPC.

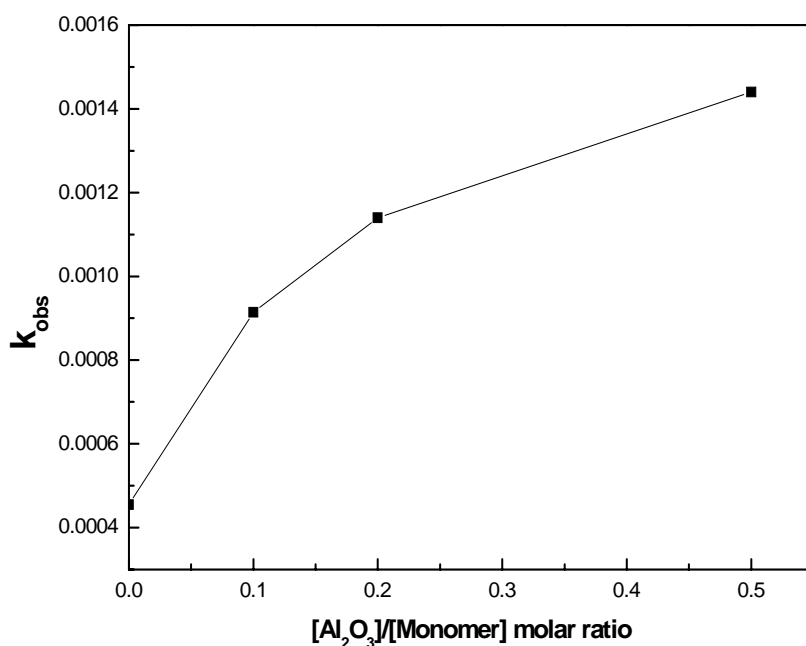


Figure S1. Dependence of observed *n*-butyl acrylate polymerization rate on $[Al_2O_3]/[monomer]$ molar ratio. Conditions: NMP initiator (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane), 0.6 mmol; NMP control agent (2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide), 0.03 mmol; BA, 75 mmol; Tetrachloroethane (TCE), 0.5 g; PhCl, 20 mL; 125°C.

General procedure for nitroxide mediated polymerization of BA in the presence of acidic alumina. In a N₂-filled dry box, a mixture of NMP initiator (33 mg, 1.0 equiv.), NMP control agent (1 mg, 0.05 equiv.), BA (3.2 g, 250 equiv.), acidic alumina (0.255 g, 1:10 to monomer) and chlorobenzene (5 ml) was sealed in 20 ml scintillation vial. The reaction mixture was allowed to stir in a 125°C oil bath for 18 h. At the end of this period, the alumina was removed by filtration, and the polymer was precipitated with a large excess of methanol. The polymer was collected by filtration and dried under high vacuum for 24 h.

Table S1. Nitroxide-mediated polymerisation (NMP) of n-butyl acrylate in the presence of acidic Al₂O₃^a.

Entry	[M] (g)	[M]/[I]	BA Conv. (%)	M _n expt. (x 10 ⁻⁴) ^b	M _n theo. (x 10 ⁻⁴)	PDI (M _w /M _n) ^b	Recycled Al ₂ O ₃ (%)
1	12.8	1500	25	5.27	4.81	1.11	98
2	9.6	1125	31	4.91	4.47	1.14	99
3	6.4	750	34	3.54	3.27	1.15	99
4 ^c	6.4	250	47	1.70	1.51	1.16	97
5 ^c	3.2	125	59	1.10	0.95	1.15	95
6	1.6	188	33	0.84	0.79	1.15	98

^aConditions: Al₂O₃, 1:10(mol ratio) to monomer; NMP initiator (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane), 1.0 equiv; NMP control agent (2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide), 0.05 equiv; 125^oC. ^bBy GPC (THF) relative to polystyrene standards. ^cRuns that using recycled Al₂O₃.

Kinetics study of nitroxide mediated polymerization of styrene in the presence and absence of acidic alumina. In a N₂-filled dry box, a round bottom flask equipped with a magnetic stir bar was charged with NMP initiator (98 mg, 1.0 equiv.), NMP control agent (3 mg, 0.05 equiv.), styrene (3.9 g, 125 equiv.), internal standard tetrachloroethane (TCE, 0.5 g), acidic alumina (0.382 g, 1:10 to monomer) and chlorobenzene (10 ml). The flask was then placed in an oil bath at 125^oC. Samples were taken at specific time intervals using a syringe and analyzed by GC. The conversion of styrene was calculated from the integration of styrene peak with respect to TCE peak. The molecular weight was measured by GPC.

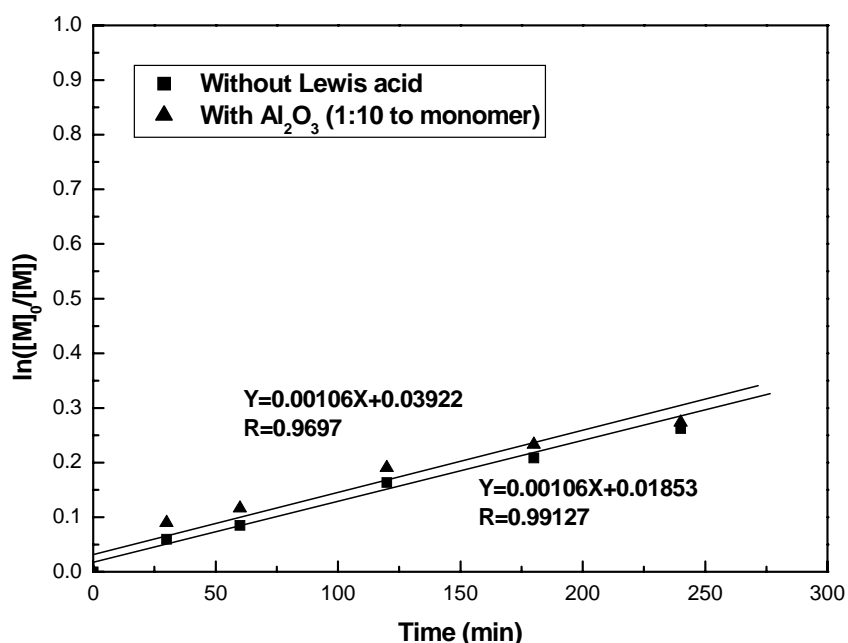


Figure S2. Kinetics study of nitroxide mediated homopolymerization of styrene in the presence and absence of Lewis acid. Conditions: NMP initiator (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane), 0.3 mmol; NMP control agent (2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide), 0.015 mmol; Styrene, 38 mmol; Tetrachloroethane (TCE), 0.5 g; PhCl, 10 mL; 125^oC.

General procedure for block copolymer formation: preparation of poly(n-butyl acrylate)-*b*-polystyrene. In a N₂-filled dry box, a mixture of NMP initiator (33 mg, 1.0 equiv.), NMP control agent (1 mg, 0.05 equiv.), BA (3.2 g, 250 equiv.), acidic alumina (0.255 g, 1:10 to monomer) and chlorobenzene (5 ml) was sealed in 20 ml scintillation vial. The reaction mixture was allowed to stir in a 125°C oil bath for 18 h. At the end of this period, the polymer was precipitated with a large excess of methanol. The colorless polymer was collected by filtration and dried under high vacuum for 24 h. The poly(n-butyl acrylate), starting block (M_n=15000, PDI= 1.11, 0.5 g, 0.033 mmol) was then redissolved in styrene (1.5 g, 14.4 mmol), and the mixture was heated at 125°C for 8 h. The solidified reaction mixture was dissolved in dichloromethane and precipitated into methanol. The polymer was collected by filtration and dried under high vacuum for 24 h to give the desired diblock copolymer as a white solid (1.41g, 61%), M_n, 55000; PDI, 1.16.

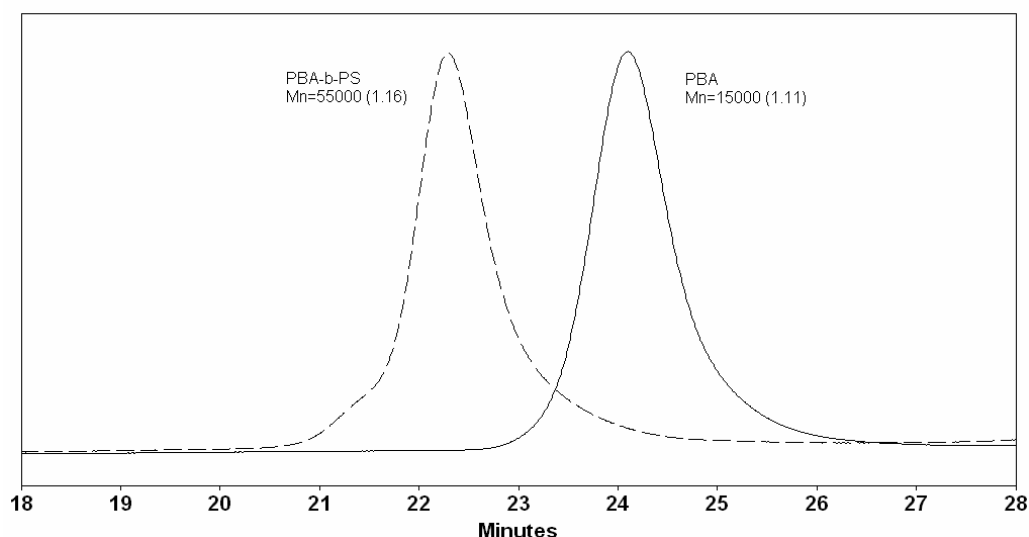


Figure S3. GPC traces for the starting poly(*n*-butyl acrylate) made by NMP in the presence of alumina (left), and the poly(*n*-butyl acrylate)-*b*-polystyrene obtained after chain extension with styrene.

Kinetics study of RAFT polymerization of MA in the presence and absence of acidic alumina. In a N₂-filled dry box, a round bottom flask equipped with a magnetic stir bar was charged with MA (2.0 g, 23.3 mmol), benzyl 1-pyrrocarbodithioate (0.068 g, 0.29 mmol), AIBN (9.5 mg, 0.058 mmol), internal standard tetrachloroethane (TCE, 0.5 g), acidic alumina (0.237 g, 1:10 to monomer) and chlorobenzene (15 ml). The flask was then placed in an oil bath at 60°C. Samples were taken at specific time intervals using a syringe and analyzed by GC. The conversion of MA was calculated from the integration of MA peak with respect to TCE peak. The molecular weight was measured by GPC.