Supporting Information To:

Where is Cu(0) Generated By Disproportionation During SET-LRP?

Nga H. Nguyen,^a Hao-Jan Sun,^a Martin E. Levere,^a Sven Fleischmann^{a,b} and Virgil Percec^{a,*}

^aRoy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania Philadelphia, Pennsylvania 19104-6323

^bBASF SE, Registered Office: 67056 Ludwigshafen, Germany

Email: percec@sas.upenn.edu

Experimental

Materials

Hydrazine hydrate (100%, Acros) (hydrazine hydrate 64%) was used as received. Copper (0) wire (20 gauge wire, (0.812 mm diameter) Fischer) was activated with and hydrazine hydrate (100%, Acros) (hydrazine 64%) prior to use.¹ Dimethyl sulfoxide (DMSO) (Fisher, Certified ACS, 99.9%) was distilled over CaH₂ and stored in a glovebox. Hexamethylated tris(2-aminoethyl)amine (Me₆-TREN) was synthesized as described in the literature.² CuBr was prepared by the reduction of CuBr₂ according to a literature procedure³ and stored in the glovebox before use.

Techniques

The glovebox was an Innovative Technology Inc. model operating under a nitrogen atmosphere, deoxygenated with a copper catalyst and with moisture level ideally maintained below 25 ppm. The Scanning Electron Microscope (SEM) experiments were performed with a JEOL 7500F HRSEM equipped with a cold field emission gun operating at a probe current of 1 pA - 2 nA and accelerating voltage of 0.1 - 30 kV. Images were collected under SEI mode using Everhardt-Thornley secondary electron detector, and the sample to detector distance was monitored by an IR-CCD chamber camera.

Element analysis was conducted with Oxford Inca Thin Window 10^2 mm EDS. Cu(0) wire samples were cut into size of 1 - 2 cm and placed on a clean Al stub before mounted on a single stub sample stage. The sample was then subjected into the SEM sample chamber without further carbon or metal coating. The sample chamber equipped with dry vacuum system and liquid nitrogen anticontamination device for clean specimen environment and the chamber vacuum was maintained below 1 x 10^{-4} Pa. The voltage was set to 15 kV with working distance kept between 4.3 mm to 6.9 mm. The magnification was set to 8,000 – 10,000 for low magnification images and 50,000 – 100,000 for high magnification images. Element analysis was performed at the same time and area where the images were collected.

Typical Procedure for Disproportionation of CuBr in DMSO in the Presence of Hydrazine-Activated Cu(0) Wire at [CuBr]/[Me₆-TREN] = 1/0.5. Me₆-TREN was deoxygenated by six cycles of freeze-pump-thaw and transferred into the glovebox. A microsyringe was kept in the glovebox to handle the ligand. CuBr (0.86 mg, 6 μ mol) was measured into a UV cuvette and transferred into the glovebox. Activated Cu(0) wire (12.5 cm of 20 gauge wire (diameter = 0.812 cm) wrapped around a stirring bar was added to the cuvette in the glovebox. Inside the glovebox, the solution of DMSO containing Me₆-TREN (1.65 mM) was prepared. 1.8 mL of the solution was delivered into the cuvette containing CuBr to achieve [CuBr] = 3.33 mM and [Me₆-TREN] = 1.65 mM. The disproportionation mixture was gently stirred for 45 min. Photographs of the disproportionation mixture were taken periodically. After that the stirring bar wrapped with Cu(0) wire was removed, and immediately dried under vacuum overnight to remove residual solvent and ligand. Cu(0) wire was analyzed by SEM.

Analysis of Activated Cu(0) Wire after SET-LRP of MA Initiated with MBP in DMSO at $[MA]_0/[MBP]_0/[Me_6-TREN]_0 = 60/1/0.1$. The monomer (MA, 2 mL, 22.2 mmol), solvent (DMSO, 1 mL), ligand (Me_6-TREN, 8.5 mg, 3.7 x 10⁻⁵ mol), and initiator (MBP, 62 mg, 3.7 x10⁻⁴ mol) were added to a 25 mL Schlenk tube. After six freeze-pump-thaw cycles, the Schlenk tube was taken to the

glovebox. The catalyst, hydrazine-activated Cu(0) wire (12.5 cm of 20 gauge (0.812 mm diameter) wrapped around a stirring bar, was added to the reaction vessel to start the polymerization inside the glovebox. After 35 min (95% monomer conversion), the Cu(0) wire was removed from the reaction mixture. Inside the glovebox, Cu(0) wire was repeatedly rinsed with deoxygenated THF and MeOH to remove residual polymer, monomer and CuBr₂ salt. It was dried under vacuum overnight prior to SEM analysis. To measure the Cu(0) consumption after each polymerization, Cu(0) wire was weighed before and after the polymerization. After polymerization, Cu(0) wire was washed 3 times in THF and 3 times in deionized water, followed by acetone, and dried under vacuum till constant weight.

References

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- 3. B. M. Rosen, X. Jiang, C. J. Wilson, N. H. Nguyen, M. J. Monteiro and V. Percec, J. Polym. Sci. Part A: Polym. Chem., 2009, 47, 5606-5628.