

RAFT Polymerization of Acrylonitrile and Preparation of Block Copolymers Using 2-Cyanoethyl Dithiobenzoate as the Transfer Agent

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SUPPORTING INFORMATION

Synthesis of 2-cyanoethyl dithiobenzoate:

Dithiobenzoic acid was synthesized according to literature procedures ¹. Dithiobenzoic acid (1.39 g, 9.0×10^{-3} mol), sodium hydride (0.26 g, 1.1×10^{-2} mol), 2-bromopropionitrile (2.23 mL 91.6×10^{-2} mol) and tetrahydrofuran (10 mL) were combined and the mixture was stirred overnight at room temperature. The solvent and excess 2-bromopropionitrile were removed on a rotary evaporator and the residue subjected to column chromatography on silicon gel (Kieselgel-60, 70-230 mesh) with chloroform as eluent to give 2-cyanoethyl dithiobenzoate (0.75 g, 40.3%). ¹H NMR, 1.79 (d, 3H, CH-CH₃); 4.80 (q, 1H, CHCH₃); 7.4, 7.6, 8.0 (m, 5H, ArH).

Synthesis of polyacrylonitrile by RAFT process:

0.015 g azobisisobutyronitrile (9.15×10^{-5} mol) and 0.057 g 2-cyanoethyl dithiobenzoate (2.77×10^{-4} mol) were added in a 25 mL Schlenk flask and degassed. 3 mL of AN (4.54×10^{-2} mol) and 6 mL ethylene carbonate were mixed together, degassed, then added into the above flask via syringe. The resulting mixture was then placed in an oil bath at 60 °C for 7 h. At the end of this time, the reaction mixture was dissolved in DMF and the polymer was precipitated by addition of the solution to methanol. The solid product was dried under vacuum yielding the desired polymer, which was suitable for chain-extension. During the reaction, samples were taken periodically and a portion of each sample was diluted with DMF for GPC measurement according to our previous procedure ². The remainder was precipitated into THF. Conversion of acrylonitrile was measured by GC analysis using THF as an internal standard. The precipitated PAN was washed with methanol and used for M_n determination by ¹H NMR in DMF.

Chain Extension to Prepare PAN-b-PBA by RAFT:

0.11 g dithiobenzoate-terminated PAN (6.47×10^{-5} mol; M_n (NMR)=1700 and $M_w/M_n=1.15$) and 1.0×10^{-3} g azobisisobutyronitrile (6.10×10^{-6} mol) were degassed in a 10 mL Schlenk flask. 0.86 mL *n*-BA (6.02×10^{-2} mol) and 2.60 mL ethylene carbonate were degassed and added to the above flask via syringe. The mixture was then placed in an oil bath at 60 °C for 49 h. Samples were taken periodically throughout the polymerization and a portion of each sample was diluted with DMF for GPC measurement. The remainder was precipitated by addition to THF. Conversion of acrylonitrile was measured by GC analysis using THF as an internal standard.

The GPC traces of the dithiobenzoate-terminated PAN and the diblock copolymer PAN-*b*-PBA are given in Figure 1 and Figure 2. Samples shown in Figure 1 were taken directly from the reaction mixture, whereas samples shown in Figure 2 were precipitated in water/methanol (1:1, vol). Figure 3 is a kinetic curve of polymerization of AN (Table 1, entry #2).

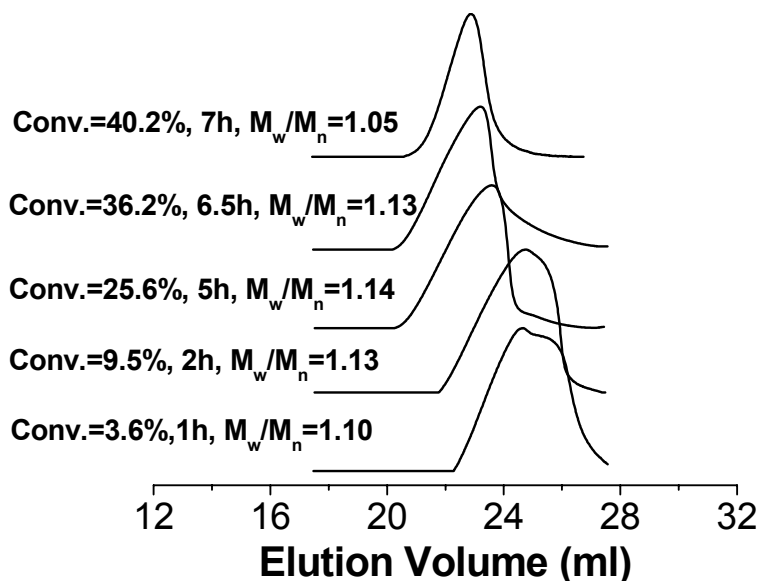


Figure 1

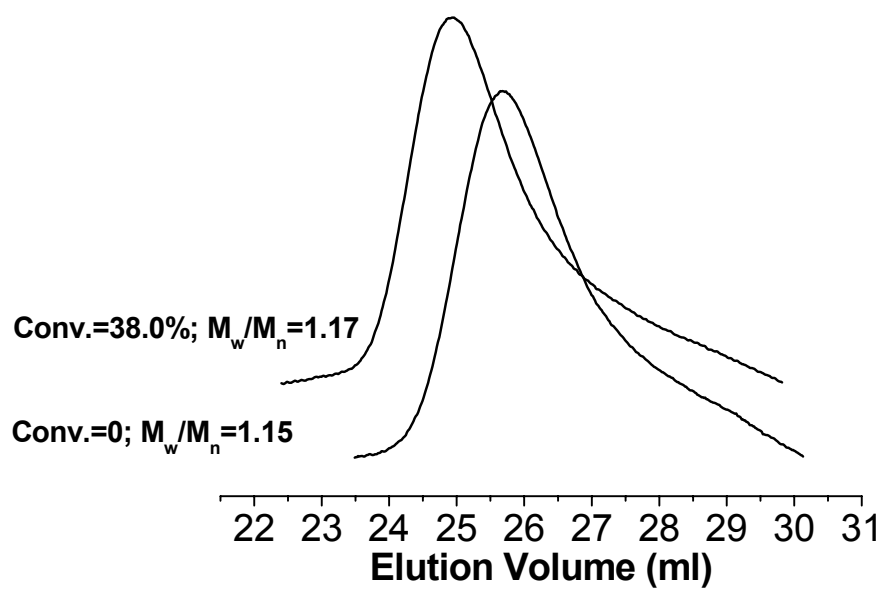


Figure 2

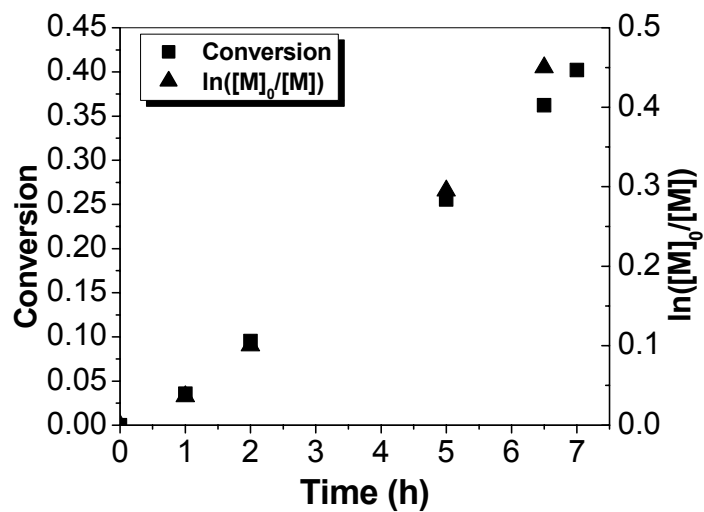


Figure 3

References:

- (1) Becke, F.; Hagen, H. *Ger.* **1968**, 274, 121.
- (2) Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, 36, 1465-1473