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Supporting Information

Emulsion Polymerization of Acrylonitrile in Aqueous Methanol

Kelly M. Meek[a], Todd R. Eaton[a], Nicholas A. Rorrer[a], David G. Brandner[a], Lorenz P. Manker[a], Eric M. Karp[a], Mary J. Biddy[a], Adam D. Bratis[a], Gregg T. Beckham[a], Amit K. Naskar[b]

[a]*National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401.*

[b]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.*

S1. Acrylonitrile Separation

A mock solution of the effluent gas was added to 400 mL DMF to replicate full capture of the product stream. The acrylonitrile-methanol-water mixture was separated from DMF via spinning band distillation (B/R Instruments 800 Micro Spinning Band), where the ternary mixture boiled at ~60 ˚C. The composition of the recovered mixture was estimated using ^{1}H NMR spectroscopy (Fig. S2) with DMSO-d_6 as the solvent, and the chemical shift was referenced to DMSO-d_6 at 2.50 ppm. It was noted that, as expected, because of the large difference in the boiling points of the azeotrope and DMF, no DMF was observed in the ^{1}H NMR spectrum of the recovered ternary mixture. The molar ratio of acrylonitrile to methanol was estimated by relative integration as 1.0 to 0.98, respectively. This molar ratio falls between the ratios used for Sample 2 and Sample 3 (Table 1) in the polymerization of PAN copolymers, and is easily adjusted to match Sample 3 (or Samples 4-6) by adding more methanol. The molar ratio of water in the solution was also estimated, but is not expected to have high accuracy, because trace amounts of water in deuterated DMSO makes quantification of water challenging. However, because additional water substantially exceeding the equimolar ratio to AN is added to the typical emulsion reaction, it is unnecessary to have an accurate quantification of water, and most important to know the ratio of acrylonitrile to methanol.

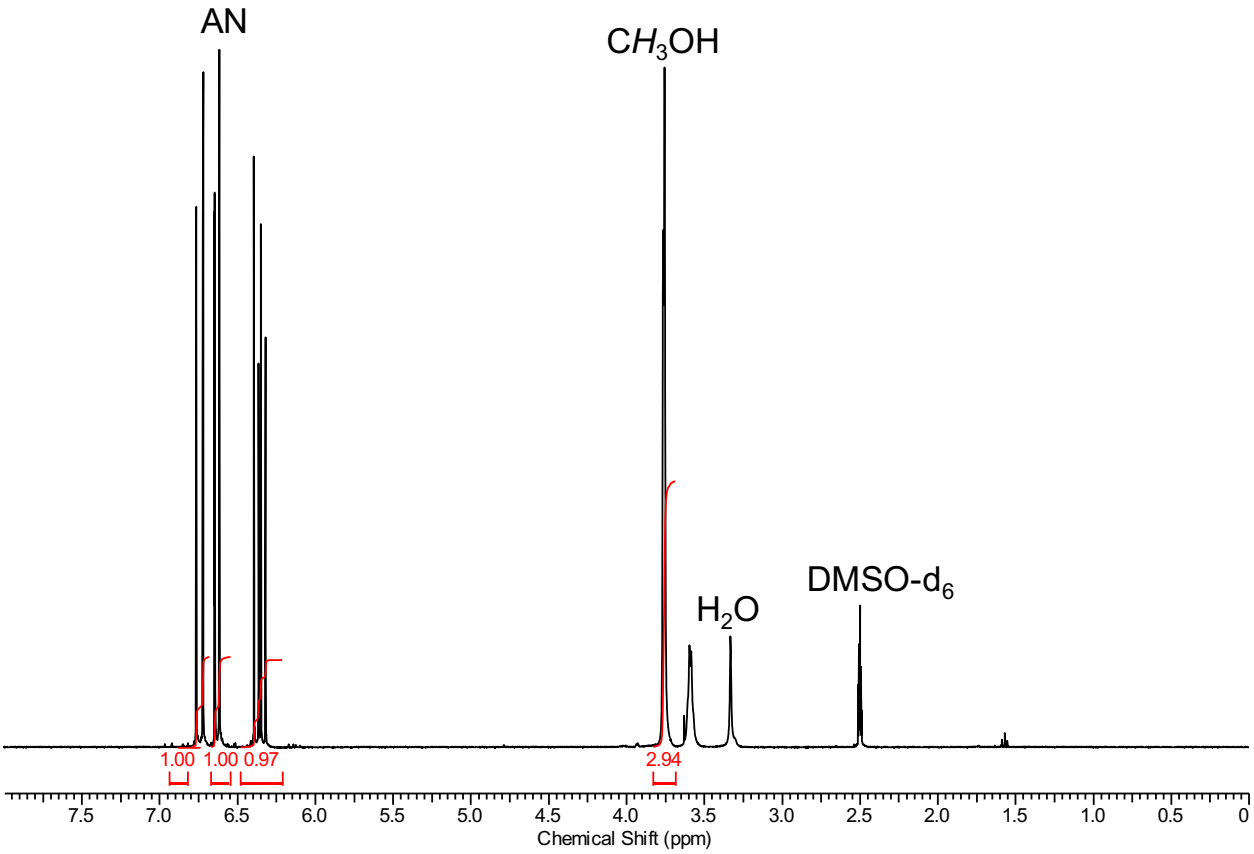

Figure S1. ^{1}H NMR spectrum of the acrylonitrile-methanol-water mixture after separation from DMF via spinning band distillation.

S2. Polymer Characterization

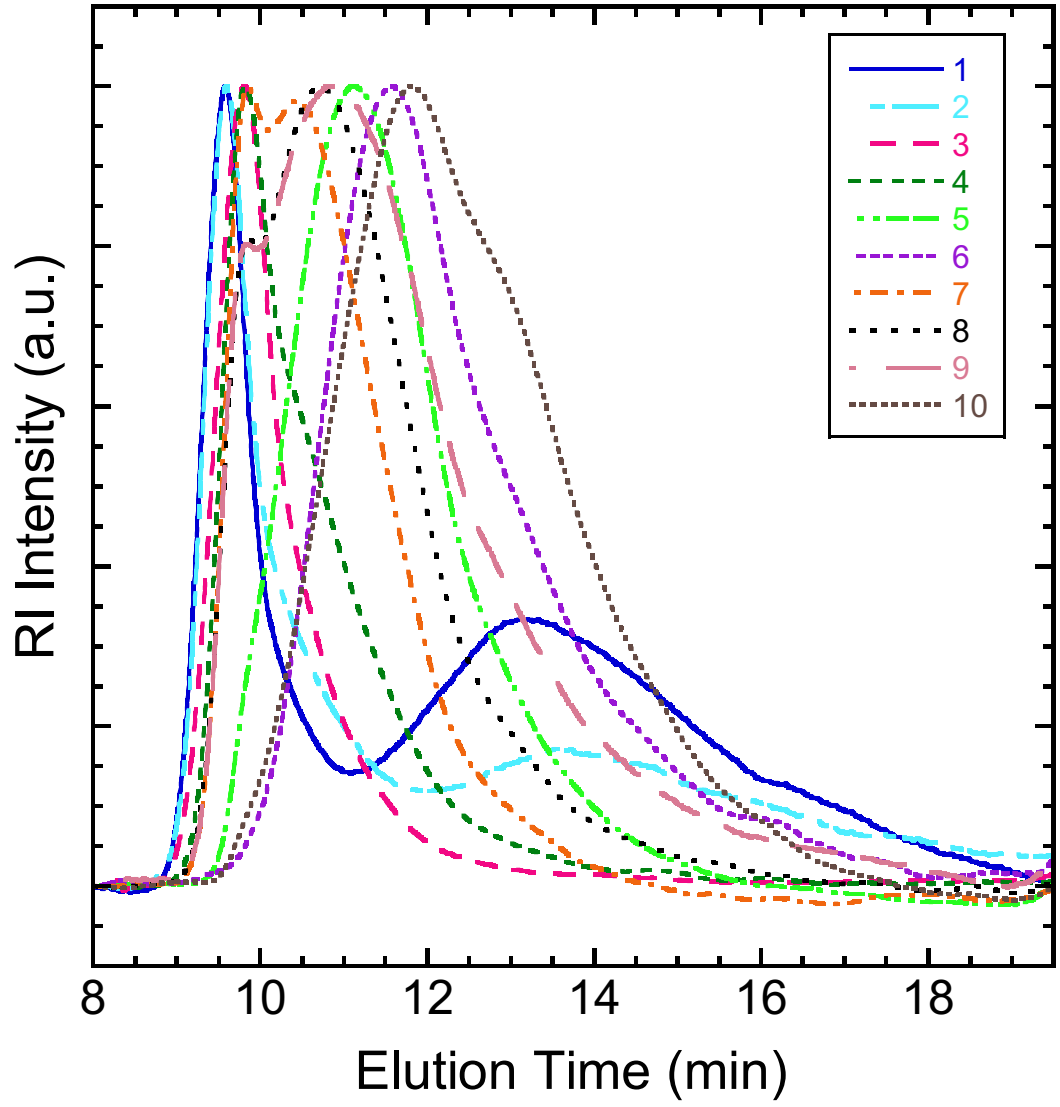

Figure S2. SEC eluograms of PAN-*r*-PMA samples.

Table S1. Molecular weight analysis of PAN-*r*-PMA.

Sample	M_N (kDa) Peak 1	PDI Peak 1	% Area Peak 1	M_N (kDa) Peak 2	PDI Peak 2	% Area Peak 2	Overall M_N (kDa)	Overall PDI
1	726.3	1.294	47.8	15.4	1.71	52.2	28.5	13.3
2	507.7	1.590	80.8	12.9	1.44	19.2	35.7	13.5
3	331.7	1.875	100	-	-	-	331.7	1.875
4	226.3	2.074	100	-	-	-	226.3	2.074
5	82.5	2.097	100	-	-	-	82.5	2.097
6	50.4	1.987	100	-	-	-	50.4	1.987
7	150.9	2.288	100	-	-	-	150.9	2.288
8	117.5	2.465	100	-	-	-	117.5	2.465
9	85.8	2.843	100	-	-	-	85.8	2.843
10	38.9	2.279	100	-	-	-	38.9	2.279