

Synthesis of Well-Defined Polyacrylonitrile by Atom Transfer Radical Polymerization

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Polyacrylonitrile (PAN) is a commercially important polymer because of its unique and well-known properties including hardness and rigidity, chemical resistance, compatibility with certain polar substances, and low gas permeability.¹ PAN is usually prepared by radical polymerization without control over molecular dimension and structure.² PAN can also be prepared by anionic polymerization,² which yields better control. However, in the anionic polymerization of acrylonitrile, the "living" character can be lost due to side reactions such as direct attack of the propagating anion on the cyano groups or attack on α -protons activated by the cyano groups.³

To avoid such side reactions, "living"/controlled free radical polymerization can be used as an alternative, as it is tolerant to a wide variety of functional groups. Originally, "living"/controlled free radical polymerization began with the iniferter system⁴ and has broadened to using stable free radicals such as TEMPO,^{5,6} various organometallic species,⁷ degenerative transfer,⁸ and atom transfer radical polymerization (ATRP).^{9–12} Fukuda et al. used TEMPO to prepare random copolymers of styrene and acrylonitrile, but homopolymerization of acrylonitrile was unsuccessful.¹³ The use of the iniferter for PAN resulted in polymers with high polydispersities ($M_w/M_n > 1.6$).¹⁴

ATRP seems to be the most versatile in terms of diversity of polymerizable monomers. Many monomers such as substituted styrenes and (meth)acrylic esters have been successfully polymerized in a controlled fashion. This paper presents the extension of ATRP to the synthesis of PAN with very low polydispersities. This was accomplished by using ATRP with 2-bromopropionitrile as the initiator and CuBr/2,2'-bipyridine (bpy) as the catalyst. Ethylene carbonate was used as the solvent to provide solubility for the catalyst and the resulting polymer. The polymerization was homogeneous throughout the reaction.¹⁵

The mechanism of polymerization of acrylonitrile by ATRP is presumably similar to that proposed for the ATRP of other vinyl monomers such as styrene and (meth)acrylates^{9,16} (Scheme 1).

However, first-order kinetic plots for all polymerizations showed curvature after initially being linear. This may be due to the interaction between the nitrile groups on the PAN and the copper ions.¹⁷ In spite of these interactions, the preparation of PAN was successfully

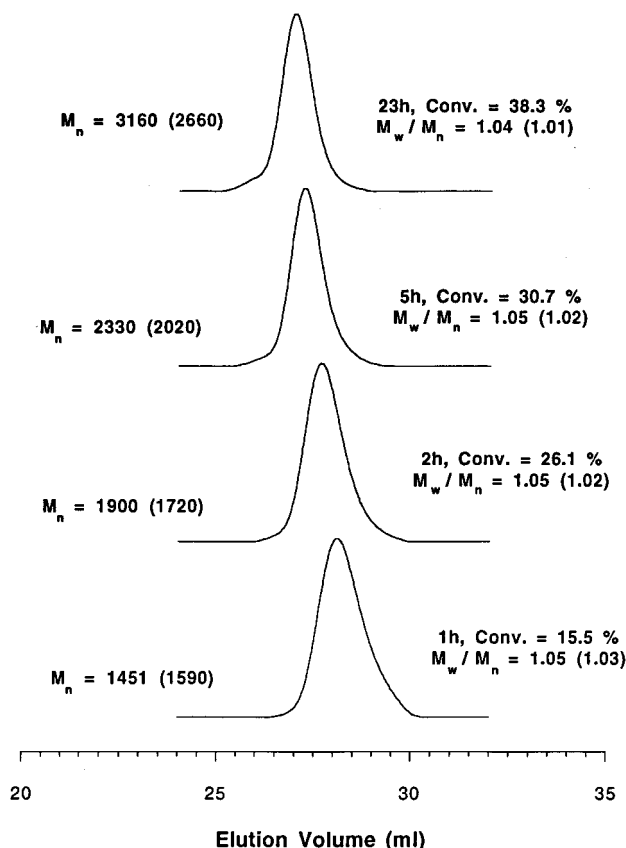


Figure 1. SEC chromatograms of polyacrylonitrile prepared by using 2-bromopropionitrile initiator in ethylene carbonate at 44 °C, $[AN]_0 = 5.25$ M, $[2\text{-bromopropionitrile}]_0 = 5.53 \times 10^{-2}$ M, $[CuBr] = [bpy]_0/3 = 5.53 \times 10^{-3}$ M, M_n determined by 1H NMR (MALDI), M_w/M_n by SEC (MALDI).

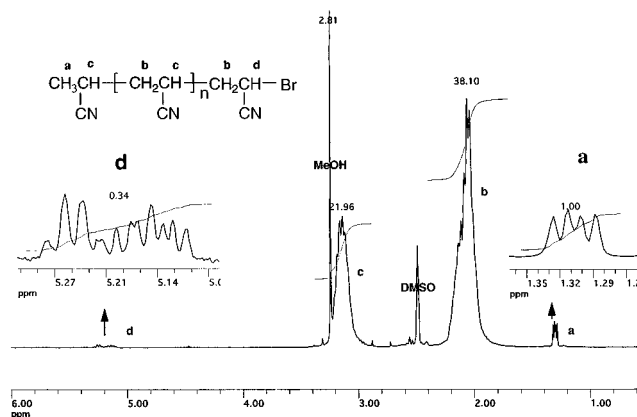
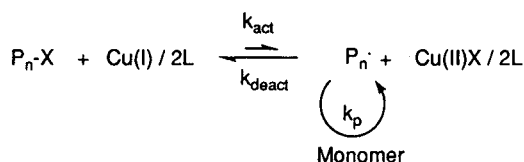


Figure 2. 1H -NMR spectrum of 2-bromopropionitrile-initiated polyacrylonitrile in ethylene carbonate at 44 °C. $[AN]_0 = 5.25$ M, $[2\text{-bromopropionitrile}]_0 = 5.53 \times 10^{-2}$ M, $[CuBr] = [bpy]_0/3 = 5.53 \times 10^{-3}$ M.

controlled by ATRP, leading to polymers with predetermined molecular weights and low polydispersities up to $M_n = 10,000$.

Figure 1 illustrates the size exclusion chromatographs (SEC) of PAN prepared by ATRP. The molecular weight increased linearly and polydispersity decreased with conversion. Polymers with very low polydispersities ($M_w/M_n = 1.06\text{--}1.04$) were obtained for the first time. The molecular weights were estimated from NMR and

Scheme 1



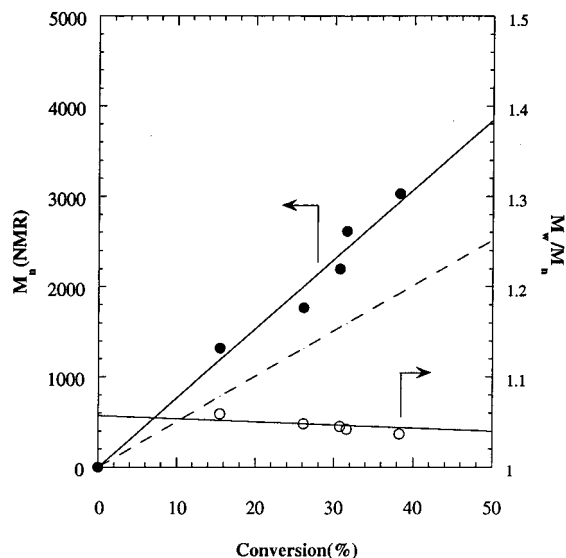


Figure 3. Evolution of M_n and M_w/M_n with conversion for polymerization of acrylonitrile initiated by 2-bromopropionitrile in ethylene carbonate at 44 °C. $[AN]_0 = 5.25$ M, $[2\text{-bromopropionitrile}]_0 = 5.53 \times 10^{-2}$ M, $[CuBr] = [bpy]_0/3 = 5.53 \times 10^{-3}$ M. the broken line shows the theoretical molecular weight.

MALDI because the calibration with polystyrene standards was not adequate.

Figure 2 shows the 1H NMR spectrum of PAN, which was obtained via ATRP using 2-bromopropionitrile as an initiator. The CH_3 protons from the initiator at 1.3 ppm and the $CHBr(CN)$ proton from the end group at 5.1–5.3 ppm in PAN were observed. From NMR data, the molecular weight was calculated by comparison of the area of the peaks from the CH_3 (or CH) protons from the end groups with the CH_2 (or CH) protons from the polymer backbone.

M_n (NMR) and M_w/M_n (SEC) are plotted versus conver-

Table 1. ATRP of Acrylonitrile using 2-Bromopropionitrile Initiator in Ethylene Carbonate at 44 °C, $[AN]_0 = 5.25$ M, $[2\text{-Bromopropionitrile}]_0 = 5.53 \times 10^{-2}$ M, $[CuBr]_0 = [py]_0/3 = 5.53 \times 10^{-3}$ M

time (h)	conv (%)	$M_{n,NMR}$	$M_{n,MALDI}$	$M_{n,th}^a$	$M_w/M_n, SEC$	$M_w/M_n, MALDI$
1	15.5	1450	1590	916	1.06	1.03
2	26.1	1900	1720	1450	1.05	1.02
5	30.7	2330	2020	1680	1.05	1.02
10	31.5	2750	2270	1720	1.04	1.02
23	38.3	3160	2660	2060	1.04	1.01

^a $M_{n,th} = MW \text{ of initiator} + MW \text{ of AN} \times \text{conversion}/100 \times [M]_0/[I]_0 = 134 + 53 \times \text{conversion}/100 \times 95$.

sion in Figure 3. The molecular weights determined by NMR increased linearly with conversion and were close to the predicted values ($DP_n = \Delta[M]/[I]_0$).

MALDI was performed to confirm the molecular weights and polydispersities of the polymers. Figure 4 shows a typical MALDI spectrum of PAN with M_n (NMR) = 3160 and M_w/M_n (SEC) = 1.04. M_n and M_w/M_n by MALDI are 2660 and 1.01, respectively. The lower value of M_n by MALDI as compared to that by NMR may be ascribed to easier desorption/ionization of shorter polyacrylonitrile chains.¹⁸ The accuracy of MALDI is often ± 4 amu in a linear mode.¹⁹ The peak at 2654 amu is within ± 4 amu with respect to the 2650.8 amu value expected for $CH_3CH(CN)[CH_2CH(CN)]_{47}Br/Na^+$.

Molecular weight values obtained by both NMR and MALDI were higher than the expected molecular weight assuming quantitative initiation (Table 1). This may suggest that not all the initiator was converted to polymer chains, presumably due to the coupling/disproportionation of the initiating radicals and formation of excess $Cu^{II}Br_2$. However, linear evolution of molecular weight with conversion determined by NMR and MALDI and low polydispersities observed by SEC support the conclusion that after the initiation step, well-defined and controlled PAN was formed by ATRP.

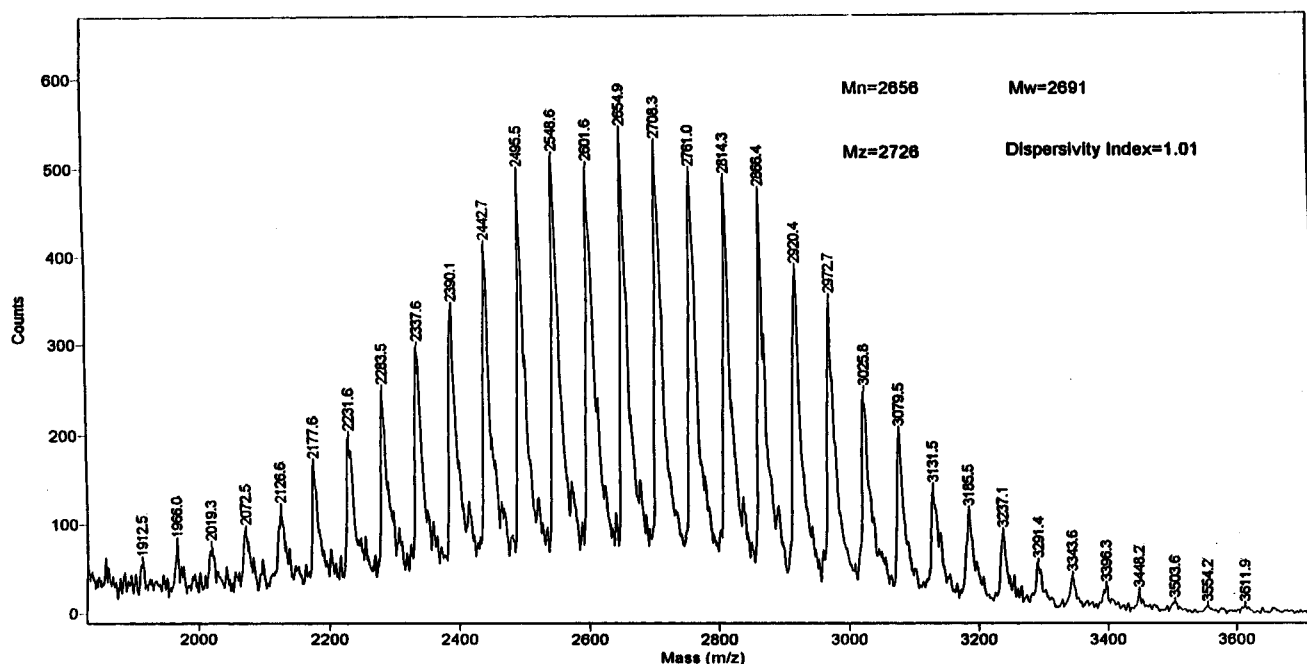


Figure 4. MALDI spectrum of PAN prepared in ethylene carbonate at 44 °C. $[AN]_0 = 5.25$ M, $[2\text{-bromopropionitrile}]_0 = 5.53 \times 10^{-2}$ M, $[CuBr] = [bpy]_0/3 = 5.53 \times 10^{-3}$ M.

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- (15) Synthesis of PAN: 2.28×10^{-2} g (1.60×10^{-4} mol) of CuBr, 7.49×10^{-2} g (4.80×10^{-4} mol) of bpy, and 25 g of ethylene carbonate were added into a 50 mL Schlenk flask. The flask was tightly sealed with a rubber septum, degassed under vacuum, and charged with argon after melting ethylene carbonate (mp = 37 °C). Acrylonitrile (10.0 mL, 1.52×10^{-2} mol) and 1.42×10^{-1} mL (1.60×10^{-3} mol) of 2-bromopropionitrile were introduced into the flask via syringe. The reaction mixture was immersed in an oil bath heated at 44 °C. Periodically, samples were removed from the reaction mixture by syringe. A portion of this sample was diluted with DMF and purified by passing through alumina to remove the copper for SEC measurement. 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 DMSO- d_6 . MALDI was performed on a Perseptive Biosystem MALDI-TOF Voyager Elite with delayed extraction using indolacrylic acid as matrix.
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