An Investigation into the CuX/2,2′-Bipyridine (X = Br or Cl) Mediated Atom Transfer Radical Polymerization of Acrylonitrile

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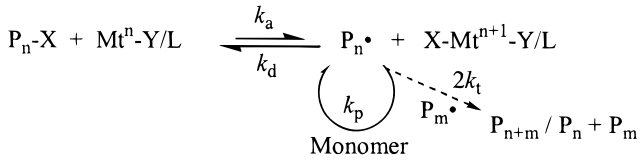
ABSTRACT: Atom transfer radical polymerization has been used to successfully synthesize polyacrylonitrile (PAN) with predictable molecular weights and narrow polydispersities. This was achieved by using CuX/2,2′-bipyridine (X = Br or Cl) as the catalyst, 2-halopropionitriles as initiators, and ethylene carbonate as a solvent. Monomer consumption showed significant curvature in the first-order kinetic plot, indicating termination is present. ^{1}H NMR spectroscopy showed that the halide end group is irreversibly removed during the polymerization. Possible reasons for this reaction are given, with the most probable being the reduction of the radical by Cu^IX to form an anion that subsequently deactivates very quickly. Such side reactions limit the molecular weight achievable to M_n < 30 000 while still keeping low polydispersity, M_w/M_n < 1.5.

Introduction

The preparation of polyacrylonitrile (PAN) homo- and copolymers is typically carried out via free radical polymerization.[1] This, however, normally does not lead to polymers with predefined molecular weights, narrow polydispersities, or functionalization. While other methods exist for more controlled polymerization of acrylonitrile (AN), such as anionic polymerization, these often involved complex catalysis or side reactions with the nitrile groups.[1,2] We recently communicated that, by use of atom transfer radical polymerization (ATRP), PAN with predefined molecular weights and narrow polydispersities can be successfully synthesized.[3] This method has the usual advantages of radical polymerizations, such as tolerance to additives, solvents, trace impurities, etc.[4]

ATRP involves a reversible atom transfer from the polymer chain end (P_nX) to a metal catalyst (Mt^n), forming a radical species that is able to propagate ($P_n^\bullet$) and oxidize the metal to $X-Mt^{n+1}$ (Scheme 1; X, Y = halogen atoms, L = ligand).[5−7] Ideally, the activation/deactivation cycle keeps the concentration of radicals low ($10^{-7}-10^{-8}$ M) while the concentration of growing chains is usually much higher ($10^{-2}-10^{-3}$ M). This enables quantitative initiation while keeping the probability of radical−radical termination low; however, termination cannot be completely avoided given the finite radical concentration. To approach this picture, knowledge of the kinetics of the polymerization is of paramount importance. In this paper we examine the ATRP of AN using Cu^IX/2,2′-bipyridine (bpy) complexes (X = Br or Cl) as the catalyst.

Scheme 1



Experimental Section

AN was obtained from Aldrich; the inhibitor was removed by passing through an alumina column. Cu^IBr and Cu^ICl were obtained from Aldrich and purified according to the procedure of Keller and Wycoff.[8] $Cu^{II}Br_2$ was also obtained from Aldrich and used without further purification. Other reagents, such as ethylene carbonate (EC), propylene carbonate, diphenyl ether, dimethylformamide, 2,2′-bipyridine (bpy), and 2-bromopropionitrile (BPN), were used as received.

A typical procedure for the synthesis of PAN by ATRP is as follows: 2.28×10^{-2} g of CuBr (1.60×10^{-4} mol), 7.49×10^{-2} g of bpy (4.80×10^{-4} mol), and 25 g of EC 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 EC (mp = 37 °C). A 10.0 mL aliquot of AN (1.52×10^{-2} mol) and then 1.42×10^{-1} mL of BPN (1.60×10^{-3} mol) were introduced into the flask via syringe. The reaction mixture was immersed in an oil bath heated at the appropriate temperature (45 or 65 °C). Periodically, samples were removed from the reaction mixture by a syringe. A portion of this sample was diluted with DMF and purified by passing through alumina to remove the copper for GPC measurement. The remainder was precipitated into THF. Conversion of AN was measured by GC analysis using THF as an internal standard. Because of the complex behavior of PAN during GPC analysis, M_n was also measured by ^{1}H NMR and MALDI-TOF MS. The precipitated PAN was washed with methanol and used for M_n determination by ^{1}H NMR in DMSO-d_6 on a Bruker AM 300 MHz spectrometer. The precipitated polymer was typically off-white or slightly yellow in color, indicating an insignificant amount of copper left in the sample. MALDI-TOF MS was performed on a Perseptive Biosystem MALDI-TOF Voyager Elite with delayed extraction using indolacrylic acid as the matrix. GPC analysis was undertaken using a system consisting of a Waters 510 HPLC pump, three Waters Ultrastyragel columns (500, 10^3, and 10^5 Å), and a Waters 410 DRI detector, with a DMF flow rate of 1.0 mL/min.

Results

The results of several AN ATRP experiments are shown in Figures 1 (number-average molecular weight, M_n, and polydispersity, M_w/M_n) and 2 (monomer conversion data). Typically, the reaction mixtures began as dark red solutions that changed to green during the reaction (after approximately 5−10 h). Molecular weights increase with conversion, and the polydispersity remained low throughout the polymerization, although they are highest for the highest catalyst concentration

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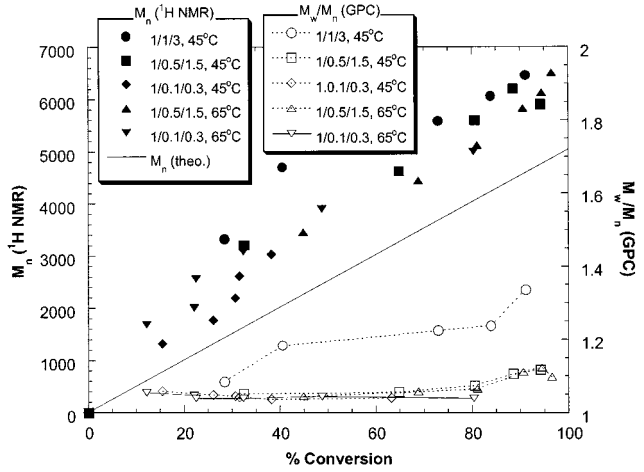


Figure 1. Number-average molecular weight (M_n), as measured by ^{1}H NMR (filled symbols), and polydispersity (M_w/M_n), as measured by GPC (open symbols), as a function of conversion for the ATRP of AN with various ($[BPN]_0/[CuBr]_0/[bpy]_0$) ratios (indicated in figure) at either 45 or 65 °C (indicated in figure), with $[AN]_0 = 5.25$ M, $[AN]_0/[BPN]_0 = 95$, and $[CuBr]_0/[bpy]_0 = 1/3$ in ethylene carbonate.

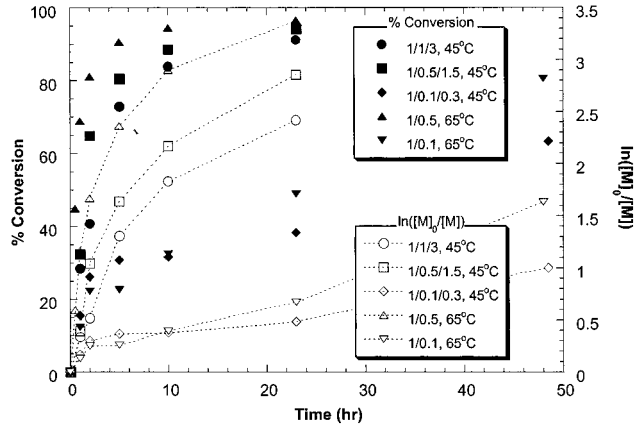


Figure 2. Percentage monomer conversion (filled symbols), and first-order kinetic plot of monomer consumption (open symbols), as a function of time for the ATRP of AN with various ($[2\text{-bromopropionitrile}]_0/[CuBr]_0/[bpy]_0$) ratios (indicated in figure) at either 45 or 65 °C (indicated in figure), with $[AN]_0 = 5.25$ M, $[AN]_0/[BPN]_0 = 95$, and $[CuBr]_0/[bpy]_0 = 1/3$ in ethylene carbonate.

(Figure 1). The molecular weights are slightly higher than the values predicted by the ratio of starting monomer and initiator concentrations (i.e., $M_n(\text{theo}) = 53 \times [M]_0/[RX]_0$). The first-order kinetic plots (Figure 2) show significant curvature, meaning that the concentration of the active species is not constant during the polymerization, in contrast to what has generally been observed in the ATRP of other monomers (styrene, methyl methacrylate, methyl acrylate).[5]

The effects of using 2-bromopropionitrile or 2-chloropropionitrile as the initiator, and either CuBr or CuCl as the catalyst on the kinetics, M_n and M_w/M_n, while keeping other conditions constant, are shown in Figures 3 and 4, respectively. Using Cl in either the initiator or catalyst results in a decrease of the rate of polymerization; however, the kinetic plot for monomer consumption still shows curvature. Molecular weights increase in a linear fashion with increasing conversion. The distribution remains narrow throughout for each polymerization; the RBr/CuBr case shows a lower polydispersity at an earlier stage, indicating a faster deactivation step for this system. The polymerization rate for the RBr/CuBr system is fastest (see Figure 3) because the weaker C−Br bond facilitates a faster rate of activation.

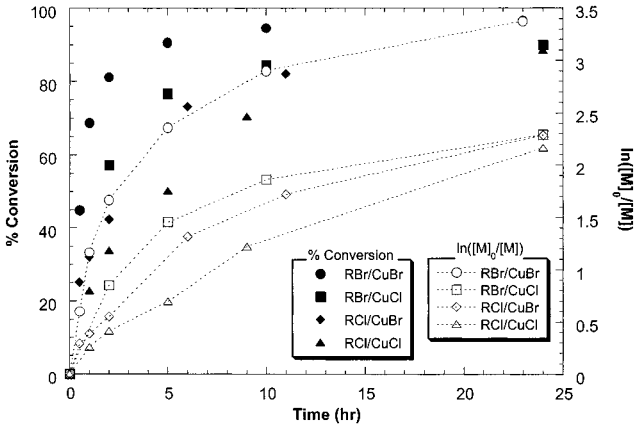


Figure 3. Percentage monomer conversion (filled symbols), and first-order kinetic plot of monomer consumption (open symbols), as a function of time for the ATRP of AN with various combinations of halo−propionitrile (RCl or RBr) initiators and Cu−halide (CuCl or CuBr) catalysts (indicated in figure), with $[AN]_0 = 5.25$ M and $[AN]_0/[RX]_0/[CuX]_0/[bpy]_0 = 95/1/0.5/1.5$ at 65 °C in ethylene carbonate.

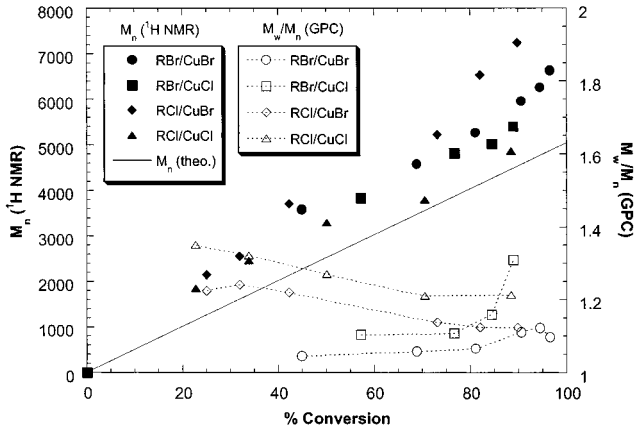


Figure 4. Number-average molecular weight (M_n), as measured by ^{1}H NMR (filled symbols), and polydispersity (M_w/M_n), as measured by GPC (open symbols), as a function of conversion for the ATRP of AN with various combinations of halo−propionitrile (RCl or RBr) initiators and Cu−halide (CuCl or CuBr) catalysts (indicated in figure), with $[AN]_0 = 5.25$ M and $[AN]_0/[RX]_0/[CuX]_0/[bpy]_0 = 95/1/0.5/1.5$ at 65 °C in ethylene carbonate.

Figure 5 shows how M_n and M_w/M_n varied throughout the polymerization when various $[AN]_0/[RX]_0$ ratios were used (i.e., attempting higher molecular weights of PAN). For the higher $[AN]_0/[RX]_0$ ratios, more catalyst was used to increase the rate of reaction. For each $[AN]_0/[RX]_0$ ratio, molecular weights increase linearly with conversion. The polydispersities are low for the lower molecular weights but tend to increase with conversion; this is especially the case for the largest $[AN]_0/[RX]_0$ ratio.

The effect of adding various initial concentrations of the deactivating Cu^{II} species and CuBr:ligand ratio was investigated. It was found that addition of <25% of $Cu^{II}Br_2$ (relative to $[Cu^{I}Br]_0$) did not markedly affect the rate of polymerization (Table 1). However, addition of 50% of $Cu^{II}Br_2$ resulted in a very long reaction time. At low $[bpy]_0/[Cu^{I}Br]_0$ ratios the rate of polymerization was

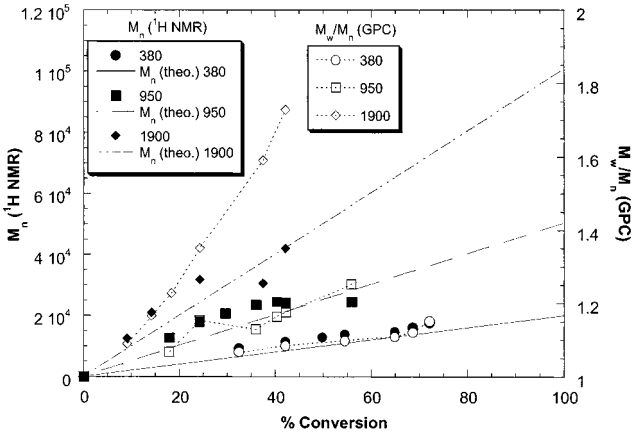


Figure 5. Number-average molecular weight (M_n), as measured by ^{1}H NMR (filled symbols), and polydispersity (M_w/M_n), as measured by GPC (open symbols), as a function of conversion for the ATRP of AN with various $[AN]_0/[BPN]_0$ ratios (indicated in figure) with $[AN]_0 = 5.25$ M at 65 °C in ethylene carbonate; $[AN]_0/[RX]_0/[CuX]_0/[bpy]_0 = 380/1/0.75/2.25$, 950/1/1/3, and 1900/1/1/3.

Table 1. Percent Monomer Conversion for the Addition of $Cu^{II}Br_2$ to the ATRP of AN ($[AN]_0 = 5.25$ M, $[AN]_0/[BPN]_0 = 190$ at 65 °C)

	% $[Cu^{II}Br_2]_0$				
time (h)	0	5	15	25	50
0.5	32.6	29.4	32.3	31.5	0.7 (48 h)
1	45.2	41.0	43.7	42.5	
1.5	53.8	49.1	51.9	49.2	
2		54.2	59.4	57.7	
3		64.8	69.1	68.1	

Table 2. Percent Monomer Conversion for the Variation of $[Bpy]_0/[Cu^IBr]_0$ Ratio on the ATRP of AN ($[AN]_0 = 5.25$ M, $[AN]_0/[BPN]_0/[CuBr]_0 = 190/1/0.5$ at 65 °C)

	$[bpy]_0/[Cu^IBr]_0$				
time (h)	0.5	1	1.5	2	3
0.5	7.64	18.2	24.4	28.1	32.6
1	10.1	24.3	33.2	38.3	45.2
1.5	13.4	29.0	39.8	44.6	53.8
2	17.7	36.0	44.2	51.7	
2.5	19.2	40.1	52.2	56.5	

slow but increased as the bpy content was increased up to 3/1 (Table 2).

The homogeneity of the reaction mixture is important in this system because of the limited solubility of PAN in various (typical) solvents, as well as in the AN monomer itself. Figures 6 and 7 show the first-order kinetic plot, M_n and M_w/M_n for reactions with EC, propylene carbonate (PC), diphenyl ether (DPE), and dimethylformamide (DMF) as diluents. PAN is soluble in EC, PC, and DMF but not soluble in DPE or AN. EC produced the fastest rate of polymerization, followed by PC and then in bulk; the other solvents produced rates that were very much slower. All first-order kinetic plots show curvature. The molecular weights agree reasonably well with the theoretical molecular weight when EC or PC is used as solvent or the reaction was performed in bulk. However, the bulk reaction showed a continuous increase in polydispersity, while when using the carbonates as solvents the polydispersities were narrow ($M_w/M_n < 1.2$). With DPE as the solvent only low conversions were reached, the molecular weights overestimate the theoretical molecular weight, and polydispersities increased with conversion. With

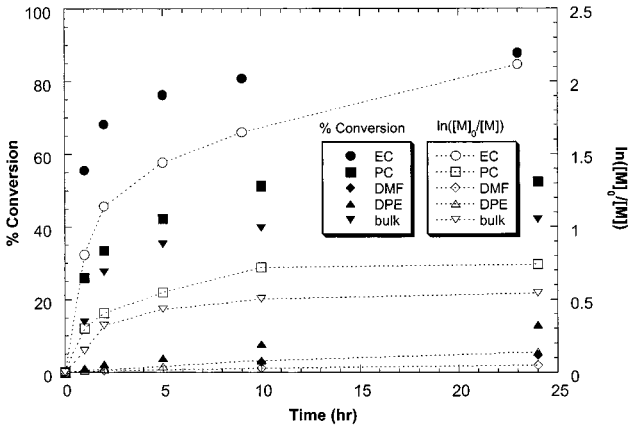


Figure 6. Percentage monomer conversion (filled symbols), and first-order kinetic plot of monomer consumption (open symbols), as a function of time for the ATRP of AN in various solvents at 65 °C (EC = ethylene carbonate, PC = propylene carbonate, DMF = dimethylformamide, DPE = diphenyl ether), with $[AN]_0 = 5.25$ M and $[AN]_0/[BPN]_0/[CuBr]_0/[bpy]_0 = 190/1/0.5/1.5$.

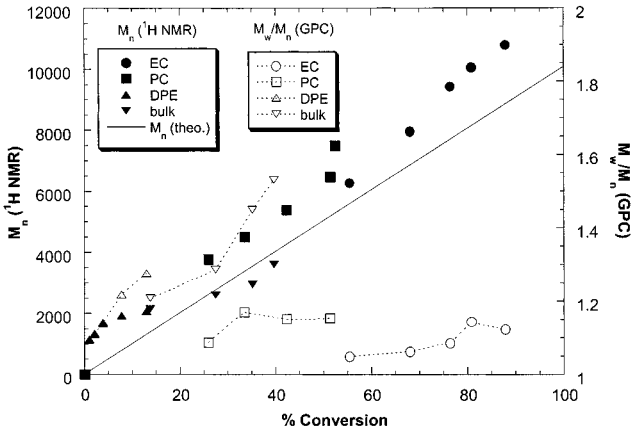


Figure 7. Number-average molecular weight (M_n), as measured by ^{1}H NMR (filled symbols), and polydispersity (M_w/M_n), as measured by GPC (open symbols), as a function of conversion for the ATRP of AN in various solvents at 65 °C (EC = ethylene carbonate, PC = propylene carbonate, DMF = dimethylformamide, DPE = diphenyl ether), with $[AN]_0 = 5.25$ M and $[AN]_0/[BPN]_0/[CuBr]_0/[bpy]_0 = 190/1/0.5/1.5$.

DMF as the solvent very little polymer was obtained and therefore not analyzed.

To examine the effect of the counterion, various Cu^I salts were used as catalysts, complexed with 3 equiv of bpy. Figure 8 indicates that the polymerizations of several Cu^I salts with different counterions, including acetate (OAc), thiophene carboxylate (Tc), and PF_6, when complexed with 3 equiv of bpy were slower than the standard CuBr/3bpy system. The molecular weights for each system are in general agreement with the theoretical molecular weight; however, only the $Cu(CH_3CN)_4PF_6$ system showed polydispersities that are comparable to those of the CuBr catalyst (Figure 9).

Polymerization of AN initiated with AIBN was performed in the presence of Cu^IBr/3bpy or $Cu^{II}Br_2$/3bpy. Figure 10 indicates that the rate of monomer consumption is markedly reduced when either Cu^IBr or $Cu^{II}Br_2$ is added to the AIBN-initiated polymerization of AN. From this it can be inferred that both copper species are interacting with the free radicals. The molecular weights also show a significant decrease when the copper species are added (Figure 11). (Note that M_n may

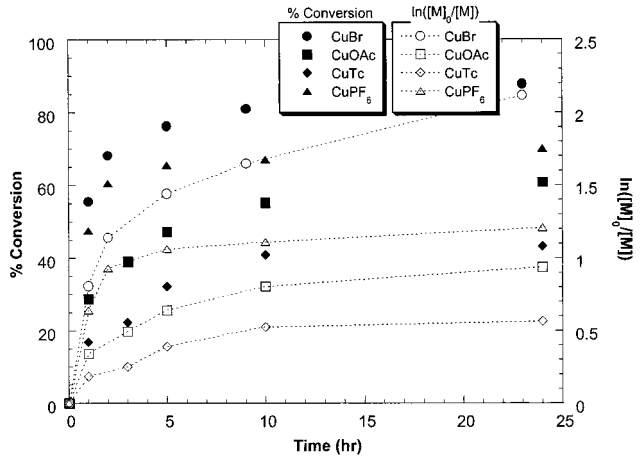


Figure 8. Percentage monomer conversion (filled symbols), and first-order kinetic plot of monomer consumption (open symbols), as a function of time for the ATRP of AN with various Cu^I salts at 65 °C in EC, with $[AN]_0 = 5.25$ M and $[AN]_0/[BPN]_0/[Cu^I\ salt]_0/[bpy]_0 = 190/1/0.5/1.5$.

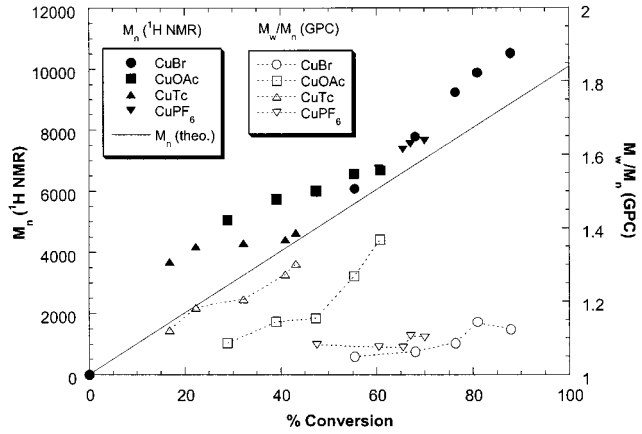


Figure 9. Number-average molecular weight (M_n), as measured by ^1H NMR (filled symbols), and polydispersity (M_w/M_n), as measured by GPC (open symbols), as a function of conversion for the ATRP of AN with various Cu^I salts at 65 °C in EC, with $[AN]_0 = 5.25$ M and $[AN]_0/[BPN]_0/[Cu^I\ salt]_0/[bpy]_0 = 190/1/0.5/1.5$.

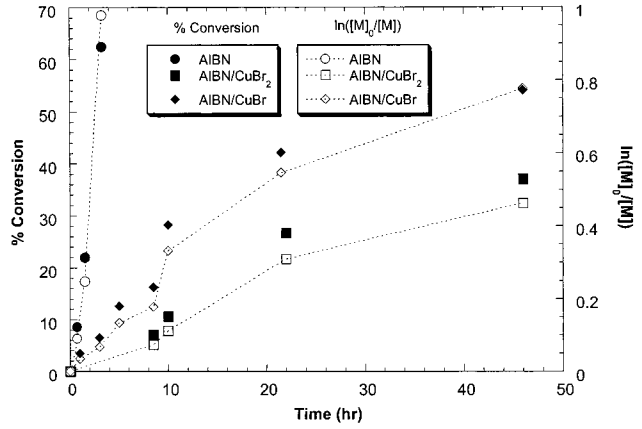


Figure 10. Percentage monomer conversion (filled symbols), and first-order kinetic plot of monomer consumption (open symbols), as a function of time for the polymerization of AN initiated by AIBN with Cu^IBr or $Cu^{II}Br_2$ at 65 °C in EC. $[AN]_0 = 5.25$ M, $[AN]_0/[AIBN]_0 = 1000$, $[Cu^IBr]_0/[bpy]_0/[AIBN]_0 = 1/3/1.8$, and $[Cu^{II}Br_2]_0/[bpy]_0/[AIBN]_0 = 1/3/2.0$.

be overestimated in these cases because the GPC was calibrated with polystyrene standards.) The addition of $Cu^{II}Br_2$ produced the lowest polydispersities of these

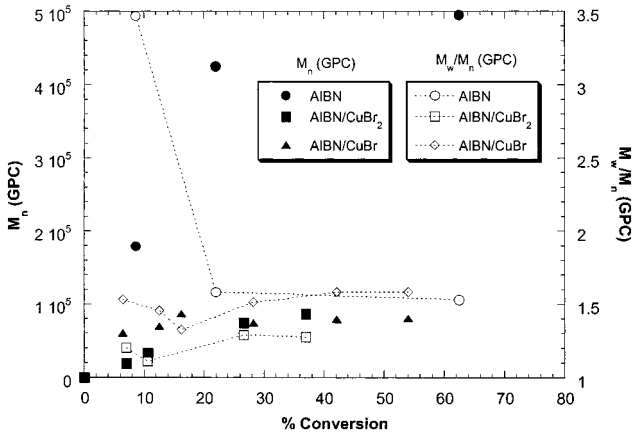


Figure 11. Number-average molecular weight (M_n), as measured by GPC (filled symbols), and polydispersity (M_w/M_n), as measured by GPC (open symbols), as a function of conversion for the polymerization of AN initiated by AIBN with Cu^IBr or $Cu^{II}Br_2$ at 65 °C in EC. $[AN]_0 = 5.25$ M, $[AN]_0/[AIBN]_0 = 1000$, $[Cu^IBr]_0/[bpy]_0/[AIBN]_0 = 1/2/1.8$, and $[Cu^{II}Br_2]_0/[bpy]_0/[AIBN]_0 = 1/2/2.0$.

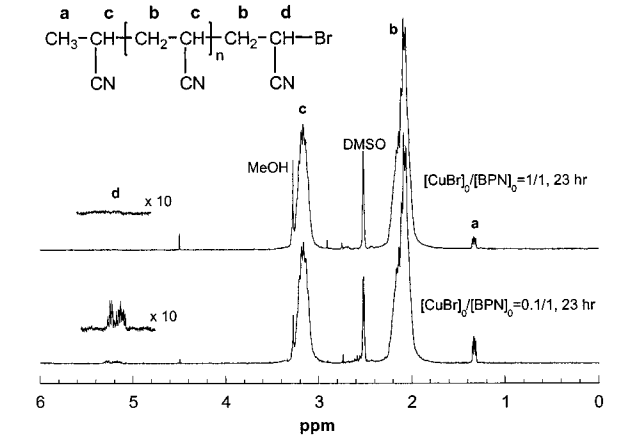


Figure 12. ^1H NMR spectra of PAN synthesized with different $[CuBr]_0/[BPN]_0$ ratios (for $[CuBr]_0/[BPN]_0 = 1/1$: % conversion = 91.1, M_n (^1H NMR) = 6580, M_w/M_n (GPC) = 1.34; for $[CuBr]_0/[BPN]_0 = 0.1/1$: % conversion = 38.3, M_n (^1H NMR) = 3160, M_w/M_n (GPC) = 1.04). Temperature = 45 °C, $[AN]_0 = 5.25$ M, $[AN]_0/[BPN]_0 = 95$, and $[CuBr]_0/[bpy]_0 = 1/3$ in EC.

reactions, and M_n tends to increase in a linear manner. This is what would be expected through "reverse ATRP", where the radicals generated abstract a Br from $Cu^{II}Br_2$, thus forming an alkyl bromide and Cu^IBr in situ—the key components in ATRP. This technique has previously produced excellent control of molecular weights and polydispersities for styrene, methyl acrylate, and methyl methacrylate.[9] In contrast, the reaction free of any Cu catalyst showed high molecular weights and high polydispersities. When Cu^IBr was present, the molecular weights were not as high as in the previous case but reached a plateau around $M_n = 80\,000$ at low conversions. The polydispersities were approximately 1.5 over the conversion regime studied here.

End group analysis was undertaken through both ^1H NMR spectroscopy and MALDI-TOF MS. Figure 12 shows ^1H NMR spectra of PAN samples taken from an ATRP of AN/BPN/CuBr/bpy = 95/1/1/3 at 45 °C. The BPN α-end group absorbs at 1.3 ppm while the ω-end group, with a Br atom adjacent to the proton, absorbs at 5.2 ppm. Integration of these signals should lead to a 3:1 ratio if all end groups are intact. The spectra in Figure 12 indicate that a significant percentage of Br

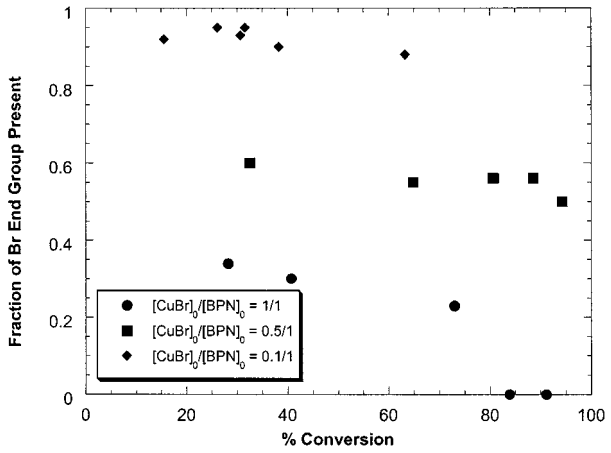


Figure 13. Fraction of Br end groups as a function of monomer conversion for different $[CuBr]_0/[BPN]_0$ ratios. Temperature = 45 °C, $[AN]_0$ = 5.25 M, $[AN]_0/[BPN]_0$ = 95, and $[CuBr]_0/[bpy]_0$ = 1/3 in EC.

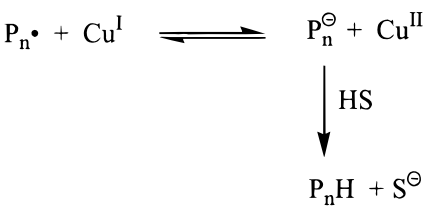
end groups were removed; this is especially the case when an equimolar amount of catalyst is used. Figure 13 shows the fraction of Br end groups as a function of conversion for three $[Cu^IBr]_0/[BPN]_0$ ratios. The Br end group functionality decreased dramatically from unity toward a final value corresponding to the ratio of $[Cu^IBr]_0/[BPN]_0$. Thus, the fraction of Br end groups lost depends on $[Cu^IBr]_0$.

Finally, a MALDI-TOF MS spectrum of PAN synthesized by ATRP is shown in Figure 14. The major series of peaks correspond to $\{CH_3CH(CN)-[CH_2CH(CN)]_n-CH_2CH(CN)Br + Na\}^+$. Also evident is another series of peaks of lower intensity corresponding to $\{CH_3CH(CN)-[CH_2CH(CN)]_n-CH_2CH(CN)H + Na\}^+$; the proportion of unsaturated chains, as well as chains that could form by radical coupling, is apparently much lower. Simulated MALDI spectra, also shown in Figure 14, suggest that these assignments are correct.[10] While it is well-known that the polymer during MALDI analysis is susceptible to dehalogenation during ionization, it is unlikely that the dehalogenated species would pick up a hydrogen atom during the MALDI analysis. Therefore, the hydrogen-terminated series is most likely to result from the polymerization reaction.

Discussion

The data presented here indicate that PAN can be synthesized with predefined molecular weights (M_n < 30 000) and narrow polydispersities (M_w/M_n < 1.5; Figures 1 and 5). This is done in a relatively simple fashion using a Cu^IBr/unsubstituted bpy catalyst system. Using EC as the solvent allows the polymerization to occur under apparently homogeneous conditions and facilitates a reasonable rate of reaction; other solvents do not appear to provide as good control of molecular weights or rates (Figures 6 and 7). However, the ATRP of AN under the conditions presented here appears to be not as successful as for other monomers (e.g., styrene, MMA, methyl acrylate) which can be carried out to much higher degrees of polymerization.[11] For example, while molecular weights increase linearly with conversion and polydispersities are very low, the curvature noticed in nearly all the kinetic plots (e.g., Figure 2) indicates that the reaction "dies", thereby reducing the functionality of the PAN and limiting the molecular weight. Furthermore, the observation that the reaction progressively turns green indicates that the deactivating

Scheme 2



Cu^{II} species is being generated, and ^1H NMR spectra (Figures 12 and 13) and mass spectra (Figure 14) data clearly show that the halide end groups are being lost.

There are several possible reasons for this behavior, including the following:

1. Radical−radical termination may be extremely fast, meaning either the rate coefficient for such termination (k_t) is very high or the radical concentration is too high.

2. There may be side reactions that lose the halogen from the end of the chain, thereby killing chain growth. Possibilities of this include the reduction of the radical to an anion by Cu^I, which following subsequent reaction with a proton source (e.g., adventitious water) produces a dead polymer chain (Scheme 2), or a more simple elimination reaction producing HBr and an unsaturated chain end.

3. The catalyst may also be undergoing reactions other than the simplified activation/deactivation cycle proposed for ATRP. For example, the copper center may be coordinated by either monomer or polymer through the cyano group, possibly either deactivating it or lowering its effective concentration.

4. The cyano group may also contribute to the observed behavior through interactions of the N-centered radical.[4]

These potential scenarios may occur concurrently with each other, thus all contributing to the nonideal living behavior. Perhaps the best clue as to why the "livingness" is limited in the ATRP of AN presented here is the loss of the halogen end groups, and from MALDI data, it appears that the end group is substituted with a hydrogen atom. This may occur through radical−radical termination by disproportionation. However, it is established that termination in AN polymerization occurs mainly through combination,[4] and furthermore, no evidence for the unsaturated end group could be found in the ^1H NMR spectra we obtained; thus, it is more likely that this substitution occurs through another mechanism. Radical−radical termination by combination could be occurring at a very fast rate, thus leading to the irreversible generation of Cu^{II}, but is inconsistent with the halide end group being replaced by a hydrogen atom.

As mentioned above, Cu^{II} is formed throughout the reaction as suggested by the reactions turning green after several hours. The addition of Cu^{II} to the reaction mixture does not affect the rate until relatively large amounts are present (>25%; Table 1), where the polymerization slows dramatically. It is therefore possible that the polymerization with only Cu^I added will proceed until a large percentage (>25%) has been converted to Cu^{II}, but the rate will decrease, because of not only the increase in Cu^{II} concentration but also the reduction in Cu^I concentration.

There are several pieces of indirect evidence for the reduction of the radical by Cu^I to form the carbanion and Cu^{II}, followed by protonation of the anion. Examination of the oxidation/reduction potentials of radicals

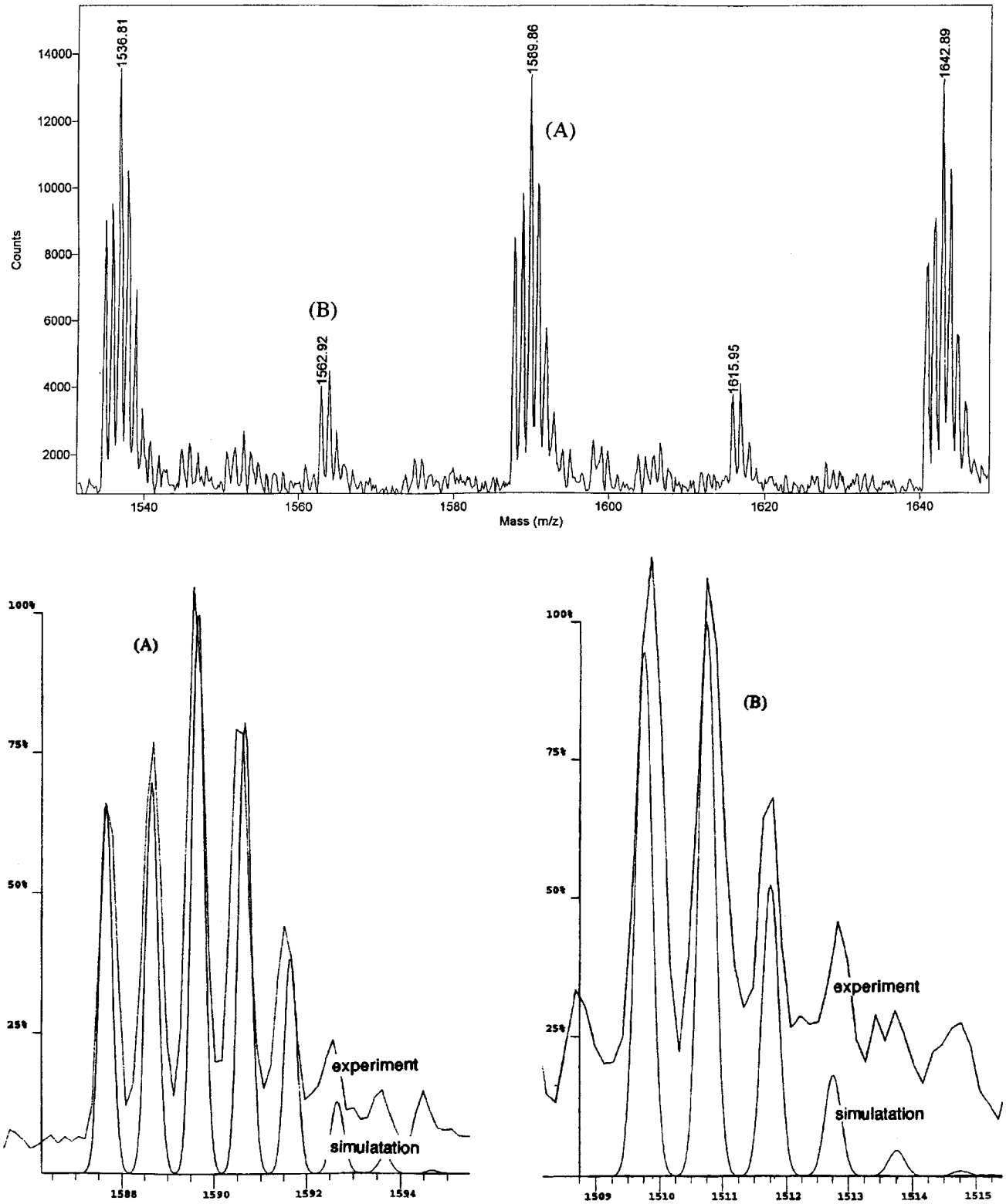


Figure 14. (a) MALDI-TOF MS spectrum of PAN. Series A: $\{CH_3CH(CN)-[CH_2CH(CN)]_n-CH_2CH(CN)Br + Na\}^+$. Series B: $\{CH_3CH(CN)-[CH_2CH(CN)]_n-CH_2CH(CN)H + Na\}^+$. Temperature = 45 °C, $[AN]_0 = 5.25$ M, and $[AN]_0/[BPN]_0/[CuBr]_0/[bpy]_0 = 95/1/0.1/0.3$ in EC; % conversion = 26.1, M_n (^{1}H NMR) = 1900, M_w/M_n (GPC) = 1.05. (b) Expanded experimental and simulated MALDI-TOF MS spectrum of PAN.

with strong electron-withdrawing substituents and the Cu^I/bpy complex indicates that reduction of the radical to the anion is quite possible.[12] We have earlier shown the methyl acrylate may be susceptible to a similar side reaction, and styrene may possibly undergo an oxidation reaction forming the styryl cation.[13,14] Since AN also forms an electrophilic radical, presumably more electrophilic than that derived from methyl acrylate, it can be reasonably assumed that similar reactions for the two monomers may occur. Furthermore, Figures 10 and 11 indicate that in radical polymerization of AN in the presence of Cu^IBr (and also $Cu^{II}Br_2$, but this results in reverse ATRP) there is some interaction between the propagating species and the catalyst. A reduction in

both the rate of polymerization and molecular weights was observed. Experiments with AIBN-initiated polymerization of methyl acrylate in the presence of $Cu^{I}(OTf)$[13] gave similar results. Using a catalyst with a lower reduction potential (i.e., $Cu^{I}(CH_3CN)_4PF_6$ without bpy as a ligand) failed to produce any polymer after 20 h (65 °C, $[AN]_0 = 5.25$ M, $[AN]_0/[BPN]_0/[Cu^{I}(CH_3CN)_4PF_6]_0 = 190/1/0.5$, in EC).

The ^{1}H NMR results (Figures 12 and 13) show that the loss of the halide end group at the end of the reaction is proportional to the starting $Cu^{I}Br$ concentration. End group loss appears to occur very quickly, with 65% lost within the first hour (~30% conversion) of the reaction with $[Cu^{I}Br]_0/[BPN]_0 = 1/1$. It is possible that the BPN also loses Br before initiation occurs. This would account for the higher molecular weights than predicted theoretically (Figure 1). In fact, a small trend in the size of this deviation can be seen with changing $[Cu^{I}Br]_0/[BPN]_0$—increasing the $[Cu^{I}Br]_0/[BPN]_0$ ratio leads to a greater discrepancy between M_n(^{1}H NMR) and M_n(theor). Another observation is that for $[Cu^{I}Br]_0/[BPN]_0 = 1/1$, where most end group loss occurs, the polydispersities are also relatively high compared with lower $[Cu^{I}Br]_0/[BPN]_0$ ratios. However, the proposed mechanism of the AN radical being reduced to an anion followed by termination, as discussed above, does not lead to the observed 1/1 stoichiometry between end group loss and $[Cu^{I}Br]_0$. If some kind of stable anionic species would be formed, each end group that is lost would require oxidation of 2 equiv of Cu^{I} to Cu^{II}, and thus in the experiments shown in Figure 13 only half the end groups would be lost compared to what is actually observed. This indicates that the process may be potentially catalytic in copper, and some of the anions produced may be reoxidized to radicals.

Interactions of the Cu with the cyano groups in both monomer and polymer are weaker than the binding of bpy to the metal center.[15] Such interactions are, however, possible because of the much greater concentration of the CN groups relative to the bpy compound.

The bulk of the polymer appears to have been formed through free radical polymerization. Several pieces of information point to this. For example, reverse ATRP, where radicals are generated from the decomposition of AIBN, works in a similar fashion as it does for styrene. Also, the polymerizations presented here are not as sensitive to moisture as an anionic mechanism would be. (The polymerizations were performed under nonrigorously dry conditions.) Also, the PAN products were not highly colored as often found in anionically prepared PAN.[16] Because the propagating species is expected to be a radical, then the iminyl form of the radical may undergo reactions that are not expected of the carbon-centered radical, thus complicating the ATRP of AN further.

Various alterations to the basic reaction conditions were performed attempting to improve the "living" behavior of the polymerization. Using Cl instead of Br slowed the rate of polymerization and increased polydispersities slightly but did not lead to linear first-order kinetic plots of monomer consumption (Figures 3 and 4). Different counterions also lead to slower rates of polymerization and higher polydispersity compared with the case of the $Cu^{I}Br$ catalyst (Figures 8 and 9). As reported above, an experiment using $Cu^{I}(CH_3CN)_4PF_6$ without bpy as a ligand, where the reduction potential of the catalyst was lowered, failed to produce any polymer after 20 h. Finally, altering or removing the solvent again led to slower rates and poorer control (Figures 6 and 7).

Other than our initial communication, there are two other reports of the synthesis of well-defined PAN in the literature. Sivaram et al.[17] found that, by using metal-free ammonium methanides as initiators, PAN could be formed through anionic polymerization at 0−30 °C with predictable molecular weights of several hundred up to 3500. This is in contrast to the anionic polymerization of AN with metal-containing carbanions, which generally do not lead to well-defined, narrow distribution, PAN. However, the mechanisms involved in the work of Sivaram et al.[17] remain unclear, and the polymers were limited to relatively low molecular weight because of solubility problems. Very recently, Hawker et al.[18] reported that the polymerization of AN, using an alkoxyamine initiator having a weaker C−O bond than TEMPO-derived alkoxyamines, resulted in PAN with molecular weights up to 50 000 and polydispersities less than 1.16. Fukuda et al.[19] succeeded in synthesizing controlled copolymers of AN and styrene using TEMPO-mediated polymerization; however, homopolymerization of AN using these conditions was unsuccessful. Other controlled polymerization methods, such as group transfer polymerization (GTP),[20] have also been unsuccessful in producing well-defined PAN. Sugimoto et al.[21] reported the controlled polymerization, by using aluminum porphyrin initiators, of the closely related monomer methacrylonitrile, where controlled polymerization has suffered similar problems as observed with AN polymerization (side reactions in anionic polymerization, poor solubility, etc.).

Conclusions

ATRP has been shown to be successful in synthesizing PAN with predefined molecular weights and narrow polydispersities using a $Cu^{I}X$/bpy (X = Br or Cl) catalyst system. However, the kinetics of the polymerization were not first order in monomer, indicating that termination was occurring. This results in molecular weights being limited to <30 000 (if $M_w/M_n < 1.5$) and a reduction of end group functionality. Several reasons for this were discussed; however, the most probable is the reduction of the radical by Cu^{I} to form an anion and Cu^{II} species. It is possible, however, that further alterations in the metal and/or ligand may produce better control, thus allowing higher molecular weight PAN, with low polydispersities and good end group functionality, to be produced.

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