

# High-Molecular-Weight Polyacrylonitrile by Atom Transfer Radical Polymerization

Chen Hou,<sup>1</sup> Rongjun Qu,<sup>1</sup> Junshen Liu,<sup>1</sup> Liang Ying,<sup>2</sup> Chengguo Wang<sup>3</sup>

<sup>1</sup>College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, China

<sup>2</sup>Office of Science and Technology, Yantai Normal University, Yantai 264025, China

<sup>3</sup>College of Materials Science and Engineering, Shandong University, Jinan 250061, China

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**ABSTRACT:** A single-pot atom transfer radical polymerization was used for the first time to successfully synthesize polyacrylonitrile with a molecular weight higher than 80,000 and a narrow polydispersity as low as 1.18. This was achieved with CuBr/isophthalic acid as the catalyst, 2-bromopropionitrile as the initiator, and *N,N*-dimethylformamide as the solvent. The effects of the solvent on the polymerization of acrylonitrile were also investigated. The induction period was shorter in *N,N*-dimethylformamide than in propylene carbonate and toluene, and the rate of the polymerization in *N,N*-dimethylformamide was fastest. The

molecular weight of polyacrylonitrile agreed reasonably well with the theoretical molecular weight in *N,N*-dimethylformamide. When chlorine was used in either the initiator or the catalyst, the rate of polymerization showed a trend of decreasing, and the molecular weight deviated from the theoretical prediction significantly. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3372–3376, 2006

**Key words:** atom transfer radical polymerization (ATRP); living polymerization

## INTRODUCTION

Carbon-fiber composites are important construction materials in applications for which high strength and modulus and high thermal and corrosion resistance are the primary requirements.<sup>1</sup> The properties of the final carbon fibers are determined by the nature of the polyacrylonitrile (PAN) precursor fibers.<sup>2</sup> A high molecular weight and a narrow polydispersity are essential requirements for the synthesis of PAN polymers satisfying the requirements for high-performance PAN fibers.<sup>3</sup> PAN is usually prepared by radical polymerization without control over the molecular dimensions and structure, whereas other methods exist for more controlled polymerization of acrylonitrile (AN), such as anionic polymerization; these often involve complex catalysis or side reactions with the nitrile groups.<sup>4</sup> Living/controlled free-radical polymerization can be used as an alternative; atom transfer radical polymerization (ATRP) is one of the most widely used methods, involving a fast dynamic equilibrium between dormant species and active radical species to provide control.<sup>5–7</sup> PAN with predefined

molecular weights and narrow polydispersity has been successfully synthesized by the use of ATRP, but the molecular weights of PAN obtained with ATRP systems are limited to less than 15,000.<sup>8–10</sup> The potential application of ATRP for high-molecular-weight polymers would require a high initiator efficiency and a moderate reaction rate during the polymerization at a high monomer-to-initiator ratio. Another possible route to high-molecular-weight polymers employs multiple steps of isolation and purification of the living polymer at intermediate stages and its use as a macroinitiator for further chain extension. Acids, which are inexpensive and nontoxic, complex more easily with copper and may therefore act as ligands. A new catalytic system based on copper complexes with isophthalic acid (IPA) was first used in this study. In this work, ATRP kinetics in high monomer-to-initiator ratio systems were examined, and the possibility of obtaining PAN with a low polydispersity index (PDI) and high molecular weight by a single-pot synthesis was evaluated. The influence of the solvent and the catalyst system on ATRP was also investigated.

## EXPERIMENTAL

### Materials

AN (Shanghai Chemical Reagents Co., Shanghai, China; analytical-reagent grade) was vacuum-distilled from CaH<sub>2</sub> just before polymerization. CuBr and CuCl (Shanghai Chemical Reagents; analytical-reagent grade)

Correspondence to: C. Hou (sdchenhou@hotmail.com).

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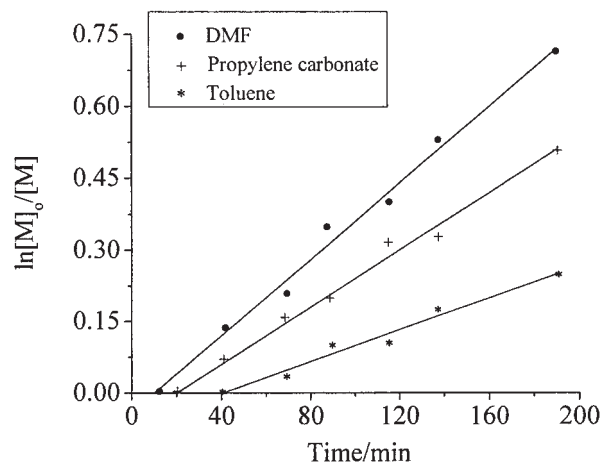
were washed with absolute ethanol and dried *in vacuo* at 60°C before use. IPA (Shanghai Chemical Reagents; analytical-reagent grade) was used as received. 2-Bromopropionitrile (BPN) and 2-chloropropionitrile (CPN) were obtained from Aldrich and used without further purification. *N,N*-Dimethylformamide (DMF; Shanghai Dongyi Chemical Reagents Co., Shanghai, China) was distilled at reduced pressure and stored until use. Propylene carbonate and toluene (Shanghai Chemical Reagents; analytical-reagent grade) were used as received.

### Polymerization

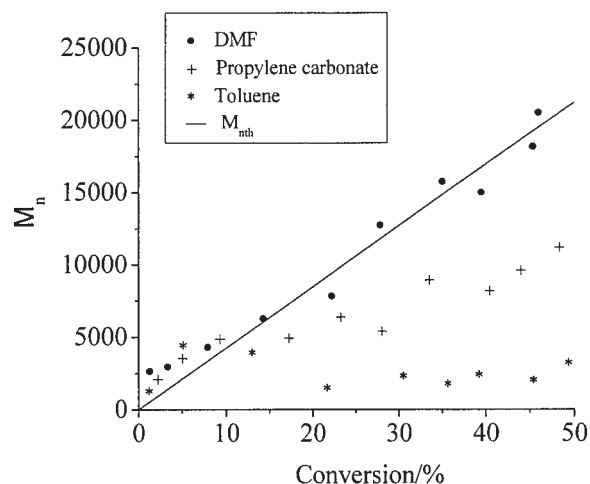
A typical example of the general procedure was as follows. A dry flask was filled with CuBr, IPA, DMF, BPN, and AN in that order. It was degassed *in vacuo* and charged with N<sub>2</sub> (four times) and was sealed under N<sub>2</sub>. The mixture was stirred at room temperature until the catalyst was dissolved. The flask was then immersed in an oil bath held at the desired temperature by a thermostat. At timed intervals, the polymerization system was stopped by the cooling of the flask in ice water. After the polymerization product was dissolved in DMF, PAN was precipitated in methanol and then dried.

### Characterization

The conversion of the monomer was determined gravimetrically. The number-average molecular weight ( $M_n$ ) and PDI were measured by gel permeation chromatography (GPC) with a Waters 515 GPC instrument (Waters Inc., Milford, Massachusetts), and all samples were run in DMF with a column temperature of 30°C.



**Figure 1** First-order kinetic plot of the monomer consumption as a function of time in different solvents during the ATRP of AN with  $[AN] = 5.0M$  and  $[AN]/[bpn]/[CuBr]/[ipa] = 800:1:1:3$  at 60°C.

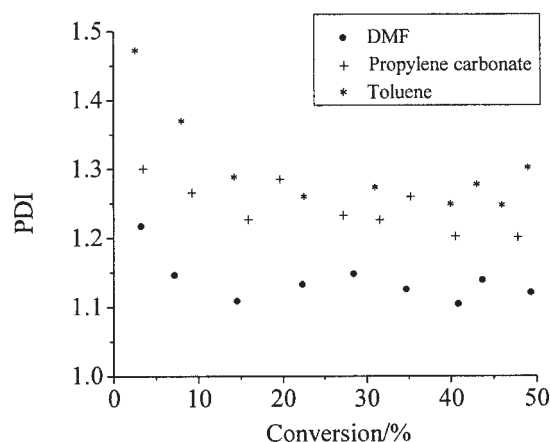


**Figure 2** Dependence of  $M_n$  on the monomer conversion in different solvents for the ATRP of AN with  $[AN] = 5.0M$  and  $[AN]/[bpn]/[CuBr]/[ipa] = 800:1:1:3$  at 60°C ( $M_{nth}$  = theoretical number-average molecular weight).

## RESULTS AND DISCUSSION

### Effect of the solvent on the polymerization

Figure 1 shows kinetic plots of  $\ln[M]_0/[M]$  versus time for the ATRP of AN catalyzed by CuBr/IPA and initiated by BPN. Polymerizations were conducted in three different solvents. The polymerizations were approximately first-order with respect to the monomer concentration. The slopes of the kinetic plots indicate that in the polymerization processes, the number of active species was constant, and the termination reactions could be neglected. As shown in Figure 1, the polymerizations of AN appeared to require an induction period. The induction period was shorter in DMF than in propylene carbonate and toluene. The rate of polymerization in DMF was fastest. The induction



**Figure 3** Dependence of PDI on the monomer conversion in different solvents for the ATRP of AN with  $[AN] = 5.0M$  and  $[AN]/[bpn]/[CuBr]/[ipa] = 800:1:1:3$  at 60°C.

**TABLE I**  
**Percentage Monomer Conversion as a Function of Time with Various Combinations of Halopropionitrile Initiators and Cu-Halide Catalysts for ATRP of AN with [AN] = 5.0M and [AN]/[BPN]/[CuBr]/[IPA] = 800:1:1:3 at 60°C**

Catalyst	Conversion (%)								
	20 min	40 min	60 min	80 min	100 min	120 min	140 min	160 min	180 min
CuBr/BPN	3.92	11.9	17.2	24.8	29.6	35.4	41.5	45.3	49.5
CuCl/BPN	3.12	10.3	16.1	23.4	28.2	34.7	38.4	42.1	46.3
CuBr/CPN	2.94	9.31	14.2	21.2	25.2	30.6	34.5	36.4	40.2
CuCl/CPN	2.56	7.85	10.3	17.5	20.3	25.7	29.8	30.1	34.6

period was perhaps caused for two reasons: the presence of oxygen and impurities and the effect of the solvent.<sup>11,12</sup> In this case, IPA could not complex with CuBr sufficiently. The polymerizations were heterogeneous because of the limited solubility of the catalyst and the ligand in the monomer in propylene carbonate and toluene. The addition of DMF increased the solubility of the catalyst in AN. In addition, the polarity of the solvent could also affect the metal complex structure. In the polar solvent DMF,  $\text{Cu}^+(\text{IPA})_2\text{Cl}^-$  may have existed, but in a less polar solvent,  $(\text{IPA})\text{CuCl}_2\text{Cu}(\text{IPA})$ , could exist.<sup>13</sup>

The rate of the homogeneous polymerization in DMF was unexpectedly faster than the heterogeneous polymerization in propylene carbonate and toluene. A similar result was reported by Shenmin and Deyue<sup>14</sup> for iron-mediated ATRP. The experimental data reported in this work are different from those reported by Pascual et al.,<sup>15</sup> who used 2,2'-bipyridine, and Ziegler et al.,<sup>16</sup> who used monodentate amines as the ligands in copper-mediated systems. They concluded that DMF affects the living nature of ATRP. In our ATRP system, DMF had no significant effect on the living nature if there was sufficient ligand to complex the transition metal.

Figure 2 indicates that the molecular weights agreed reasonably well with the theoretical molecular weight when DMF was used as the solvent. When propylene carbonate was used as the solvent, the plot of the molecular weight shows an obvious curvature. With toluene as the solvent, only AN oligomer was reached. The high molecular weight at conversions lower than 10% indicated that there was some termination or side

reaction at the beginning of the reaction because the radicals were not immediately deactivated.

Figure 3 shows that PDI of PAN decreased with increasing monomer conversion, reaching values of 1.15 at about 20% conversion for DMF systems. Thus, the DMF-based system provided the desired characteristics of a high initiation efficiency, a low polydispersity, and a fast polymerization rate. This indicates that this system could potentially be used for even higher molecular weight PAN.

#### Effect of the catalyst on the polymerization

The effects of using either CuBr or CuCl as the catalyst and either BPN or CPN as the initiator on the ATRP of AN, with other conditions kept constant, are shown in Tables I–III. Using chlorine in either the initiator or catalyst resulted in a decrease in the rate of polymerization. The polymerization rate for the CuBr/BPN system was fastest because the lower carbon–bromine (C–Br) bond dissociation energy facilitated a faster rate of activation.<sup>17</sup> The molecular weights increased in a linear fashion with increasing conversion for CuBr/BPN and CuCl/BPN systems. The molecular weight increased with the monomer conversion for the CuBr/CPN and CuCl/CPN systems also but deviated from the theoretical prediction significantly under the reaction conditions; this may have been due to the early termination by radical–radical coupling caused by fast initiation.<sup>18</sup> The molecular weight distribution remained narrow throughout each polymerization; the CuBr/BPN case showed a lower polydispersity at the earlier stage, indicating a faster deacti-

**TABLE II**  
**Dependence of  $M_n$  on the Monomer Conversion with Various Combinations of Halopropionitrile Initiators and Cu-Halide Catalysts for ATRP of AN with [AN] = 5.0M and [AN]/[BPN]/[CuBr]/[IPA] = 800:1:1:3 at 60°C**

Catalyst	$M_n \times 10^4$									
	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%
CuBr/BPN	2300	4310	6400	8470	10,600	12,800	15,000	16,500	19,000	22,000
CuCl/BPN	2600	4500	6700	8500	11,000	12,100	16,000	16,500	17,600	20,400
CuBr/CPN	2800	4750	6500	8400	10,000	11,400	12,600	13,700	15,500	19,400
CuCl/CPN	3100	5000	6000	7000	8500	11500	12,400	12,900	14,600	18,500

TABLE III  
Dependence of PDI on the Monomer Conversion with Various Combinations of Halopropionitrile Initiators and Cu-Halide Catalysts for ATRP of AN with  $[AN] = 5.0M$  and  $[AN]/[BPN]/[CuBr]/[IPA] = 800:1:1:3$  at  $60^\circ C$

Catalyst	PDI										
	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	
CuBr/BPN	1.15	1.12	1.11	1.14	1.16	1.14	1.12	1.13	1.15	1.13	
CuBr/CPN	1.24	1.19	1.17	1.13	1.14	1.19	1.21	1.24	1.29	1.31	
CuCl/BPN	1.31	1.28	1.24	1.18	1.17	1.15	1.24	1.27	1.24	1.26	
CuCl/CPN	1.38	1.34	1.30	1.21	1.13	1.16	1.29	1.36	1.42	1.53	

vation step for this system. The polydispersities were low for the lower molecular weights but tended to increase with conversion; this was especially the case for the CuCl/CPN system.

### Synthesis of high-molecular-weight PAN

To get high-molecular-weight PAN, we then used  $[AN]/[bpn]$  ratios of 3200:1 and 6400:1, with the catalyst concentrations higher than the initiator concentrations ( $[CuBr]/[bpn] = 3$  and  $6$ , respectively), to enhance the apparent polymerization rate and thus avoid very long reaction times. The kinetic results presented in Figure 4 demonstrate that the polymerization rate was proportional to the monomer concentration, corresponding to a constant radical concentration during ATRP. Davis et al.<sup>19</sup> and Shipp and Matyjaszewski<sup>20</sup> drew the same conclusion and reported that there was reduced termination with initiator dilution in  $[AN]/[bpn] = 3200$  and  $[AN]/[bpn] = 6400$  experiments.

Figure 5 reveals that the molecular weight was controlled well with increasing conversion even in these systems with relatively few chains. The molecular

weight distribution remained narrow, and PDI = 1.18 was achieved for a molecular weight as large as 80,000 (Fig. 6). This was the first successful attempt at a single-pot ATRP starting with high initiator dilution and leading to PAN with a molecular weight higher than 80,000 and a narrow polydispersity as low as 1.2. In comparison, Grimaud and Matyjaszewski<sup>21</sup> reported higher polydispersities at  $M_n = 103,900$ . Hovestad et al.<sup>22</sup> observed the loss of PDI control for monomer-to-initiator ratios larger than 500.

### CONCLUSIONS

Laboratory studies of the ATRP of AN have shown that PAN with a molecular weight higher than 80,000 and a narrow polydispersity as low as 1.18 can be obtained by a one-pot synthesis in DMF with a CuBr/IPA/BPN initiation system. Polymerizations of AN appear to require an induction period. The induction period is shorter in DMF than in propylene carbonate and toluene, and the rate of the polymerization in DMF is fastest. DMF provides very good control at a polymerization rate quite acceptable for obtaining high-molecular-weight PAN. Using Cl in either the

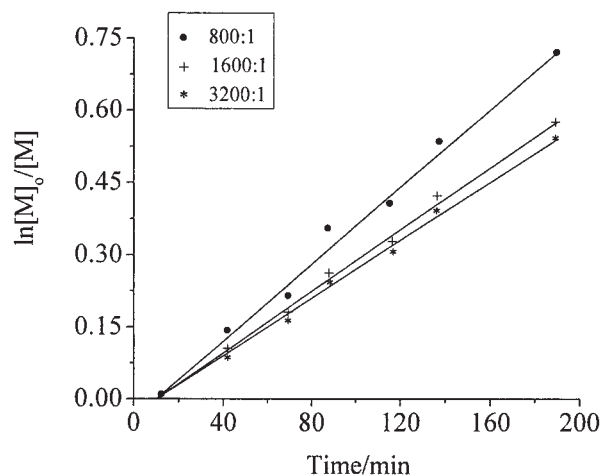


Figure 4 First-order kinetic plot of the monomer consumption as a function of time with different  $[AN]/[bpn]$  ratios during the ATRP of AN with  $[AN] = 5.0M$  and  $[CuBr]/[ipa] = 1:3$  at  $60^\circ C$  in DMF.

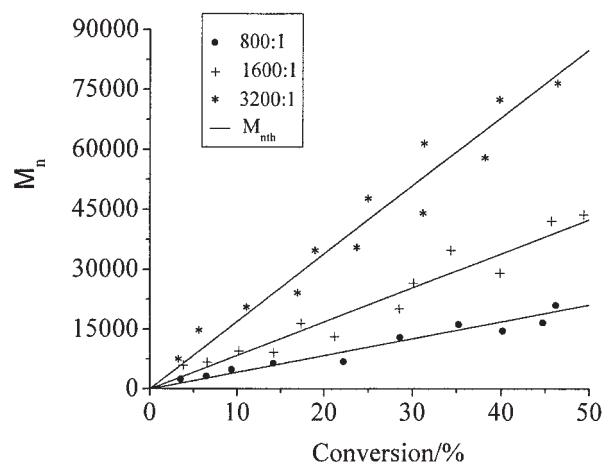
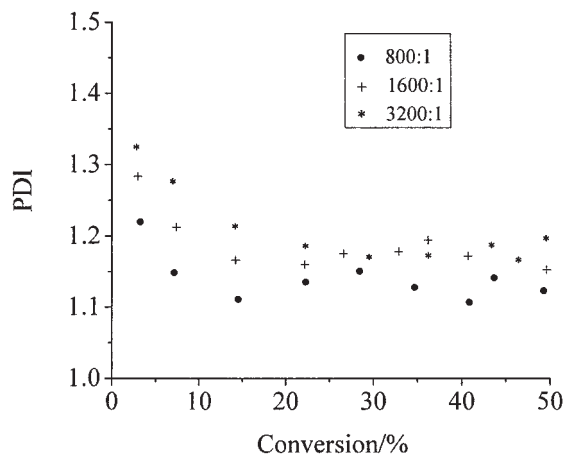


Figure 5 Dependence of  $M_n$  on the monomer conversion with different  $[AN]/[bpn]$  ratios for the ATRP of AN with  $[AN] = 5.0M$  and  $[CuBr]/[ipa] = 1:3$  at  $60^\circ C$  in DMF ( $M_{nth}$  = theoretical number-average molecular weight).



**Figure 6** Dependence of PDI on the monomer conversion with different  $[AN]/[bpn]$  ratios for the ATRP of AN with  $[AN] = 5.0M$  and  $[CuBr]/[ipa] = 1:3$  at  $60^{\circ}C$  in DMF.

initiator or the catalyst results in a decrease in the rate of polymerization, and the molecular weight deviates from the theoretical predication significantly. The polydispersity shows a trend of increasing along with conversion, especially for the  $CuCl/CPN$  system.

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