Well-Defined High-Molecular-Weight Polyacrylonitrile via Activators Regenerated by Electron Transfer ATRP

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Introduction. Polyacrylonitrile (PAN) is an important precursor for high value carbon-based materials, such as carbon-fiber composites with high chemical and mechanical resistance,[1] and mesoporous carbons for use in photoelectronic devices.[2−4] Two of the essential requirements that PAN precursors for high-performance carbon materials must possess are high molecular weight (MW) and well-controlled architecture.[5,6] Normally, commercially available high-molecular-weight PAN (MW < 10^6) is prepared by conventional radical polymerization,[7] and therefore it is difficult to control molecular weight distribution (typically, $M_w/M_n > 3$). Similarly, it is difficult to control the chain architecture and microstructure of the polymer. A commonly employed alternative for preparing high-MW PAN with low polydispersity is anionic polymerization, but this technique yields branched structures which affects the mechanical performance of PAN fibers prepared from this polymer.[8] The primary objective of this study was the preparation of well-defined, linear, high-MW PAN by applying a new robust polymerization technique: activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP).

Controlled radical polymerization (CRP), which has undergone significant progress in the past decade, enables the facile synthesis of polymers with controlled molar mass, low polydispersity, well-defined architecture, and site-specific functionalities.[9−24] All the major CRP processes, atom transfer radical polymerization (ATRP),[25,26] nitroxide-mediated polymerization (NMP),[27,28] and reversible addition−fragmentation chain transfer polymerization (RAFT)[29,30] have been successfully used to prepare PAN with low-to-moderate chain length and narrow molecular weight distribution. However, there has been no report on a CRP of PAN with molecular weight in excess of 100 000 g/mol and narrow MWD. For example, our group reported that in a standard ATRP of AN the highest achievable molecular weight with low polydispersity ($M_w/M_n < 1.5$) was lower than 30 000 g/mol.[26] One possible reason for this limitation is a side reaction between the growing radicals and the copper catalysts. The Cu^IX catalyst can participate in the outer-sphere electron transfer (OSET) reactions resulting in reduction of a radical to a carbanion that rapidly abstracts adventitious protons, resulting in loss of control over the reaction.[26]

Recently, activators regenerated by electron transfer (ARGET) ATRP, a new initiation process for a controlled/“living” radical polymerization, has been developed.[31−36] This method allows an ATRP process to be conducted with a very active copper catalyst in significantly low concentration (several ppm) in the presence of an excess of appropriate reducing agent (e.g., metallic copper, tin(II) 2-ethylhexanoate, glucose, or ascorbic acid) without losing control over the polymerization. In an ARGET ATRP, the excess Cu^{II} deactivator formed by the persistent radical effect[37−39] is continuously regenerated to ATRP activator, the Cu(I) species, by an excess of reducing agents. The use of reducing agents allows starting ATRP with the oxidatively stable Cu(II) species; it may also compensate for the presence of air or some other radical traps in the system so that the polymerization can be performed well in the presence of limited amounts of air. Therefore, this robust catalytic system, ARGET ATRP, is a huge step toward development of a viable process for industrial scale production.

We have determined that the use of ARGET ATRP also enables formation of high-MW polymers with low polydispersity because the minute amount of copper catalyst drastically suppresses side reactions caused by ATRP catalysts. Our recent research has revealed that high-MW styrene−acrylonitrile (SAN) copolymers could be successfully prepared by ARGET ATRP.[40] The M_n of SAN copolymer approached 200 000 with a polydispersity PDI < 1.3. In this paper, we report the appropriate reaction conditions (i.e., initiators, reducing agents, solvents, and temperatures) for the synthesis of well-defined high-MW PAN by ARGET ATRP.

Results and Discussion. ARGET ATRP of acrylonitrile was conducted with $Cu^{II}Cl_2$/tris[(2-pyridyl)methyl]amine (TPMA) as the catalyst. In order to ensure that the polymerization continued, the concentration of the reducing agent (e.g., tin(II) 2-ethylhexanoate ($Sn(EH)_2$)) was about 10 times that of the copper catalyst. Since PAN is not soluble in AN monomers, 2.5 vol equiv of an appropriate solvent to monomer was added to the reaction to allow the polymerization to be conducted under homogeneous conditions. Gel permeation chromatography (GPC) of PAN in *N*,*N*-dimethylformamide (DMF) as the eluent significantly overestimates the molecular weight of the PAN in comparison with linear polystyrene standards.[41] Because of this, GPC with a multiangle laser light scattering detector (MALLS-GPC) was used to determine the absolute molecular weights of the PAN. After comparing the results from the two procedures, it was concluded that the measured absolute molecular weights by MALLS were 2.5−2.7 times smaller than those estimated from linear polystyrene standards GPC (M_w GPC) (as shown in Table S1 of the Supporting Information). In the following discussion, the absolute molecular weights of all the polymers were characterized as $M_{n,GPC}/2.5$ with acceptable errors, where $M_{n,GPC}$ was the number-average molecular weight measured by GPC using linear polystyrenes as the calibration standards.

Entries 1−3 in Table 1 show the results of three ARGET ATRP of AN carried out with $Sn(EH)_2$ as the reducing agent in ethylene carbonate (EC) at 65 °C. Typically, molecular weights increased with conversion and polydispersity remained low throughout the polymerization. Two different catalyst concentrations, 75 and 25 ppm vs monomer, were used (Table 1, entries 1 and 2) to study the effect of different amounts of copper catalyst on the polymerization. The SEC (size exclusion chromatography) traces in Figure 1 exhibited a smooth shift of the entire molecular weight distribution toward high molecular weight in both reactions. Polydispersity increased with increase in monomer conversion. This increase in PDI was accompanied by the appearance of a tail, and eventually a low-molecular-weight shoulder, which may indicate the formation of dead chains caused by side reactions. When the GPC curves from

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Table 1. ARGET ATRP of Acrylonitrile[a]

	molar ratio											
entry	initiator	AN	$Cu^{II}Cl_2$	RA[b]	TPMA	Cu (ppm)	solvent	T (°C)	time (h)	conv[c] (%)	$M_{n,GPC}$[d]/2.5 (×103)	PDI[d]
1	BPN:1	2000	0.15	1.0	1.15	75	EC	65	69.5	55.8	57.0	1.47
2	BPN:1	2000	0.05	0.5	0.55	25	EC	65	69.5	52.8	76.2	1.27
3	EBiB:1	2000	0.05	0.5	0.55	25	EC	65	118.0	69.0	93.5	1.29
4	BPN:1	4000	0.20	2.0	2.20	50	EC	65	49.9	50.0	128.0	1.28
5	BPN:1	4000	0.20	2.0	2.20	50	DMSO	65	43.5	49.0	132.1	1.27
6	BPN:1	4000	0.20	2.0	2.20	50	DMSO	40	288.0	69.0	161.3	1.18
7	BPN:1	10000	0.50	5.0	5.50	50	DMSO	65	122.2	42.7	216.2	1.45
8	diBiB:0.5	4000	0.20	2.0	2.20	50	DMSO	65	90.0	69.8	284.8	1.80

[a] $[AN]_0 = 4.34$ M. [b] RA = reducing agent, $Sn(EH)_2$ for entries 1−3; glucose for entries 4−8. [c] Measured by ^1H NMR spectroscopy in DMSO-d_6. [d] Measured by GPC in DMF with polystyrene calibration.

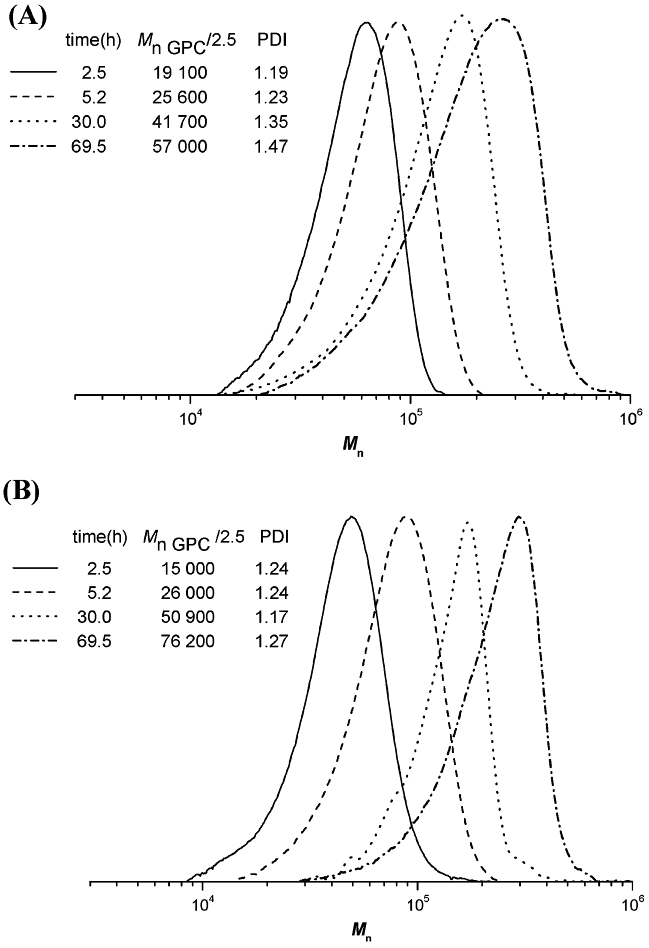

Figure 1. Evolution of SEC traces for ARGET ATRP of acrylonitrile with 75 ppm (A) and 25 ppm (B) of copper catalyst (Table 1, entries 1 and 2) in ethylene carbonate at 65 °C. $[AN]_0 = 4.43$ M. (A) AN/BPN/$Cu^{II}Cl_2$/TPMA/$Sn(EH)_2$ = 2000:1:0.15:1.15:1. (B) AN/BPN/$Cu^{II}Cl_2$/TPMA/$Sn(EH)_2$ = 2000:1:0.05:0.55:0.5.

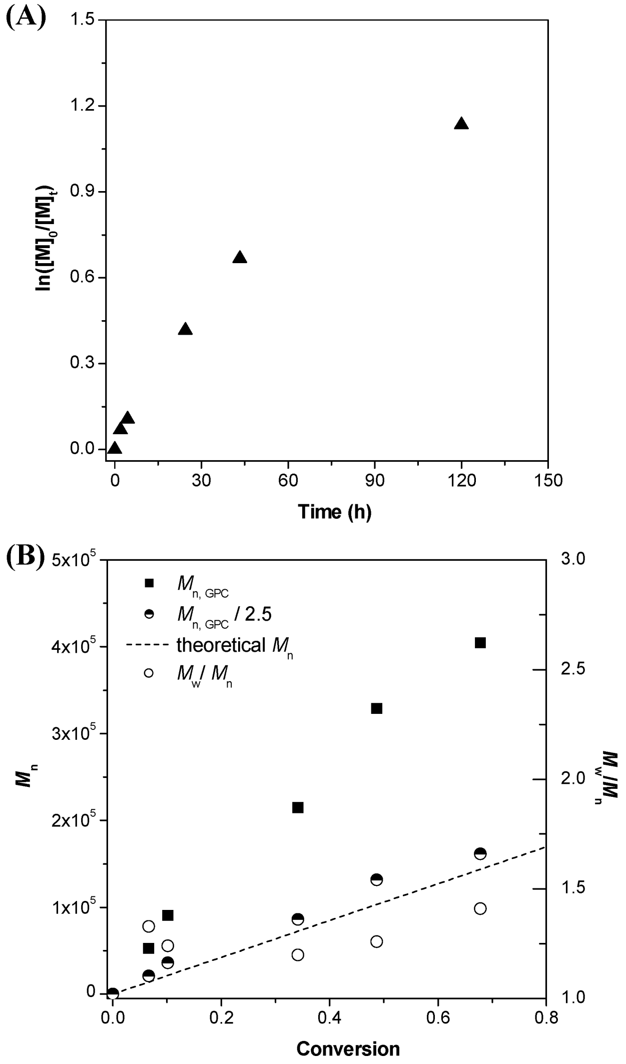

Figure 2. Kinetics (A) and evolution of molecular weights and M_w/M_n (B) with monomer conversion in ARGET ATRP of AN with glucose as the reducing agent in DMSO at 65 °C (Table 1, entry 5). AN/BPN/$Cu^{II}Cl_2$/TPMA/$Sn(EH)_2$ = 4000:1:0.20:2.20:2.0. $[AN]_0 = 4.43$ M.

the polymer prepared with 75 ppm copper catalyst are compared with the results from the one with 25 ppm copper catalyst, the polymer formed in the presence of the lower level of catalyst contained less dead chains and consequently had lower polydispersities. This phenomenon indicates that lowering the amount of copper catalyst is the key to controlling the ATRP of AN; furthermore, keeping the catalyst concentration as low as possible is an effective procedure to overcome the previous MW limit. A less reactive initiator, ethyl 2-bromoisobutyrate (EBiB), was also used for ARGET ATRP of AN (Table 1, entry 3). High-MW ($M_{n,GPC}/2.5 > 90$K) polymer with low polydispersity (PDI < 1.3) was prepared in 69% yield.

In order to reduce the absolute amount of any metals used in an ARGET ATRP, the organic reducing agent glucose was examined for the ARGET ATRP of AN because of its enhanced solubility in polar solvents and its lower environmental impact. The polymerization was also well controlled as shown in Table 1, entry 4.

Ethylene carbonate solvent is a solid at room temperature (mp ∼ 37 °C), which complicates the setting up the reaction; therefore another solvent, with a lower melting point, dimethyl sulfoxide (DMSO), was also examined (Table 1, entry 5). The first-order kinetic plot of the polymerization of AN in DMSO (Figure 2A) after 60 h (>50% conversion) showed some curvature, indicating the decrease of radical concentration due

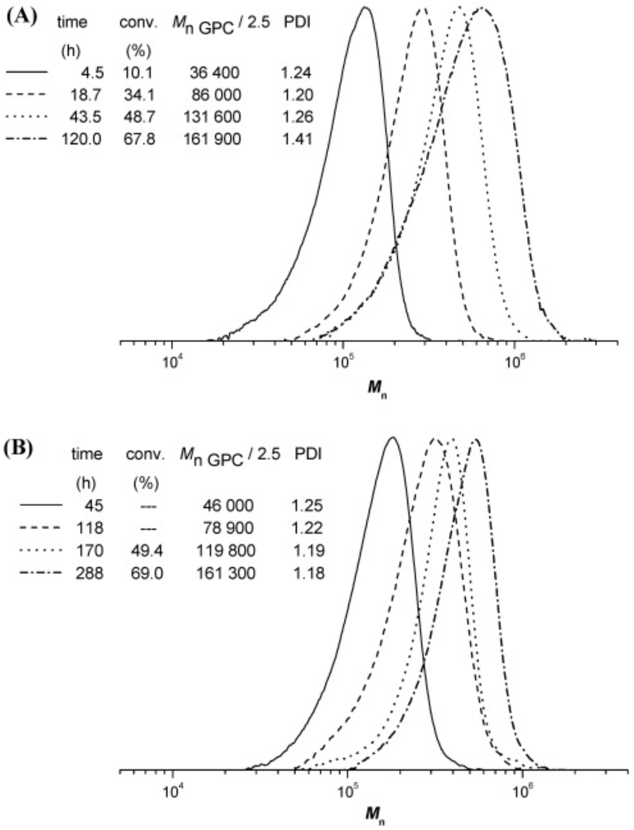

Figure 3. Evolution of SEC traces for ARGET ATRP of AN with glucose as the reducing agent in DMSO. (A) At 65 °C (Table 1, entry 5) and (B) at 40 °C (Table 1, entry 6). AN/BPN/$Cu^{II}Cl_2$/TPMA/Sn(EH)$_2$ = 4000:1:0.20:2.20:2.0. $[AN]_0$ = 4.43 M.

to small contribution of side reaction with copper catalyst (either OSET or oxidation). Figure 2B shows that molecular weights increased in a linear fashion with increasing conversion and that the absolute molecular weights ($M_{n,GPC}/2.5$) were close to the theoretical values determined by the ratio of initial monomer and initiator concentrations (i.e., $M_{n,theo} = 53[AN]_0/[BPN]_0$). This means that the initiator efficiency of the polymerization was close to unity.

Typically, the relative rate of side reactions in radical polymerization increases with temperature. This is also applicable to the side reactions in the ATRP processes, meaning that at lower reaction temperatures the side reactions are suppressed. Figure 3 exhibits the SEC traces of AGRET ATRP of AN in DMSO at 65 and 40 °C (Table 1, entries 5 and 6). The polydispersities of polymers prepared at 40 °C were lower than those prepared at higher temperature and continued to decrease throughout the reaction, indicating that side reactions were effectively reduced at lower temperature, although the polymerization occurred over a longer time. The final molecular weight of the PAN approached 161 000, and polydispersity was only 1.18.

The attempts to prepare well-defined PAN with even higher molecular weights were also carried out (Table 1, entries 7 and 8). With a higher ratio of $[AN]_0/[BPN]_0$ (~10 000), the absolute molecular weight of the PAN exceeded 200 000 at monomer conversion 40%. However, the reaction rate was slow, and the polydispersity was relatively high (~1.45). The use of ethylene glycol bis(2-bromoisobutyrate) as a difunctional initiator in an ARGET ATRP, which allows the linear PAN chains to grow in two directions, resulted in preparation of PAN with $M_n >$ 280 000, although the molecular weight distribution was relatively broader. This could be due to intrinsic transfer and termination reactions typical for any radical process.

Conclusions. This paper reports the successful synthesis of well-defined high-molecular-weight polyacrylonitrile by ARGET ATRP. The very small amount of copper catalyst (typically 25−75 ppm) used in the system effectively suppressed the occurrence of side reactions, such as OSET reduction of an active growing radical to a carbanion by Cu^IX. Well-controlled polymerizations were carried out with both Sn(II) and glucose as an organic reducing agent, yielding PAN with high molecular weight (>100 000) and low polydispersity (<1.30).

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Supporting Information Available: Experimental details for synthetic procedures and analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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