

# An Iron-Based Reverse ATRP Process for the Living Radical Polymerization of Acrylonitrile

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**ABSTRACT:** A hexa-substituted ethane thermal iniferter, diethyl-2,3-dicyano-2,3-di(*p*-tolyl) succinate (DCDTS), was firstly used as the initiator in the reverse atom transfer radical polymerization (RATRP) of acrylonitrile. FeCl<sub>3</sub> coordinated by isophthalic acid (IA) was used as the catalyst in this system. The polymerization in *N,N*-dimethylformamide not only shows the best control of molecular weight and its distribution but also provides rather rapid reaction rate with the ratio of [AN] : [DCDTS] : [FeCl<sub>3</sub>] : [IA] at 500 : 1 : 2 : 4. The polymers obtained

were end-functionalized by chlorine atom, and they were used as macroinitiators to proceed the chain extension polymerization in the presence of FeCl<sub>2</sub>/IA catalyst system via a conventional ATRP process and polyacrylonitrile obtained was with  $M_n = 39,260$ , PDI = 1.25. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1575–1580, 2007

**Key words:** atom-transfer radical polymerization; living polymerization; kinetics

## INTRODUCTION

Carbon fiber composites are important construction materials in applications where high strength and modulus, high thermal and corrosion resistance, and light weight are the prime requirements.<sup>1</sup> The properties of the final carbon fibers are determined by the nature of acrylic precursor fibers. High molecular weight and narrow polydispersity are essential requirements for synthesis of polyacrylonitrile (PAN) polymers satisfying the requirements for high-performance acrylic precursor fibers.<sup>2</sup> PAN is usually prepared by radical polymerization without control.<sup>3</sup> Living/controlled free-radical polymerization can be used as an alternative. Atom-transfer living radical polymerization (ATRP) is one of the most widely used methods. ATRP of acrylonitrile (AN) has been studied systemi-

cally.<sup>4–7</sup> However, transition-metal-catalyzed ATRP has two major drawbacks: toxicity of the halide species RX and oxidation of the catalyst by oxygen in air. To overcome these drawbacks, the use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state has been reported and referred to as reverse ATRP (RATRP) by Matyjaszewski and coworkers, and Kamigaito et al.,<sup>8–11</sup> and the other researchers.<sup>10–13</sup> It is important to find new initiators and new catalytic systems that are less toxic to human health for RATRP. Azo- and peroxide compounds were employed as the initiator in the RATRP system.<sup>14,15</sup> It is well known that the decomposition of conventional initiators is irreversible, which makes the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature. The development of new-type initiators for RATRP, using carbon–carbon bond initiator, is of interest. This new-type initiator could provide the initiation step of RATRP, in which the initiator reversibly decomposes to primary radicals, unlike other conventional initiators resulting in suitable amounts of primary radicals being generated. Qiu and coworkers<sup>16</sup> has introduced a carbon–carbon bond thermal initiator, diethyl-2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), instead of AIBN into RATRP system for methyl methacrylate polymerization. Acids were generally believed to deactivate the metal organic catalyst, resulting in poor control of the polymerization. However, acids, which are inexpensive and nontoxic, complex more easily with iron and can be used as a ligand. Zhu<sup>17</sup> has reported ATRP of styrene catalyzed by FeCl<sub>2</sub>/succinic acid.

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In this study, a new catalytic system based on iron complexes with isophthalic acid was firstly used. The first successful attempt of the well-controlled RATRP of AN in *N,N*-dimethylformamide with a thermal iniferter, DCDTS, and FeCl<sub>3</sub> complexed with isophthalic acid as a catalyst was described. Effect of FeCl<sub>3</sub>/IA catalyst system on RATRP of AN was investigated.

## EXPERIMENTAL

### Materials

Analytical-reagent-grade acrylonitrile (AN, Shanghai Chemical Reagents Co., Shanghai, China) was vacuum distilled from CaH<sub>2</sub> just before polymerization. Analytical-reagent-grade FeCl<sub>3</sub> (anhydrous) was prepared from FeCl<sub>3</sub> · H<sub>2</sub>O (Shanghai Chemical Reagents Co., Shanghai, China) treated with thionyl chloride according to reference procedure<sup>18</sup> and dried under vacuum at 60°C before use. DCDTS was prepared according to the method reported previously.<sup>19</sup> Analytical-reagent-grade isophthalic acid (IA) (Shanghai Chemical Reagents Co., Shanghai, China) was used as received without purification. *N,N*-dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents Co., Shanghai, China) was distilled at reduced pressure and stored over type 4-Å molecular sieves before use. Analytical-reagent-grade propylene carbonate, toluene, and dimethylsulfoxide (Shanghai Chemical Reagents Co., Shanghai, China) were used as received.

### Polymerization

A typical example of the general procedure was as follows. FeCl<sub>3</sub>, IA, and DMF were added to a dry tube under stirring, four cycles of vacuum nitrogen were applied to remove the oxygen. After the catalyst was dissolved, AN with DCDTS dissolved in advance was added via an argon-washed syringe. The tube was then sealed under nitrogen and immersed in an oil bath held at the desired temperature by a thermostat. After a definite time, the polymerization was terminated by cooling the flask in ice water. The polymerization product was dissolved in DMF. The resultant mixture was then poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C under vacuum.

### Characterization

The conversion of the monomer was determined gravimetrically. The molecular weight ( $M_n$ ) and polydispersity index (PDI) of AN polymers were measured by gel permeation chromatography (GPC). GPC was performed with a Waters model 515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL min<sup>-1</sup> through a combination of Waters HR1, HR3, and HR4

styragel columns. Poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 30°C with purified high-performance-liquid-chromatography-grade DMF as an eluent. A Waters model 2410 differential refractometer was used as the detector.

The molecular weight ( $\overline{M}_n$ ) of AN polymers was determined by the intrinsic viscosity measurements. The intrinsic viscosity  $[\eta]$  of AN polymers was measured at 25°C in DMF using an Ubbelohde viscometer,<sup>20</sup> and the molecular weight was calculated from the following equation:

$$[\eta] = 3.92 \times 10^{-4} \overline{M}_n^{0.75} \quad (1)$$

To compare with the aforementioned measurements of the molecular weight of AN polymers, the theoretical molecular weight ( $M_{th}$ ) was used. According to the characteristics of living polymerization,  $M_{th}$  could be calculated from the following equation:<sup>21</sup>

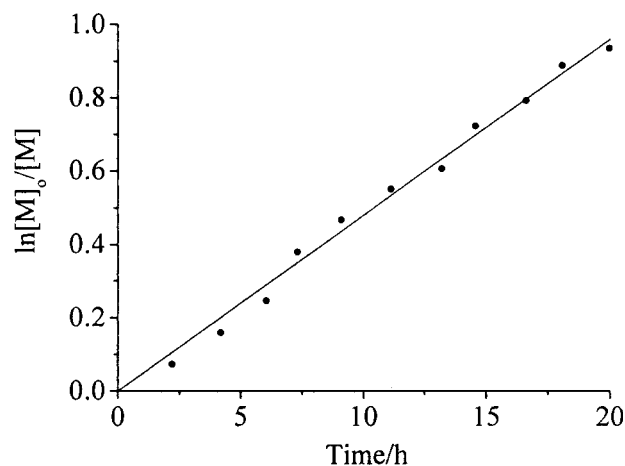
$$M_{th} = \frac{[AN]}{2[DCDTS]} \times M_{wAN} \times \text{Conversion} \quad (2)$$

where  $M_{wAN}$  is the molecular weight of AN.

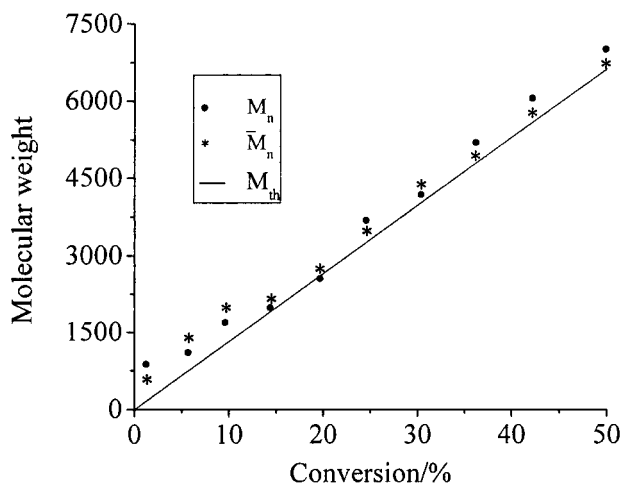
## RESULTS AND DISCUSSION

### Polymerization of AN with the DCDTS/FeCl<sub>3</sub>/IA initiating system

AN was polymerized catalyzed by FeCl<sub>3</sub>/IA with DCDTS as the initiator at 70°C ([AN] : [DCDTS] : [FeCl<sub>3</sub>] : [IA] = 500 : 1 : 2 : 4). After heating, a change of color from deep orange to light yellow was observed as described by Moineau et al.<sup>22</sup> This corresponds to the decomposition of DCDTS and the establishment of the equilibrium between Fe<sup>3+</sup> and Fe<sup>2+</sup>.



**Figure 1** First-order kinetic plot of monomer consumption as a function of time during RATRP of AN with [AN] = 8.0M and [AN] : [DCDTS] : [FeCl<sub>3</sub>] : [IA] = 500 : 1 : 2 : 4 at 70°C.



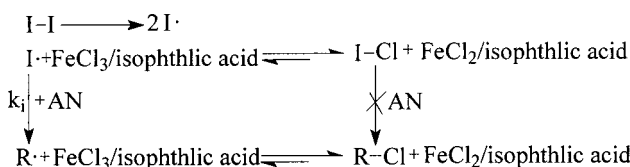
**Figure 2** Dependence of  $M_n$  on the monomer conversion for RATRP of AN with  $[AN] = 8.0M$  and  $[AN] : [DCDTS] : [FeCl_3] : [IA] = 500 : 1 : 2 : 4$  at  $70^\circ C$ .

Figure 1 shows kinetic plots of  $\ln[M]_0/[M]$  versus time. The linearity of the plot indicates that the polymerization is approximately first-order with respect to the monomer concentration. The slope of the kinetic plots indicates that in the polymerization process, the number of active species is constant. The monomer conversion reached about 61.7% within 20 h. The corresponding value of the apparent rate constant ( $k_p^{app}$ ) calculated from the kinetic plot is  $1.33 \times 10^{-5} s^{-1}$ .

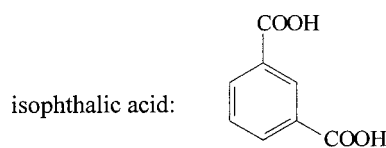
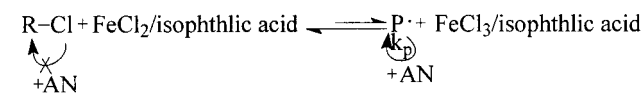
Figure 2 represents  $M_n$  and  $\bar{M}_n$  of the resulting polymers increases linearly with conversion. The high molecular weight at conversion less than 10% indicates there might have been too many primary radicals produced from the decomposition of DCDTS at the beginning of the reaction, which could not become dormant species by halogen transfer and undergo termination by combination reactions. A similar phenomenon has been observed.<sup>23</sup> The values of  $M_n$  determined by GPC agree well with those of  $\bar{M}_n$  determined by the intrinsic viscosity. Both  $M_n$  and  $\bar{M}_n$  agree reasonably well with the theoretical molecular weight ( $M_{th}$ ). The initiation efficiency  $f$  of DCDTS is calculated from  $f = M_{th}/M_n$  to be 0.91 (conversion = 61.7%). These results reveal that the polymerization of AN with DCDTS/ $FeCl_3$ /IA initiating system is a living/controlled radical polymerization process. A polymerization mechanism is proposed, as described in Scheme 1. In the initiation step, after the homolytic decomposition of one DCDTS (I-I) into two primary radicals (I $\cdot$ ), these radicals can add to the monomer. Then, the activated monomer radicals (R $\cdot$ ) react with  $FeCl_3$ /IA through chlorine atom transfer and generate the lower oxidation state metal complex,  $FeCl_2$ /IA. Finally, the polymer propagates via a conventional ATRP process.

The values of PDI of AN polymers are shown in Figure 3. The polydispersity are narrow (PDI = 1.18) when the conversion is from 15 to 50%. A broader

#### Initiation:



#### Propagation:

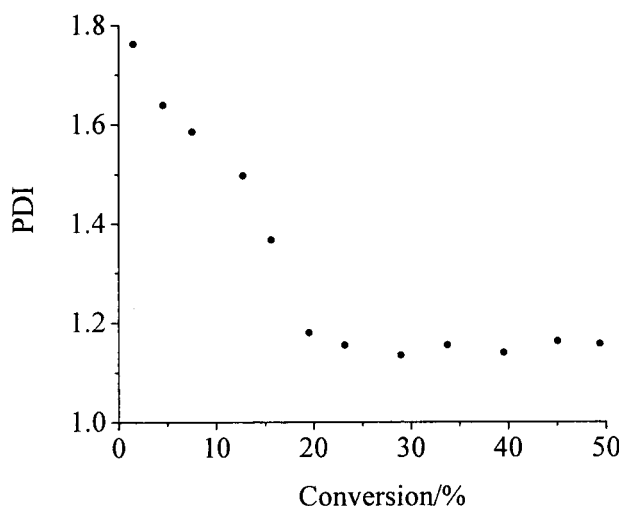


**Scheme 1** Mechanism of reverse ATRP of AN including the ligand structure.

polydispersity is obtained when the conversion is less than 15%. The slow rate of the primary radicals at  $70^\circ C$  produced from the decomposition of DCDTS changing into dormant species is responsible for the broader polydispersity during the initial polymerization in the reaction system. In other words, the RATRP system will set up as the conversion goes beyond 15%.

#### Effect of $FeCl_3$ /IA catalyst system on RATRP of AN

It has been reported that IA might decrease the initiator efficiency, leading to an increase in the observed molecular weight.<sup>24</sup> To further investigate the effects of IA, a series of experiments of RATRP of AN were carried out. The results have been compiled in Table I. In this study, different conclusions are drawn. As



**Figure 3** Dependence of PDI on the monomer conversion for RATRP of AN with  $[AN] = 8.0M$  and  $[AN] : [DCDTS] : [FeCl_3] : [IA] = 500 : 1 : 2 : 4$  at  $70^\circ C$ .

TABLE I  
Data for RATRP of AN Catalyzed by FeCl<sub>3</sub>/IA

Entry	[DCDTS] : [FeCl <sub>3</sub> ] : [IA]	Time (h)	Conversion (%)	$M_{th}$	$M_n$	$\overline{M}_w$	PDI	$k_p^{app}$ (10 <sup>7</sup> s <sup>-1</sup> )	Initiation efficiency
1	1:1:2	20	69.2	9169	11,610	11,780	1.25	1.64	0.79
2	1:2:4		61.7	8175	8980	9010	1.18	1.33	0.91
3	1:3:6		43.6	5777	6280	6320	1.17	0.79	0.92
4	1:4:8		32.9	4359	4690	4580	1.15	0.55	0.93
5	1:2:2		65.6	8692	9550	9620	1.19	1.48	0.91
6	1:2:5		53.5	7089	8440	8390	1.18	1.06	0.84
7	1:2:6		42.6	5645	7240	7280	1.20	0.77	0.78
8	1:1:4		66.5	8811	11,590	11,640	1.24	1.52	0.76
9	1:4:4		40.1	5313	5780	5820	1.16	0.71	0.92
10	1:5:4		28.9	3829	4070	4110	1.14	0.47	0.94

[AN] = 8.0M; [AN] : [DCDTS] = 500 : 1;  $T = 70^\circ\text{C}$ .

more FeCl<sub>3</sub>/IA catalyst system was added (entries 1, 2, 3, 4), slower polymerization rates and narrower molecular-weight distributions were observed, and the initiation efficiency also increased from 0.79 to 0.93, which suggests that the concentration of FeCl<sub>3</sub> has a favorable influence on the activation as well as equilibrium of RATRP. With increasing the amount of IA in the catalyst system (entries 2, 5, 6, 7), the rate of polymerization and initiation efficiency showed a trend of decrease while the molecular weight distribution of polymers remained narrow. This illustrates that a large amount of IA not only poison the metal catalyst, but also it has a role in producing a more significant side reaction, such as a reaction with active species, or catalyzing the elimination of the initiator. When the ratio of [FeCl<sub>3</sub>]/[IA] was changed from 1 : 4 to 5 : 4 (entries 2, 8, 9, 10), the molecular weight distribution of polymers decreased from 1.24 to 1.14, and the initiation efficiency increased from 0.76 to 0.94, but the rate of polymerization decreased prominently. This

implies that FeCl<sub>3</sub> itself is an effective catalyst in RATRP.

#### Effect of solvent on the polymerization

To study effect of solvents on RATRP of AN, DMF, propylene carbonate and toluene were used as solvents, respectively. Figure 4 shows kinetic plots of  $\ln[M]_0/[M]$  versus time for reverse ATRP of AN in three different solvents. The polymerizations are approximately first-order with respect to the monomer concentration. As shown in Figure 4, the rate of polymerization in DMF is unexpectedly faster than in propylene carbonate and toluene. A similar result was reported by Shenmin<sup>25</sup> for iron-mediated ATRP. The experimental data reported in this study are different from those reported by Pascual,<sup>26</sup> who used 2,2'-bipyridine, and Ziegler,<sup>27</sup> who used monodentate amines as the ligands in copper-mediated systems. They concluded that DMF affects the living nature of

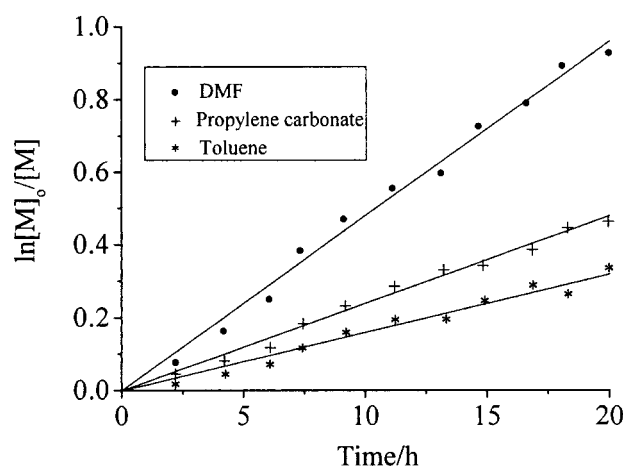


Figure 4 First-order kinetic plot of monomer consumption as a function of time in different solvents during reverse ATRP of AN with [AN] = 8.0M and [AN] : [DCDTS] : [FeCl<sub>3</sub>] : [IA] = 500 : 1 : 2 : 4 at 70°C.

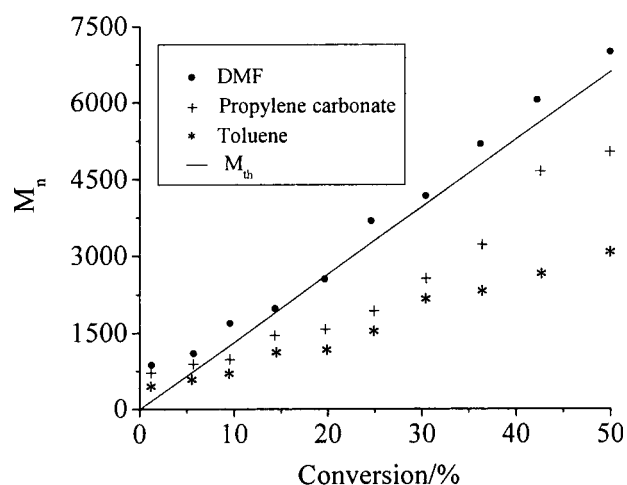


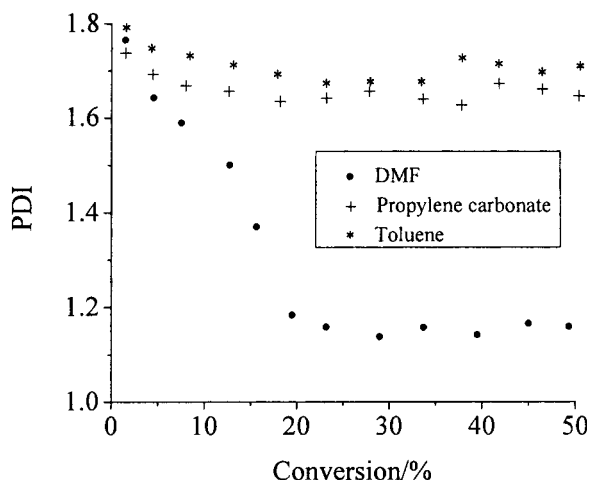
Figure 5 Dependence of  $M_n$  on the monomer conversion in different solvents for reverse ATRP of AN with [AN] = 8.0M and [AN] : [DCDTS] : [FeCl<sub>3</sub>] : [IA] = 500 : 1 : 2 : 4 at 70°C.

ATRP. In our RATRP system, DMF has no significant effect on the living nature if there is sufficient ligand to complex the transition metal. Figure 5 indicates that the molecular weights measured by GPC agree reasonably well with the theoretical molecular weight when DMF was used as the solvent. When using propylene carbonate as the solvent, the plot of the molecular weight shows an obvious curvature. When using toluene as the solvent, only AN oligomer was obtained. The thermal decomposition rate of DCDTS in propylene carbonate and toluene is not high and this may be the reason for increasing number of chains and the molecular weight departure from the theoretical molecular weight. It can be seen from Figure 6 that PDI of PAN decreases with increasing monomer conversion, reaching values of 1.18 at about 15% conversion for DMF systems.

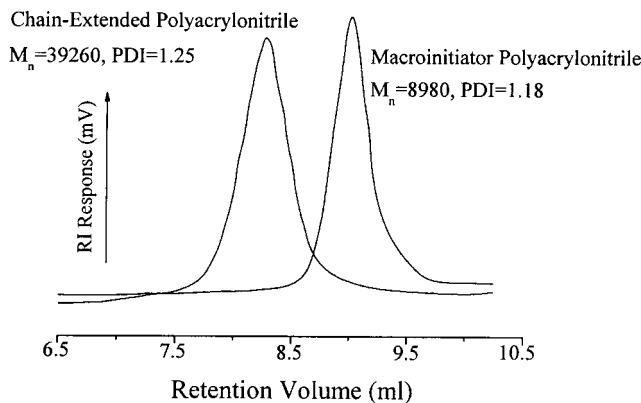
The polymerization is quite sensitive to the polarity of the solvent. When using propylene carbonate and toluene as the solvent, the polymerizations were heterogeneous due to the limited solubility of  $\text{FeCl}_3$  and IA in monomer. IA can not complex with  $\text{FeCl}_3$  sufficiently and fails to catalyze the polymerization. Addition of DMF increases the solubility of the catalyst in monomer and provides a homogeneous catalyst system. In addition, the polarity of the solvent can also affect the metal complex structure. In a polar solvent DMF,  $\text{Cl}^- \text{Fe}^{2+}(\text{IA})_2\text{Cl}^-$  may exist, but in a less polar solvent,  $(\text{IA})\text{FeCl}_3\text{Fe}(\text{IA})$  could exist.<sup>28</sup> Thus the DMF-based system provides the desired characteristics of high initiation efficiency, low polydispersity, and a fast polymerization rate.

### Chain extension of PAN

According to the initiation mechanism of DCDTS<sup>27</sup> and the mechanism polymerization of RATRP using DCDTS/ $\text{FeCl}_3$ /IA system, the well-defined PAN with



**Figure 6** Dependence of PDI on the monomer conversion in different solvents for reverse ATRP of AN with  $[\text{AN}] = 8.0\text{M}$  and  $[\text{AN}] : [\text{DCDTS}] : [\text{FeCl}_3] : [\text{IA}] = 500 : 1 : 2 : 4$  at  $70^\circ\text{C}$ .



**Figure 7** GPC curves of polyacrylonitrile before and after a chain extension reaction.

an  $\omega$ -chlorine atom end groups will be obtained in the polymerization of AN using DCDTS/ $\text{FeCl}_3$ /IA system. Therefore, the obtained PAN can act as a macroinitiator for the extension polymerization. It is reported that the limited solubility of PAN, even in its own monomer-AN, prevented the formation of high polymer using ATRP.<sup>29,30</sup> Thus in this study, DMF was used as the solvent to enable the formation of high molar mass PAN. The extension polymerization of the obtained PAN ( $M_n = 8980$ ,  $\text{PDI} = 1.18$ ) with AN was carried out in DMF at  $80^\circ\text{C}$  in the presence of the  $\text{FeCl}_2$ /IA catalyst system. As shown in Figure 7, when  $[\text{AN}] = 8.0\text{M}$ ,  $[\text{AN}] : [\text{PAN}] : [\text{FeCl}_2] : [\text{IA}] = 500 : 1 : 2 : 4$ ,  $t = 35$  h, the conversion was 95%. PAN obtained was with  $M_n = 39,260$ ,  $\text{PDI} = 1.25$ . It clearly demonstrates the chain extension of PAN takes place. The initiation efficiency  $f$  of the extension polymerization is calculated from  $f = M_{\text{th}}/M_n$  [ $M_{\text{th}} = 8980 + 53 \times ([\text{AN}]/[\text{PAN}] \times \text{conversion})$ ] to be 0.87.

### CONCLUSIONS

The new catalyst system, DCDTS/ $\text{FeCl}_3$ /IA, was successfully used in the RATRP of AN in DMF. When the ratio of  $[\text{AN}] : [\text{DCDTS}] : [\text{FeCl}_3] : [\text{IA}]$  equals  $500 : 1 : 2 : 4$ , the polymerization was best controlled. Increasing the dosage of the catalyst system would decrease the rate of polymerization and enhanced the degree of the controlled polymerization. PAN obtained was end-functionalized by chlorine atoms and can act as a macroinitiator for the extension polymerization. The resultant fibers obtained from AN polymers satisfy the requirements for high-performance PAN fibers and can be used to prepare carbon fibers.

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