

# ATRP of Acrylonitrile Catalyzed By FeCl<sub>2</sub>/Succinic Acid Under Microwave Irradiation

Chen Hou, Rongjun Qu, Chunnuan Ji, Chunhua Wang, Changmei Sun

College of chemistry and Materials Science, Yantai Normal University, Yantai 264025, China

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**ABSTRACT:** A single-pot atom-transfer radical polymerization (ATRP) under microwave irradiation was first used to successfully synthesize polyacrylonitrile. This was achieved by using FeCl<sub>2</sub>/succinic acid as the catalyst and 2-chloropropionitrile as the initiator. Using the same experimental conditions, the apparent rate constant under microwave irradiation was found to be higher than that under conventional heating. The FeCl<sub>2</sub>/succinic acid ratio of 1 : 2 not only gives the best control of molecular weight and its distribution but also provides rather rapid reaction rate.

When FeCl<sub>2</sub> was replaced with CuCl, ATRP of AN does not show an obvious living characteristics. To demonstrate the active nature of the polymer chain end, the polymers were used as macroinitiators to proceed the chain-extension polymerization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1598–1601, 2006

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

## INTRODUCTION

Atom-transfer radical polymerization (ATRP) is a new technique of living radical polymerization,<sup>1–3</sup> which has many advantages and great industrialization prospects in comparison with other living radical polymerizations. However, the main problem of ATRP is the larger amount of catalyst needed and the lower activity of the initiation system. Usually, a higher temperature and a greater catalyst concentration are required for a higher polymerization rate; these results in a reduced molecular weight, much lower than that obtained with the conventional radical polymerization process. To solve these problems, a new catalyst system with higher reactivity or additional measures to enhance the reactivity of the present catalyst system is needed. Microwave, as peculiar source of energy, has been widely applied to enhance chemical reactions.<sup>4,5</sup> The main benefit of performing reactions under microwave irradiation (MWI) is the significant rate enhancement, that is, it can enhance the reactivity of reaction system. MWI applied to enhance chemical reactions has become a hot topic.

Polyacrylonitrile (PAN) polymers with narrow polydispersity are essential precursors for synthesis of high-performance PAN fibers.<sup>6,7</sup> Recently, all ATRPs of acrylonitrile (AN) have almost been studied by a

conventional heating (CVH) method,<sup>8–13</sup> and there were no reports on ATRP under MWI. For this reason, MWI was applied to ATRP of AN by our group. Succinic acid, which is nontoxic and commercially available, complexes with iron easily.<sup>14</sup> In this study, a new catalytic system based on iron complexes with succinic acid was used. The living radical polymerization of AN with a new iron-based ATRP process under MWI was first described. Effects of the ratio of metal to ligand were investigated. Effects of the different transition metals on the polymerization were also discussed.

## EXPERIMENTAL

### Materials

Acrylonitrile (AN, Shanghai Chemical Reagents Co., A.R. grade) was vacuum distilled from CaH<sub>2</sub> just before polymerization. FeCl<sub>2</sub> (Shanghai Chemical Reagents Co., A.R. grade) was washed with absolute ethanol and dried under vacuum at 60°C before use. Succinic acid (SA, Shanghai Chemical Reagents Co., A.R. grade) was used as received. 2-chloropropionitrile (CPN) was obtained from Aldrich and used without further purification. *N,N*-Dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents Co.) was distilled at reduced pressure and stored over type4-Å molecular sieves before use.

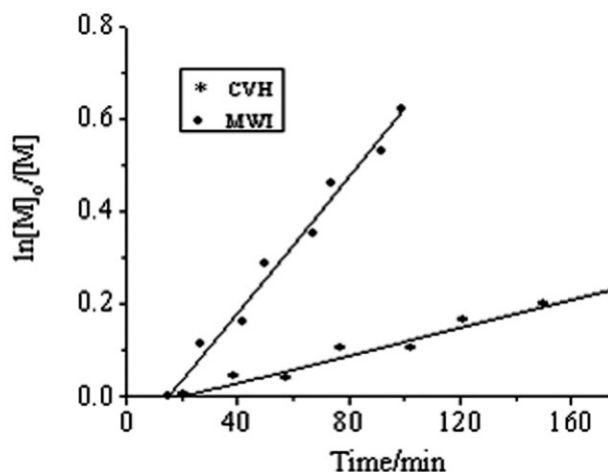
### Apparatus

A self-improved domestic microwave oven (Samsung) was used. Its irradiation power (*P*) was from 90 to 900 W. The reactor was a three-necked bottle (1000-mL) with a refluxing solvent used for controlling the reac-

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

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**Figure 1** Kinetics of ATRP of AN under MWI and CVH with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{CPN}] : [\text{FeCl}_2] : [\text{SA}] = 400 : 1 : 1 : 2$ .

tion temperature (the boiling point of the solvent). Dry and sealed glass tubes filled with  $\text{FeCl}_2$ , SA, CPN, and AN were placed in the refluxing solvent, so that polymerization could take place.

### Procedures of polymerization

A dry glass tube was filled with  $\text{FeCl}_2$ , SA, CPN, and AN. Three freeze-pump-thaw cycles were performed, and the tube was sealed in vacuo and placed in the self-improved microwave oven with a reflux of  $\text{CCl}_4$  at the boiling point ( $76.8^\circ\text{C}$ ) for a certain time under MWI (MWI power = 450 W), whereas under CVH, the tube was kept at  $76.8^\circ\text{C}$  in an oil bath. The polymerizations were stopped at a desired time by the cooling of the tubes in ice water. Afterward, the tubes were opened, and the contents were transferred and 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  $60^\circ\text{C}$  under vacuum.

### Characterization

The conversion of the monomer was determined gravimetrically. The molecular weight ( $M_n$ ) and polydispersity index (PDI) 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  $1.0\text{ mL min}^{-1}$  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  $30^\circ\text{C}$  with purified high-performance liquid chromatography grade DMF as an eluent. A Waters model 2410 differential refractometer was used as the detector.

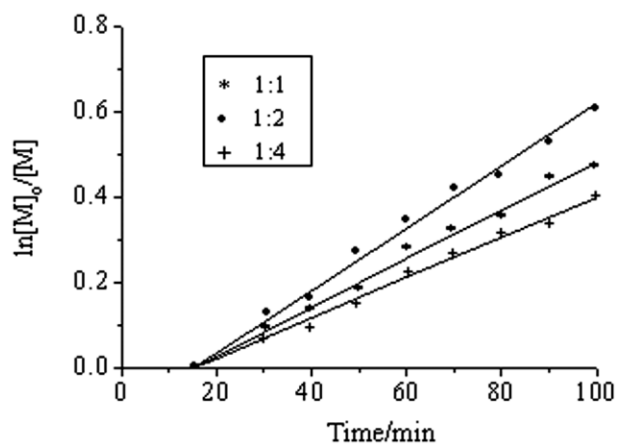
To compare with the aforementioned measurements of  $M_n$ , the molecular weight ( $\overline{M}_n$ ) of AN polymers was determined by the intrinsic viscosity measurements. The intrinsic viscosity  $[\eta]$  of AN polymers was measured at  $30^\circ\text{C}$  in DMF using an Ubbelohde viscometer,<sup>15</sup> and the molecular weight was calculated from the following equation

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

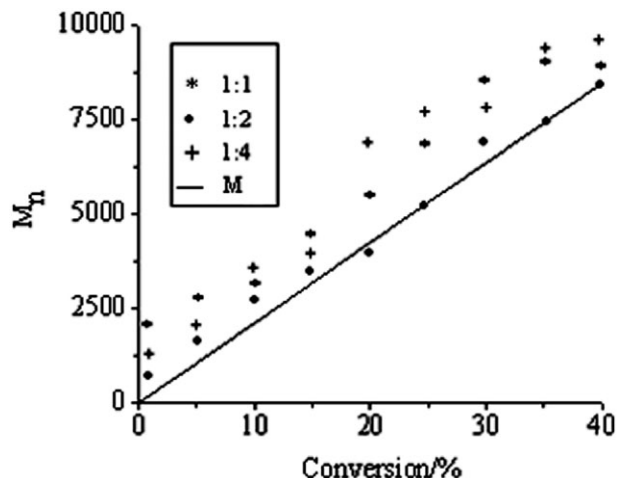
## RESULTS AND DISCUSSION

### ATRP of AN

ATRP of AN catalyzed by  $\text{FeCl}_2/\text{SA}$  was carried out. Figure 1 shows the kinetic plots of  $\ln([\text{M}]_0/[\text{M}])$  versus time for ATRP of AN, using different polymerization processes (MWI and CVH). A change of color from light yellow to deep orange was observed. This corresponds to the decomposition of CPN and the establishment of the equilibrium between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . 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, and the termination reactions can be neglected. According to the slopes of the kinetic plots, the apparent rate constant ( $k_p^{\text{app}}$ ) was calculated. The  $k_p^{\text{app}}$  under MWI ( $1.03 \times 10^{-4}\text{ s}^{-1}$ ) is much higher than that under CVH ( $2.22 \times 10^{-5}\text{ s}^{-1}$ ), which indicates that applying MWI can greatly enhance the rate of polymerization. As shown in Figure 1, ATRP of AN appears to require an induction period. The induction period becomes shorter under MWI (15 min) than that under CVH (20 min). The induction period is perhaps caused for two reasons: the presence of oxygen and impurities and the slow formation of the catalytic center.<sup>16,17</sup>



**Figure 2** Kinetics of ATRP of AN at various ratios of  $[\text{FeCl}_2]/[\text{SA}]$  under MWI with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{CPN}] : [\text{FeCl}_2] = 400 : 1 : 1$

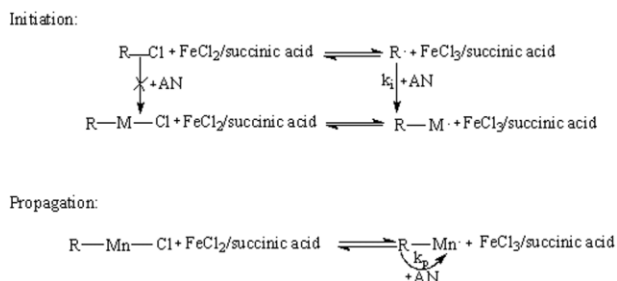


**Figure 3** Dependence of  $M_n$  on the monomer conversion at various ratios of  $[\text{FeCl}_2]/[\text{SA}]$  under MWI for ATRP of AN with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{CPN}] : [\text{FeCl}_2] = 400 : 1 : 1$ .

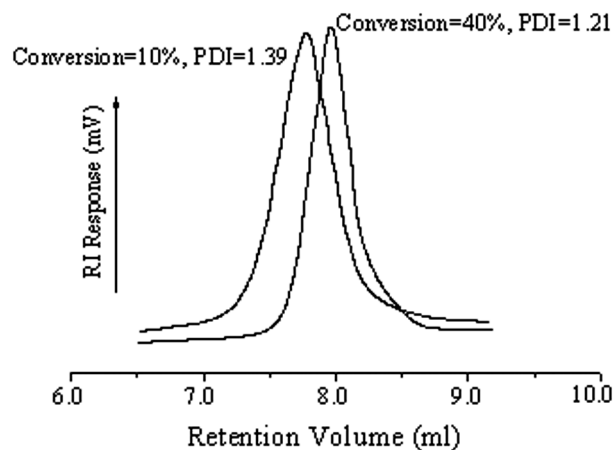
A similar result was reported by Zhu et al.<sup>18</sup> for copper-mediated ATRP of methyl methacrylate under MWI. They reported that MWI increases the dissolution of transition metals in the system; this may be one of the reasons that applying MWI to polymerization can enhance the rate of polymerization.

#### Effect of the ratio of $\text{FeCl}_2/\text{SA}$ on ATRP of an under MWI

A series of experiments of ATRP of AN under MWI were carried out at the different  $\text{FeCl}_2/\text{SA}$  ratios. Figure 2 shows kinetic plots of  $\ln[M]_0/[M]$  versus time for ATRP of an catalyzed by  $\text{FeCl}_2/\text{SA}$  and initiated by CPN. The polymerizations are approximately first-order with respect to the monomer concentration. The monomer conversion reached about 38.1, 46.2, 32.9 corresponding to 1 : 1, 1 : 2, 1 : 4 of  $[\text{FeCl}_2]$  to  $[\text{SA}]$  ratios within 100 min, respectively. The value of the apparent rate constant ( $k_p^{\text{app}}$ ) calculated from the kinetic plot is  $8.01 \times 10^{-5}$ ,  $1.03 \times 10^{-4}$ ,  $6.67 \times 10^{-5} \text{ s}^{-1}$  corresponding to 1 : 1, 1 : 2, 1 : 4 of  $[\text{FeCl}_2]$  to  $[\text{SA}]$  ratios. The apparent rate constant corresponding to the ratio of 1 : 2 is the highest one. Lower or higher concentrations of ligand result in the low reaction rate.



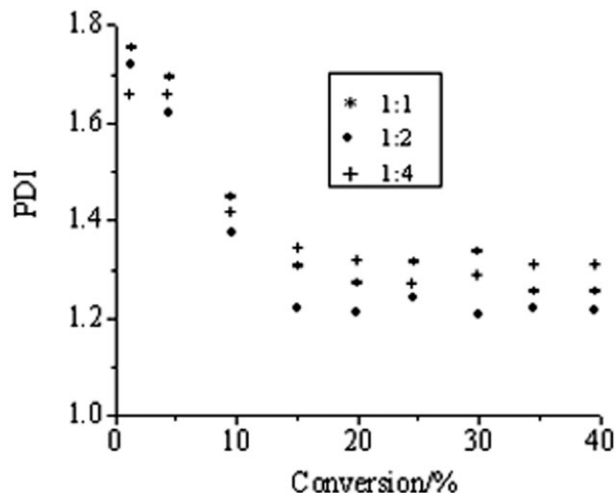
**Scheme 1** Polymerization mechanism of ATRP of AN.



**Figure 4** GPC curves of polyacrylonitrile at different conversion with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{CPN}] : [\text{FeCl}_2] : [\text{SA}] = 400 : 1 : 1 : 2$ .

Figure 3 represents the molecular weights of the resulting polymers increases linearly with conversion. The higher molecular weight at conversion less than 15% indicates that there might have been too many primary radicals produced from the decomposition of CPN at the beginning of the reaction, which could not become dormant species by halogen transfer and undergo termination by combination reactions. The molecular weights match the theoretical values very well when the ratio of  $[\text{FeCl}_2]/[\text{SA}]$  is 1 : 2. The plot of the molecular weight shows an obvious curvature corresponding to 1 : 1, 1 : 4 of  $[\text{FeCl}_2]$  to  $[\text{SA}]$  ratios.

These results reveal that the polymerization of AN with CPN/ $\text{FeCl}_2/\text{SA}$  initiating system is a living/controlled radical polymerization process. A polymerization mechanism is proposed, as described in Scheme 1. The initiating radicals are generated from



**Figure 5** Dependence of PDI on the monomer conversion at various ratios of  $[\text{FeCl}_2]/[\text{SA}]$  for ATRP of AN under MWI with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{CPN}] : [\text{FeCl}_2] = 400 : 1 : 1$ .

TABLE I  
Data for ATRP of AN Catalyzed by  $\text{CuCl}/\text{SA}$   
Under MWI

Time (min)	Conversion (%)	$M_{th}$	$M_n$	$\bar{M}_n$	PDI
20	0	—	—	—	—
40	8.42	1,785	58,750	60,380	2.12
60	18.5	3,922	73,520	74,060	2.18
80	30.3	6,424	91,230	89,750	2.35

R—Cl, which is activated in the presence of a transition metal complex in its lower oxidation state ( $\text{FeCl}_2$ /succinic acid).

Figure 4 shows the GPC curves of PAN at different conversion with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{CPN}] : [\text{FeCl}_2] : [\text{SA}] = 400 : 1 : 1 : 2$ . The polydispersity index reached about 1.39, 1.21 corresponding to 10, 40% of monomer conversion, respectively. It is obvious that the polydispersity index of the resulting polymers shows a trend of decrease with the increase of polymerization conversion. It can also be seen from Figure 5 that a broader polydispersity is obtained when the conversion is less than 10%, and the polydispersity index of the resulting polymers is narrow when the conversion goes beyond 15%. This suggests that the conventional radical polymerization takes place during the initial polymerization in the reaction system. The polydispersity index is 1.21 when the ratio of  $[\text{FeCl}_2]/[\text{SA}]$  is 1 : 2, and the polydispersity index becomes higher corresponding to 1 : 1, 1 : 4 of  $[\text{FeCl}_2]$  to  $[\text{SA}]$  ratios, respectively.

The aforementioned results illustrate that a large amount of acid 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.

#### Effect of the different transition-metal ions

The effect of the different transition metals on ATRP under MWI was investigated in the polymerization of AN with  $[\text{AN}] = 6.0\text{M}$  and  $[\text{AN}] : [\text{AIBN}] : [\text{CuCl}] : [\text{SA}] = 400 : 1 : 1 : 2$ . Table I shows the outcomes for the polymerization of AN with  $\text{CuCl}/\text{SA}$  as the catalyst system. From Table I, we can see that there is an induction period. After this period, the molecular weight increases with monomer conversion, which shows somewhat living characteristics. However, the measured molecular weight is much higher than the calculated values, and the molecular weight distribution is rather wide. This is presumably due to the coordination of carboxyl group to the copper catalyst, so the living species seems rather active, which leads to radical-radical termination as reported by Xia and Matyjaszewski.<sup>19</sup>

#### Chain extension of polyacrylonitrile

An additional method toward verifying the functionality of a polymer prepared by ATRP is as a macroinitiator for the same or other monomers.<sup>20</sup> The chain extension polymerization of AN with PAN ( $M_n = 8450$ ; PDI = 1.21) as the macroinitiator under MWI was successfully performed. The polyacrylonitrile (PAN) obtained was with  $M_n = 35,680$ ; PDI = 1.28. It clearly demonstrates the chain extension of PAN takes place. However, the molecular weight distribution (1.28) is a little broader than that of the macroinitiator (1.21), because a part of the macroinitiator probably is not active. The chain-extension polymerization of the obtained PAN verifies the active nature of the precursor chain end.

#### CONCLUSIONS

The new catalyst system,  $\text{FeCl}_2/\text{SA}$ , was successfully used in ATRP of AN under MWI. The apparent rate constant under MWI is higher than that under CVH in the same experimental conditions. When the ratio of  $\text{FeCl}_2/\text{SA}$  equals 1 : 2, the polymerization was best controlled. When  $\text{FeCl}_2$  was replaced with  $\text{CuCl}$ , ATRP of AN does not show an obvious living characteristics. PAN obtained can act as a macroinitiator for the extension polymerization.

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