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$FeCl_3$/Acetic Acid-mediated Reverse Atom Transfer Radical Polymerization of Acrylonitrile

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Reverse atom transfer radical polymerization (RATRP) has been successfully applied in the synthesis of polyacrylonitrile (PAN) with $FeCl_3$/acetic acid as catalyst in the presence of conventional initiator azobisisobutyronitrile (AIBN) at 65°C in N,N-dimethylformamide (DMF). A $FeCl_3$ to acetic acid ratio of 1:2 not only gave better control on polymer's molecular weight and its distribution, but also provided a rapid polymerization rate compared with any other molar ratio of $FeCl_3$ to acetic acid. The polymerization rate increased with increasing temperature and the apparent activation energy was calculated to be 80.6 $kJ\cdot mol^{-1}$. In comparison with dimethyl sulfoxide, acetonitrile, cyclohexanone and ethyl acetate, DMF was considered to be the best solvent of the polymerization for its polarity. Analysis of ^{1}H-NMR further confirmed the living nature of the polymerization.

Keywords: Reverse atom transfer radical polymerization, acrylonitrile, $FeCl_3$/acetic acid, "living"/control

1 Introduction

Narrow polydispersity is an essential requirement for the synthesis of PAN satisfying the requirement for high-performance PAN fibers (1). Conventional radical polymerization was the most used technique to prepare PAN due to its convenience compared with other polymerizations. However, PAN prepared via this method showed poor control on the molecular weight, molecular weight distribution and molecular structure for the nature (slow chain initiation, fast chain propagation and quick chain termination or chain transfer) of conventional radical polymerization (2, 3). "Living"/controlled radical polymerization can be an alternative to resolve such a problem. (4, 5). Atom transfer radial polymerization (ATRP), presented by Wang (6, 7), is one of the most efficient methods in the field of "living"/controlled radical polymerizations. A collection of literatures have reported the successful synthesis of PAN with predefined molecular weight and narrow polydispersity index (8–11). However, ATRP has two major drawbacks for the toxicity of initiator alkyl halide, RX, and the oxidation of catalyst M_nX. Reverse atom transfer radical polymerization, RATRP (12, 13), was developed to improve ATRP by introducing conventional initiator and oxidation state transition metal catalyst instead of alkyl halide (RX) and reduction state transition metal catalyst in ATRP.

Ligand was used to improve the solubility of the transition metal in organic phase and adjust the oxidation-reduction potential of the transition metal. The usually used nitrogen-based ligands in RATRP were toxic and expensive. Searching new catalytic systems, with less toxicity and less cost, has been taken into account. Acids were believed to be harmful and complex more easily with iron than copper as ligands. A series of acids, such as lactic acid (14), iminodiacetic acid (15, 16), succinic acid (17, 18), isophthalic acid (19–22) and acetic acid (23), have been investigated. In this paper, RATRP of AN was successfully carried out with $FeCl_3$/acetic acid as a catalytic system in the presence of AIBN in DMF.

2 Experimental

2.1 Materials

The monomer, AN (>98%), was purchased from Chengdu Chemical Reagents Co. (Chengdu, China). It was purified under air distillation and stored in the refrigerator before use. AIBN was used as initiator and treated by ethanol. $FeCl_3$ was purchased from Sinopharm Chemical Reagent Co. and used without further purification. Acetic acid (Tianjin Chemical Reagent Co., Tianjin, China) was used as received. Methanol (CH_3OH) (>99.5%), Hydrochloric acid (HCl) and DMF were used as received unless mentioned.

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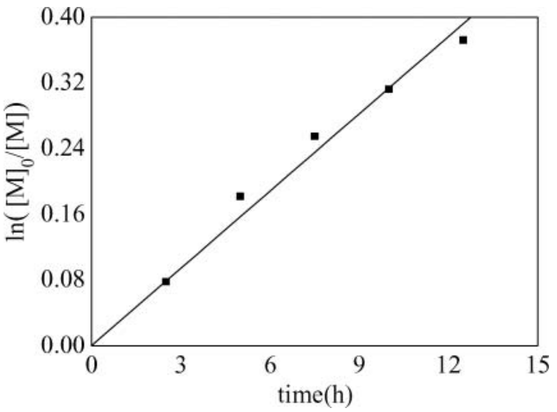


Fig. 1. First-order kinetic plot of RATRP of AN catalyzed by $FeCl_3$/acetic acid with [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2 at 65°C in DMF, [AN] = 6.0 M.

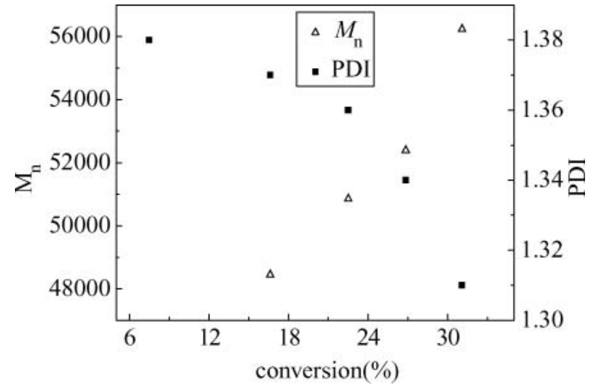


Fig. 2. Plots of M_n and PDI of PAN versus monomer conversion for RATRP catalyzed by $FeCl_3$/acetic acid with [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2 at 65°C in DMF, [AN] = 6.0 M.

2.2 Polymerization

A typical polymerization procedure was as follows: $FeCl_3$, acetic acid, AIBN, AN and DMF were added to a dry two-neck flask in that order. It was degassed in vacuum and charged with N_2 three times. Then, the flask was placed in the water bath thermostated at a desired temperature. After a definite time, the polymerization was terminated by immersing the flask into an ice bath and exposing the mixture to air. The resulting solution was dissolved into DMF, washed with a limited amount of hydrochloric acid to remove the iron catalyst residue, and precipitated with an excess of methanol-water solution (V:V = 1:1). Finally, the resulting mixture was filtered and dried under vacuum for 24 h.

2.3 Characterizations

The monomer conversion was measured gravimetrically. M_n and the molecular weight distribution (M_w/M_n) were determined by Gel Permeation Chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL/min through a combination of Waters HT3, HT4, and HT5 styragel columns. Linear poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 35°C with purified high-performance-liquid-chromatography-grade DMF as eluent. A Waters 2414 differential refractometer was used as the detector. H-NMR spectrum was recorded on a Bruker Avance 400 NMR spectrometer using DMSO-d6 as a solvent.

3 Results and Discussions

3.1 RATRP of AN Catalyzed by $FeCl_3$/Acetic Acid

A series of RATRPs of AN were carried out with [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2 at 65°C in DMF. $FeCl_3$/acetic acid and AIBN were selected as the catalyst complex and initiator, respectively. The concentration of monomer AN was set as 6 M. A change of solution color from deep orange to light yellow was observed in the initiation step of polymerization, demonstrating the activation of $FeCl_3$/acetic acid was achieved. The kinetic plot for RATRP of AN has been shown in Figure 1. The linearity of ln($[M]_0$/[M]) vs. reaction time indicated the polymerization was first order with respect to monomer concentration and the concentration of propagation radicals was constant. According to the slope, the apparent rate constant (k_p^{app}) was calculated to be 8.27×10^{-6} s^{-1}.

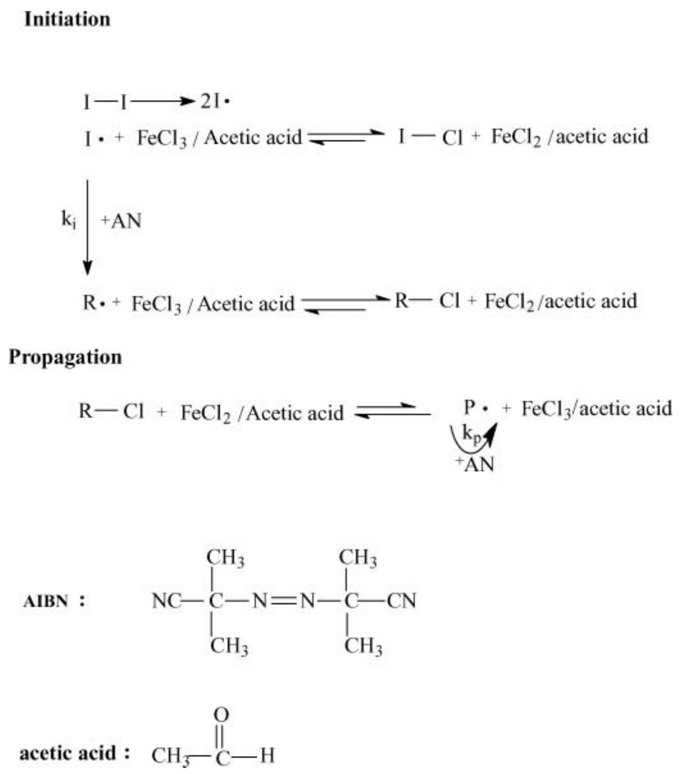
Figure 2 presents the evolution of molecular weight (M_n) and the polydispersity index (PDI) of PAN with monomer conversion. M_n increased with the increase of monomer conversion, showing the living characteristic of the polymerization by eliminating coupling termination and other side reactions. PDI was less than 1.4 and became narrower with monomer conversion, indicating the deactivation rate of primary radicals produced from decomposition of AIBN was raised and the equilibrium of dormant species and active radical species was established step by step in the polymerization process.

The proposed mechanism is described in Scheme 1. In the initiation step, AIBN was first homolytically decomposed

Table 1. Effect of ratio of $FeCl_3$ to acetic acid on the polymerization

[$FeCl_3$]: [acetic acid]	*Conversion/%*	*M_n*	*PDI*	*$k_p^{app} \times 10^6/s^{-1}$*
1:1	29.96	53620	1.36	7.91
1:2	31.07	56240	1.31	8.27
1:4	26.74	50460	1.32	6.91
1:6	28.44	37230	1.42	7.44

[AN] = 6.0 M, [AN]:[AIBN]:[$FeCl_3$] = 500:1:1, T = 65°C, t = 12.5 h , in DMF.



Sch. 1. Proposed polymerization mechanism of RATRP of AN including the initiator and ligand structures.

into two primary radicals. Then, primary radicals reacted with monomers to generate propagation radicals, or with $FeCl_3$/acetic acid to generate dormant species. Finally, the equilibrium was established to provide control and the polymerization proceeded according to the route of ATRP.

3.2 Effect of Ratio of $FeCl_3$ to Acetic Acid on RATRP of AN

To investigate the effect of different ratio of $FeCl_3$ to acetic acid on the polymerization, a variety of experiments were conducted and the results have been summarized in Table 1. As seen from Table 1, PDI was narrower with the ratio of $FeCl_3$ to acetic acid as 1:2 than 1:1. The polymerization rate also increased with the increase of $FeCl_3$ to acetic acid ratio from 1:1 to 1:2 and k_p^{app} was 7.91×10^6 $s^{-1}$with $FeCl_3$ to acetic acid at 1:1 while 8.27×10^6 s^{-1} was observed with the ratio at 1:2. With more acetic acid added to reaction system, both polymerization rate and k_p^{app} decreased. Broader PDI was also observed with the increase of the amount of acetic acid. It was concluded that the ratio of 1:2 gave the best control on the polymerization within the range of $FeCl_3$ to acetic acid ratio we studied. Neither increasing nor decreasing the ratio resulted in good control over RATRP of AN.

3.3 Effect of the Amount of Initiator AIBN and Catalyst $FeCl_3$ on RATRP of AN

Experiments were performed to study the effects of the ratio of AIBN to $FeCl_3$ and the concentration of AIBN on the polymerization with the ratio of $FeCl_3$ to acetic acid fixed at 1:2. As seen from entries 1–3 in Table 2, decreasing the ratio of AIBN to $FeCl_3$ resulted in the obvious decrease of polymerization rate and k_p^{app}, while better control on the polymerization was obtained with narrower PDI. It may be attributed to the fact that the catalyst $FeCl_3$ can enhance the activity of RATRP of AN, making quick equilibrium of polymerization true. Entries1, 4–6 gives the results of the effect of different concentration of initiator AIBN on the polymerization with [AIBN]:[$FeCl_3$]:[acetic acid] = 1:1:2. Best control on the polymerization was achieved when the molar ratio of [AN]:[AIBN] was 500:1, namely, the concentration of AIBN was 0.012 mol/L.

3.4 Effect of Polymerization Temperature on RATRP of AN

Table 3 shows the effect of polymerization temperature on RATRP of AN in DMF with [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2. The apparent rate constant increases with increasing temperature. Increasing temperature can significantly accelerate the rate of polymerization by increasing both the rate constant of radical propagation and the equilibrium constant of atom transfer. However, both the rate of chain termination and that of other side reactions were raised at elevated temperature, which should result in

Table 2. Effect of ratio of [AIBN]:[$FeCl_3$]:[acetic acid] on RATRP of AN

[AN]:[AIBN]:[$FeCl_3$]: [acetic acid]	*[AIBN]/mol/L*	*Conversion/%*	*M_n*	*PDI*	*$k_p^{app} \times 10^6/s^{-1}$*
500:1:1:2	0.012	31.07	56240	1.31	8.27
500:1:2:4		15.32	35540	1.29	3.70
500:1:3:6		10.36	28040	1.26	2.43
400:1:1:2	0.015	31.93	35840	1.40	8.55
600:1:1:2	0.010	31.36	46150	1.37	8.36
700:1:1:2	0.009	31.27	48230	1.39	8.33

[AN] = 6.0 M, T = 65°C, t = 12.5 h, in DMF.

Table 3. Effect of polymerization temperature on RATRP of AN

Temperature/°C	*Conversion/%*	$k_p^{app} \times 10^6/s^{-1}$
60	17.15	4.18
65	31.07	8.27
70	42.44	12.27
75	48.37	14.69

[AN] = 6.0 M, t = 12.5 h.

Table 4. Effect of solvents on RATRP of AN

Solvent	*Conversion/%*	M_n	*PDI*	$k_p^{app} \times 10^6/s^{-1}$
DMF	31.07	56240	1.31	8.27
DMSO	45.27	71760	1.66	13.39
acetonitrile	10.87	21590	1.40	2.56
cyclohexanone	7.34	19950	1.33	1.69
ethyl acetate	4.40	16860	1.33	1.00

[AN] = 6.0 M, [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2, T = 65°C, t = 12.5 h.

broader PDI due to the loss of control on polymerization. The desirable temperature was 65°C for good control on RATRP of AN with PDI at 1.31.

$$\Delta H^0_{\mathrm{eq}} = \Delta H_{\mathrm{app}} - \Delta H_{\mathrm{prop}} \qquad (1)$$

An Arrhenius plot obtained from the experimental data (Table 3) is given in Figure 3. The apparent activation energy was calculated to be 80.6 kJ·mol^{-1}. According to Equation 1 and ΔH_{prop} = 22.3 kJ·mol^{-1}. ΔH^0_{eq} is calculated to be 58.3 kJ·mol^{-1}. Where ΔH^0_{eq} is the enthalpy of the equilibrium, ΔH_{app} is the apparent enthalpy of activation and ΔH_{prop} is the activation enthalpy of propagation.

3.5 Effect of Solvent on RATRP of AN

For comparison purpose, DMF, dimethyl sulfoxide (DMSO), acetonitrile, cyclohexanone and ethyl acetate were used as solvents for RATRP of AN. Results in Table 4 give the M_n, PDI and k_p^{app} for RATRP of AN in five solvents. The polymerization rate in DMSO was faster than that in any other solvents, whereas the PDI was relatively broader. Narrowest PDI was obtained with DMF as solvent and the polymerization rate was moderate. The polarity of DMF could accelerate the interaction of catalyst system and active radical species by the formation of homogeneous reaction system. As a result, DMF was selected as the appropriate solvent of RATRP of AN.

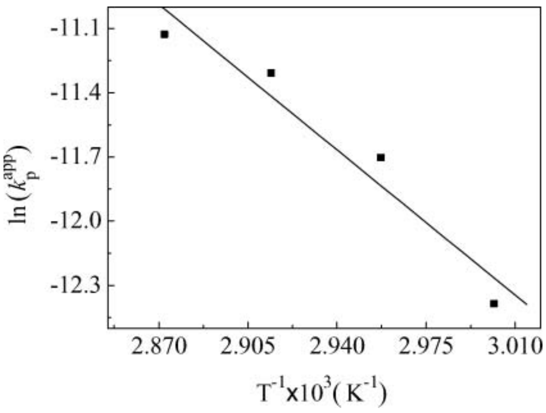


Fig. 3. Plot of k_p^{app} vs. polymerization temperature with [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2, [AN] = 6.0 M, *t* = 12.5 h, in DMF.

3.6 Analysis of Chain End by ^{1}H-NMR

The end-group of PAN synthesized via RATRP has been analyzed by ^{1}H-NMR spectroscopy, as shown in Figure 5. The peak at $\delta = 2.3$ ppm (b) was attributed to the methylene proton of acrylonitrile unit of the resulting polymer. NMR signal at $\delta = 5.2$–5.6 (d) corresponding to methylidyne attached to the end of chain could be clearly seen. It deviated from the chemical shift ($\delta = 3.0$–3.3, c) of other methylidyne protons of acrylonitrile unit for the electronic-attracting function of Cl at the end of chain. Peak ($\delta = 1.4$ a) corresponding to methyl proton indicated that AIBN moieties were attached to the main chain. From the results above, it could be suggested that polymerization proceeded according to the mechanism of "living"/controlled free radical polymerization.

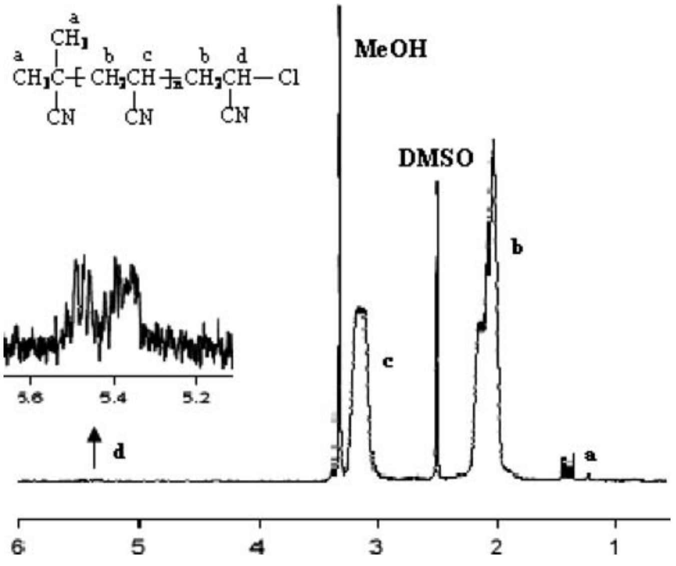


Fig. 4. ^{1}H-NMR spectrum of PAN with [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] = 500:1:1:2 at 65°C in DMF, [AN] = 6.0 M, t = 12.5 h.

4 Conclusions

RATRP of AN was successfully conducted with the initiation system AIBN/$FeCl_3$/acetic acid at 65°C in DMF. The kinetic plot of polymerization was first order with respect to monomer conversion. The molecular weight increased with monomer conversion and PDI was narrow. Best control on the polymerization was gotten with the condition of [AN]:[AIBN]:[$FeCl_3$]:[acetic acid] at 500:1:1:2. Effect of polymerization temperature was investigated and the apparent activation energy was calculated to be 80.6 kJ·mol^{-1}. The optimum solvent for RATRP of AN was DMF in comparison with others investigated above. ^{1}H-NMR analysis of PAN further verified the "living"/controlled character of RATRP of AN.

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