Reverse Atom Transfer Radical Polymerization of Acrylonitrile Catalyzed by FeCl₃/Lactic Acid

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Reverse atom transfer radical polymerization (RATRP) of acrylonitrile (AN) was carried out using azobisisobutyronitrile (AIBN) as initiator, ferric trichloride anhydrous (FeCl₃)/lactic acid (LA) as catalyst system; a ratio of FeCl₃/LA was 1:2 gave the best control. RATRP of AN with N,N-dimethylformamide (DMF) as solvent gave the moderate polymerization rate and the narrowest polydispersity index (PDI). When FeCl₃ was replaced by CuBr₂, RATRP of AN showed a longer induction period. When Cu was added to the CuBr₂-based catalyst system, the induction period was reduced. ^{1}H-NMR spectra of PAN verified the possibility of controlled/living polymerization for future chain extension.

Keywords: RATRP, FeCl₃/LA, AN

1 Introduction

The discovery of living anionic polymerization by Michael Szwarc had a tremendous effect on polymer science (1, 2). The breakthrough occurred in 1995 when Sawamoto et al. (3) and Matyjaszewski et al. (4) found the novel polymerizable method atom transfer radical polymerization (ATRP), which has become one of the preferred methods for the preparation of well-defined polymer materials (3,5–7). ATRP is based on the reversible reaction of a low oxidation-state metal complex with an alkyl halide (RX) (8) and relies on involving a fast dynamic equilibrium between dormant species R-X and active radical species R to provide control (6, 9–10). However, the toxicity of the halide species RX and the oxidation of the catalyst Mn_t/L_X by oxygen in air limits its widespread use for industrial utilization. Reverse atom transfer radical polymerization (RATRP), using conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state, was first reported by Matyjaszewski and his coworkers (11–13). Scheme 1 shows the general mechanism of RATRP. In the RATRP system, the reaction was initiated by a conventional radical initiator, such as AIBN, with the transition metal in its higher oxidation state, e.g. copper (II), and iron (III). A great deal of excellent work on RATRP has been reported (14–19).

The interest of the recent research is focused on developing new ligands and transition-metals that influence the reactivity of the catalyst. The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for atom transfer. Many ligands have been used in ATRP, such as nitrogen ligands (20–21), phosphorus ligands (20, 22–24), miscellaneous ligands (25–27), etc., but these ligands are expensive and toxic. Organic acids were generally believed to deactivate the metal organometallic catalyst, resulting in poor control of the polymerization. However, acids as ligand have many advantages, e.g., they are inexpensive, nontoxic, complexing more easily with iron (28). Some results about organic acid as a ligand have been obtained (29–34). Polyacrylonitrile (PAN) is an important precursor for polymer materials (35–36), therefore, it is necessary to prepare well-defined PAN. Xiong (29) has reported the preparation of PMMA via RATRP using LA as ligand. However, LA acts as a ligand to prepare well-defined PAN and has not been reported to the best of our knowledge.

In this paper, we report a RATRP system to prepare well-defined PAN. In this RATRP system, AIBN was selected to be initiator, and FeCl₃/LA was chosen to be catalyst system. Effects of the catalyst system, the amount of AIBN and solvents were also investigated.

2 Experimental

2.1 Materials

AN (Tianjin FuChen Chemical Reagents Co., Tianjin, China) was distilled under normal pressure and stored

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Initiation:

$$I{-}I \longrightarrow 2I\cdot$$

$$I\cdot + Mt^{n+1}X/Lm \rightleftharpoons I{-}X + Mt^{n}X/Lm$$

$$R\cdot + Mt^{n+1}X/Lm \rightleftharpoons R{-}X + Mt^{n}X/Lm$$

Propagation:

$$R{-}X + Mt^{n}X/Lm \rightleftharpoons R\cdot + Mt^{n+1}/Lm$$

Polymerization

Sch. 1. The general mechanism of RATRP.

Fig. 1. Kinetic plot for RATRP of AN at 65°C in DMF with [AN] = 6.0M and [AN]:[AIBN]:[FeCl$_3$]:[LA] = 500:1: 1:2.
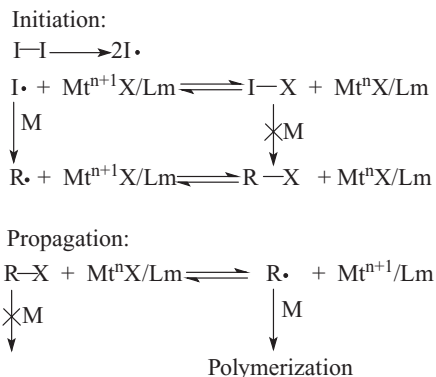
at 5°C. AIBN (Tianjin FuChen Chemical Co. Tianjin, China), FeCl$_3$ (Sinopharm Chemical Reagent Co., Shanghai, China), LA (Tianjin Regent Chemical Co. Tianjin, China), copper powder (Cu) (Sinopharm Chemical Reagent Co., Shanghai, China), Copper (II) bromide (CuBr$_2$) (Tianjin FuChen Chemical Reagents Co., Tianjin, China), dimethyl sulfoxide (DMSO) (Tianjin Regent Chemical Co. Tianjin, China), Acetonitrile (CH$_3$CN) (Tianjin FuChen Chemical Reagents Co., Tianjin, China) and DMF (Tianjin FuChen Chemical Reagents Co., Tianjin, China) were used as received. All other chemical reagents were used as received.

2.2 RATRP Polymerization Procedure

In a typical experiment, AN (19.8 ml, 0.3 mol), AIBN (6×10^{-4}mol), FeCl$_3$(6×10^{-4}mol) and LA (0.09 ml,1.2×10^{-3}mol) were mixed in a dry two-neck round-bottom flask which was bathed in ice-water. Then the mixture was degassed *in vacuo* and charged with N$_2$ (three times) and sealed finally with N$_2$. After this, the flask was immersed in a thermostated oil-bath held at the desired temperature. At timed intervals, the reaction was terminated by cooling the flask in the ice water. The production was dissolved with DMF, and precipitated by methanol-water (V:V, 1:1). The production was dried 24 h under vacuum.

2.3 Characterization

Percentage conversion of AN was determined gravimetrically. Molecular weight and molecular weight distribution were determined by GPC, conducted with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL min^{-1} through a combination of WatersHT3, HT4, and HT5 styragel columns. A Waters 2414 differential refractometer was used as the detector. Linear poly-(methyl methacrylate) standards were used for calibration. The analysis was undertaken at 35°C with purified chromatography-grade DMF as an eluent. The ^{1}H-NMR
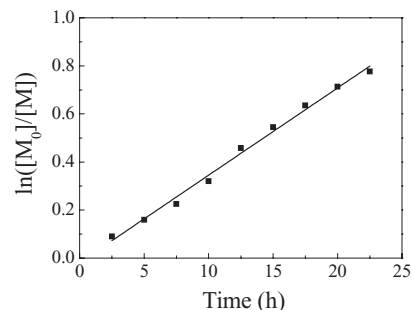
spectra were recorded at 25°C in DMSO-d6 on a Bruker Avance DMX500 NMR instrument operating at 500 MHz for ^{1}H, and using the standard Bruker software. Chemical shifts are reported in ppm with respect to TMS as internal standard.

3 Results and Discussion

3.1 Synthesis of PAN using RATRP

RATRPs of AN catalyzed by FeCl$_3$/LA were carried out at 65°C in DMF awith molar ratio of [AN]:[AIBN]:[FeCl$_3$]:[LA] at 500:1:1:2. Figure 1 showed the kinetic plot of ln[M]$_0$/[M] vs. polymerization time for RATRP of AN. The linear kinetic plot of monomer conversion suggested that, a constant radical concentration was maintained, the termination reactions could be neglected. According to the slopes of the kinetic plot, the apparent rate constant (k_p^{app}) was calculated to be 7.95×10^{-6} s^{-1}.

Figure 2 indicated the values of molecular weights and PDI of the resulting polymers measured by GPC. The PDI remained within the 1.78–1.21 range as shown in Figure 2. A broader PDI was obtained when the conversion was less
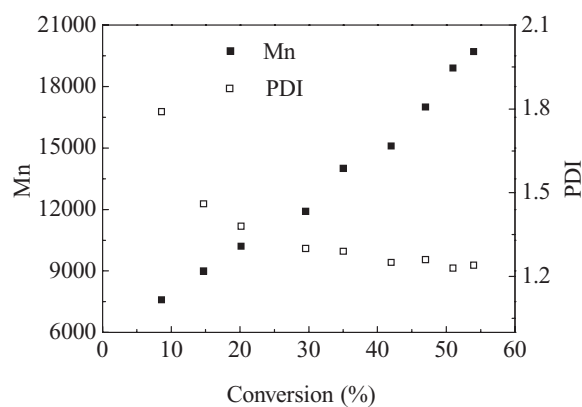

Fig. 2. Dependence of Mn and PDI on monomer conversion for RATRP of AN at 65°C in DMF with [AN] = 6.0M and [AN]:[AIBN]:[FeCl$_3$]:[LA] = 500:1:1:2.

Table 1. Effect of Catalyst System on RATRP of AN at 65°C with [AN] = 6.0M and [AN]:[AIBN] = 500:1

Entry	[AIBN]:[FeCl₃]:[LA]	Time/h	Conversion (%)	Mn	PDI
1	1:1:1		28	18600	1.37
2	1:1:2		35	14000	1.29
3	1:1:4	12.5	26	31000	1.43
4	1:1:6		24	31500	1.41
5	1:2:4		15	24100	1.32
6	1:3:6		10	41300	1.43

than 20%. The slow rate of the primary radicals at 65°C produced from the decomposition of AIBN changing into dormant species was responsible for the broader PDI during the initial polymerization in the reaction system. The conversion reached 54% with almost linear increase in Mn with total conversion. However, the PAN's Mn measured by GPC are not accurate, as such methods can overestimates the molecular weight of the PAN in comparison with linear PMMA standards (37, 38).

3.2 Effect of Catalyst System on RATRP of AN

To studythe effect of catalyst system on RATRP of AN, a series of experiments were carried out. Table 1 summarized experiment results in which AN was polymerized in the presence of different ratio of [FeCl₃]/[LA]. The conversion of AN had the highest values when the ratio of [AIBN]:[FeCl₃]:[LA] was 1:1:2. This indicated that the RA-TRP of AN had the highest polymerization rate (Table 1, entry 1–4). Lower or higher concentrations of LA resulted in a low reaction rate. A large amount of LA could poison the metal catalyst, but a low amount of LA couldn't complex with all FeCl₃. Also, the ratio of AIBN and FeCl₃/LA was studied (Table 1, entry2, 5-6). It was found that the conversion of AN decreased with increasing the ratio of
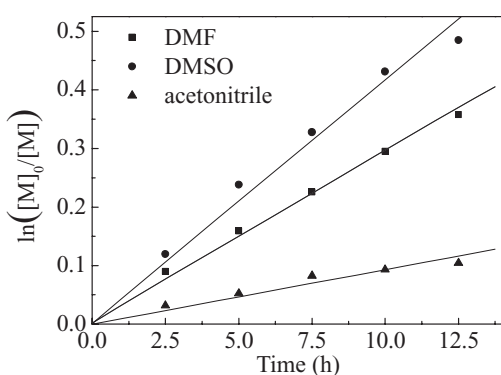
Fig. 3. First-order kinetic plot of the monomer consumption as a function of time in different solvents during the RATRP of AN with [AN] = 6.0 M and [AN]:[AIBN]:[FeCl3]:[LA]: = 500:1:1:2 at 65°C.

Table 2. Effect of solvents on RATRP of AN at 65°C with [AN]=6.0M and [AN]:[AIBN]:[FeCl₃]:[LA] =500:1:1:2

Solvents	Time/h	Conversion (%)	Mn	PDI
DMF		35.	14000	1.29
DMSO	12.5	38	67800	1.48
Acetonitrile		10	68870	1.30

[AIBN]:[FeCl₃]:[LA], while the PDI and Mn increased with increasing the ratio of [AIBN]:[FeCl₃]:[LA]. As can be seen from Table 1, the Mn didn't linear increase with the conversion. The reason maybe that initiators did not have 100% efficiency or polymer chain terminations or transfers happened during reactions at different reaction conditions.

3.3 Effect of Solvent on RATRP of AN

To study the effect of solvent on the RATRP of AN, DMF, DMSO, and acetonitrile were used as solvents. Figure 3 showed kinetic plots of ln[M]₀/[M] vs. time for the RA-TRP of AN in the three solvents. The polymerizations were approximately first-order with respect to the monomer concentration. As shown in Figure 3, the rate of polymerization in DMSO was unexpectedly faster than in that DMF and Acetonitrile. The results of the experiments were shown in Table 2. Although the conversion and the polymerization rate were the highest, the PDI was also the broadest for DMSO system. In these three systems, the system of DMF as solvent was the best, which had the moderate polymerization rate and the narrowest PDI (1.29). The results could be interpreted that the polymerization was quite sensitive to the polarity of the solvent. The polarity of DMF was stronger than DMSO and Acetonitrile. So addition of DMF to the reaction system increased the solubility of the catalyst in monomer and provided a homogeneous catalyst system. Thus, the system of DMF as solvent provided the desired characteristics of high initiation efficiency, low PDI, and a fast polymerization rate.

3.4 Effect of Concentration of AIBN on RATRP of AN

To clarify the role of AIBN in the RATRP system, the effect of different amounts of AIBN on the AN polymerizations was studied at 65°C in DMF with [AN] = 6.0M and [AN]:[FeCl₃]:[LA] = 500:1:2. The results were shown in Table 3. The conversion of AN decreased from 35% to

Table 3. Effect of Concentration of AIBN on RATRP of ARN at 65°C in DMF with [AN]=6.0M and [AN]:[FeCl₃]:[LA] =500:1:2

[AN]:[AIBN]	[AIBN](mol/L)	Time/h	Conversion (%)	Mn	PDI
500:1	0.012		35	14000	1.29
600:1	0.010	12.5	28	53700	1.34
700:1	0.009		26	67190	1.60

Table 4. Effect of the different transition-metal ions on RA-TRP of AN at 65°C in DMF with [AN] = 6.0M and [AN]:[AIBN]:[Catalyst]:[LA] = 500:1:1:2.
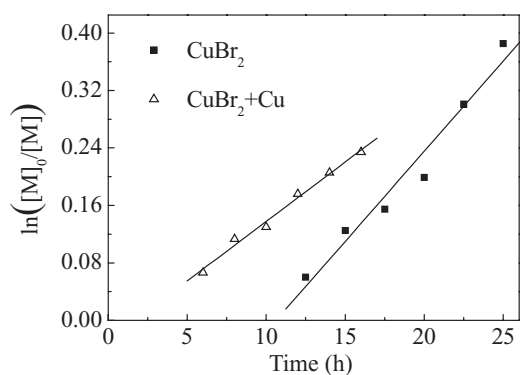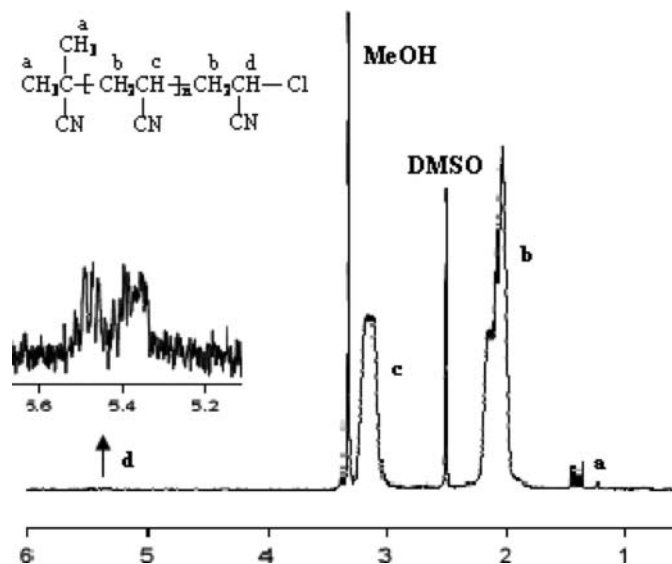
Catalyst	Time/h	Conversion (%)	Mn	PDI
FeCl$_3$	12.5	35	14000	1.29
CuBr$_2$	25	30	30950	1.34

26% with decreasing concentration of AIBN, and the PDI and Mn increased from 1.29 to 1.60.

3.5 Effect of the Different Transition-Metal Ions on RATRP of AN

Transition-metal ions had an important role in catalyst system of RATRP. In order to clarity the effects of the different transition-metal ions on RATRP of AN, a series of experiments were carried out; the results are shown in Table 4. It was found that not only the conversion of FeCl$_3$-based catalyst system was higher than CuBr$_2$-based catalyst system, but also the PDI of the former was narrower than the latter. This indicated that the activity of FeCl$_3$-based catalyst system was higher and the control of reaction was better. Figure 4 showed kinetic plots of ln[M]$_0$/[M] vs. time for the RATRP of AN with CuBr$_2$ as catalyst system. The polymerization was approximately first-order with respect to the monomer concentration, but there was a long induction period (>10 h).

In order to reduce the induction period, Cu was added to the reaction system. Figure 4 also showed kinetic plots of ln[M]$_0$/[M] vs. time for the RATRP of AN with CuBr$_2$ and Cu as catalyst system, and [CuBr$_2$]:[Cu] = 1:1. When a small amount of Cu was added to the polymerization of AN by RATRP, the polymerization kept approximately first-order with respect to the monomer concentration, and the induction period was also reduced (<5 h). This illustrated that even with the faster polymerization rate in the presence of Cu, the control of the polymerization was maintained (The

Fig. 5. ^{1}H-NMR spectrum of AIBN initiated PAN imenthylene carbonate at 44°C. [AN]:[AIBN]:[FeCl$_3$]:[LA] = 500:1:1:2.

final polymer of PDI shows only a small increase). From Figure 4, we can also see that the use of Cu resulted in an increase in the rate of polymerization. A similar result had been reported by Krzysztof Matyjaszewski (39); he thought that the addition of the Cu was a reducing agent in the reaction system. Cu slowly reduced excess deactivator, Cu^{2+} to enhance the rate, while there was still a sufficient concentration of Cu^{2+} to maintain control of the polymerization, and reduction of Cu^{2+} by Cu regenerated Cu$^+$, further enhancing the polymerization rate.

3.6 ^{1}H-NMR Spectra of PAN

The chain end of the PAN prepared via RATRP using AIBN as an initiator was analyzed by ^{1}H-NMR spectroscopy, as shown in Figure 5. CHCl(CN) proton from the end group at 5.3-5.5 ppm (d in Figure 5) in PAN were observed. The chemical shift $\delta = 3.3$ ppm corresponded to the CH(CN) (c in Figure 5). The chemical shift $\delta = .1$ ppm (b in Figure 5) was attributed to the CH$_2$. The chemical shift $\delta = 1.3$ ppm (a in Figure 5) was attributed to the CH$_3$. The ^{1}H-NMR spectra of PAN verified the chloro atom was at the end of polymer chain which was a typical characteristic of ATRP, and also verified the possibility of controlled/living polymerization for future chain extension.

4 Conclusions

Well-defined PAN was synthesized by the RATRP, which was catalyzed by a new catalyst system, FeCl$_3$/LA. When the ratio of FeCl$_3$/LA was 1:2, the reaction was the best controlled. The RATRP of AN with DMF as solvent showed the best control, which had the narrowest PDI.

Fig. 4. Kinetic plots of ln[M]$_0$/[M] vs. time for the RATRP of AN with [AN] = 6.0 M and [AN]:[AIBN]:[CuBr$_2$]:[Cu]:[LA]: = 500:1:1:1:2 at 65°C.

The rate of $FeCl_3$-based catalyst system was faster than the $CuBr_2$-based catalyst system, and there was a long induction period when $CuBr_2$ was used as the catalyst system. Copper powder added to the $CuBr_2$-based catalyst system can reduce the induction period. The ^{1}H-NMR spectra of PAN verified the possibility of controlled/living polymerization for future chain extension.

Acknowledgments

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