

Reverse Atom Transfer Radical Polymerization of Acrylonitrile Under Microwave Irradiation

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ABSTRACT: Reverse atom transfer radical polymerization was first used to successfully synthesize polyacrylonitrile under microwave irradiation. FeCl_3 , coordinated by isophthalic acid, was used as the catalyst, and 2,2'-azobisisoheptonitrile was used as the initiator. *N,N*-Dimethylformamide was used as the solvent to improve the solubility of the ligand. Under the same experimental conditions, the apparent rate constant under microwave irradiation was higher than that under conventional heating. The polymerization not only showed the best control of the molecular weight and its distribution but also pro-

vided a rather rapid reaction rate with the [acrylonitrile]/[2,2'-azobisisoheptonitrile]/[FeCl_3]/[isophthalic acid] ratio of 300 : 1 : 1 : 2. The polymers obtained were used as macroinitiators to initiate the chain extension and successfully synthesize acrylonitrile polymers with a molecular weight higher than 50,000 and a narrow polydispersity as low as 1.30. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2646–2650, 2008

Key words: atom transfer radical polymerization (ATRP); kinetics (polym.); living polymerization

INTRODUCTION

Atom transfer radical polymerization (ATRP), which was discovered by Wang and Matyjaszewski¹ and Sawamoto et al.² independently, has been an extremely active area of polymer synthesis.^{3–6} This technique provides a powerful tool for synthesizing polymers with well-controlled molecular architectures, predictable molecular weights, and narrow polydispersities. However, transition-metal-catalyzed ATRP has two major drawbacks: the toxicity of the halide species (RX) and the oxidation of the catalyst (M_n^t/LX) 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 called reverse atom transfer radical polymerization

(RATRP) by Matyjaszewski and coworkers^{7,8} and other researchers.^{9,10} The main problems of RATRP are the larger amount of catalyst needed and the lower activity of the initiation system. To solve these problems, a new catalyst system with higher reactivity or additional measures to enhance the reactivity of the catalyst system is needed. Microwaves, a peculiar source of energy, have been widely applied to enhance chemical reactions.^{11,12} The main benefit of performing reactions under microwave irradiation (MWI) is the significant reaction rate enhancement and the higher initiator efficiency.

Acids are 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 may therefore act as ligands. Zhu and Yan¹³ reported RATRP of methyl methacrylate catalyzed by FeCl_2 /isophthalic acid (IA).

RATRP of acrylonitrile (AN) have mostly been studied with a conventional heating (CVH) method,^{14,15} and there have been no reports on RATRP under MWI. For this reason, MWI was applied to RATRP of AN in this study.

Given these concepts, a new catalytic system based on iron complexes with IA was first used, and *N,N*-dimethylformamide (DMF) was used as the solvent to improve the solubility of the ligand. This is the first successful attempt at the well-controlled RATRP of AN under MWI in DMF with the conventional initiator 2,2'-azobisisoheptonitrile (ABVN). Effects of the initiator and catalyst on the polymerization were

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examined. The living characteristics were confirmed by the chain extension of polyacrylonitrile.

EXPERIMENTAL

Materials

Analytical-reagent-grade AN was obtained from Shanghai Chemical Reagents Co. (Shanghai, China), and the inhibitor was removed by passage through an alumina column.¹⁶ Analytical-reagent-grade FeCl₃ (anhydrous) was prepared from FeCl₃·6H₂O (Shanghai Chemical Reagents) treated with thionyl chloride according to a reference procedure¹⁷ and dried *in vacuo* at 60°C before use. Analytical-reagent-grade IA (Shanghai Chemical Reagents) was used as received. ABVN (Shanghai Chemical Reagents) was used as an initiator and recrystallized from ethanol and dried in a desiccator. DMF (Shanghai Dongyi Chemical Reagents Co., Shanghai, China) was distilled at reduced pressure and stored over 4-Å molecular sieves before use.

Apparatus

A self-improved domestic microwave oven (Samsung, Suzhou, China) was used. Its irradiation power was 90–900 W. The reactor was a three-necked bottle (250 mL) with a refluxing solvent used for controlling the reaction temperature (the boiling point of the solvent). Dry and sealed glass tubes filled with FeCl₃, IA, DMF, ABVN, and AN were placed in the refluxing solvent, and the polymerization took place.

General procedures of polymerization

FeCl₃, IA, and DMF were added to a dry glass tube under stirring. Four cycles of vacuum nitrogen were applied to remove oxygen. After the catalyst was dissolved, AN with ABVN dissolved in advance was added via an argon-washed syringe. The tube was then sealed under nitrogen and placed in the self-improved microwave oven with a reflux of CCl₄ at the boiling point (76.8°C) for a certain time with MWI (MWI power = 550 W), whereas with CVH, the tube was placed 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°C *in vacuo*.

Characterization

The number-average molecular weight (M_n) and polydispersity index (PDI) were determined by gel per-

meation chromatography (GPC). GPC was performed with a Waters (Milford, MA) model 515 solvent delivery system at a flow rate of 1.0 mL/min through a combination of Waters HR1, HR3, and HR4 Styragel 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. Poly(methyl methacrylate) strands were used to calibrate the columns.

The conversion of the monomer was determined gravimetrically.

According to the living characteristics of RATRP, the theoretical molecular weight (M_{th}) was calculated with the following equation:

$$M_{th} = \frac{[AN]}{2[ABVN]} \times M_{wAN} \times \text{Conversion} \quad (1)$$

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

The initiation efficiency (f) of the initiator was calculated with the following equation:

$$f = \frac{M_{th}}{M_n} \quad (2)$$

where M_n is the GPC-determined number-average molecular weight.

RESULTS AND DISCUSSION

RATRP of AN under MWI and comparison with CVH

RATRP of AN catalyzed by FeCl₃/IA was carried out with both MWI and CVH processes with the [AN]/[ABVN]/[FeCl₃]/[IA] ratio of 300 : 1 : 1 : 2. After heating, a change in the color from deep orange to light yellow was observed during the polymerization as described by Moineau et al.¹⁸ This corresponded to the decomposition of ABVN and the establishment of the equilibrium between Fe³⁺ and Fe²⁺. The dependence of the conversion on the reaction time under MWI and CVH processes is shown in Figure 1. The monomer conversions increased with the reaction time, and the conversion under MWI was higher than that under CVH. The monomer conversion reached about 66.5% within 170 min. With the same temperature and [AN]/[ABVN]/[FeCl₃]/[IA] ratio, the monomer conversion reached only 20.9% within 170 min under CVH. This clearly demonstrates that MWI enhances the polymerization rate greatly.

Figure 2 shows the kinetic plots of ln([M]₀/[M]) versus time for RATRP of AN using different polymerization processes (MWI and CVH), where [M]₀ is the AN concentration in the feed and [M] is the AN

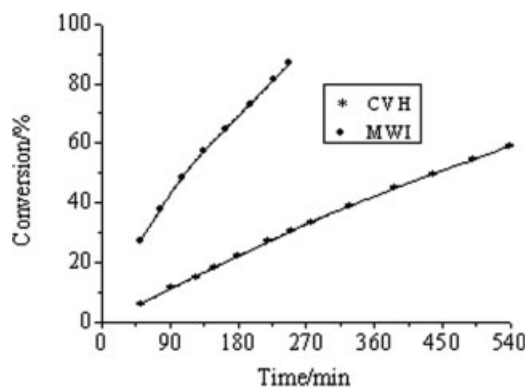


Figure 1 Dependence of the conversion on the reaction time under MWI and CVH with $[AN] = 7.0M$ and $[AN]/[ABVN]/[FeCl_3]/[IA] = 300 : 1 : 1 : 2$.

concentration in the polymerization system. The linearity of the plot indicates that the polymerization was 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 was constant, and the termination reactions could be neglected. According to the slopes of the kinetic plots, the apparent rate constant (k_p^{app}) was calculated. k_p^{app} under MWI ($10.8 \times 10^{-5} s^{-1}$) was much higher than that under CVH ($2.33 \times 10^{-5} s^{-1}$), and this indicates that applying MWI can greatly enhance the rate of polymerization. A similar result was reported by Zhu¹⁹ for copper-mediated ATRP of methyl methacrylate under MWI. They reported that MWI increased 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. As shown in Figure 2, RATRP of AN appeared to require an induction period. The induction period became shorter under MWI (4 min) than that under CVH (8 min). The induction period was perhaps caused by the slow formation of the catalytic center and the presence of oxygen and impurities.²⁰

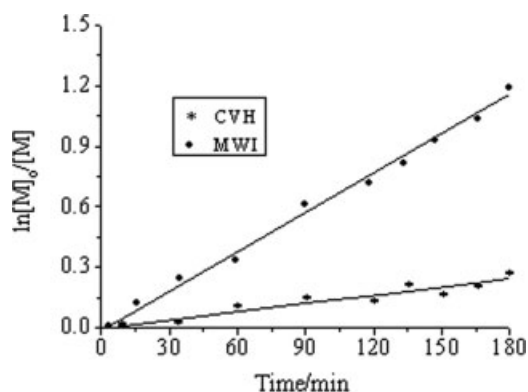


Figure 2 Kinetics of RATRP of AN under MWI and CVH with $[AN] = 7.0M$ and $[AN]/[ABVN]/[FeCl_3]/[IA] = 300 : 1 : 1 : 2$.

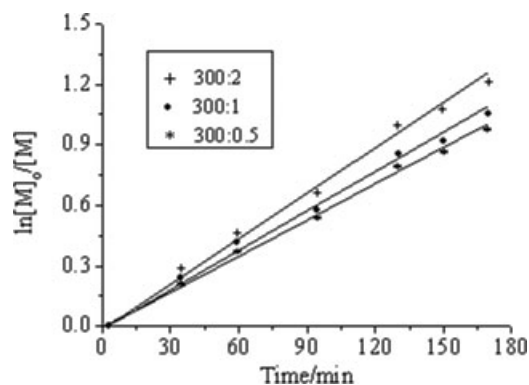


Figure 3 Kinetics of RATRP of AN at various $[AN]/[ABVN]$ ratios under MWI with $[AN] = 7.0M$ and $[AN]/[FeCl_3]/[IA] = 300 : 1 : 2$.

Effect of the concentration of ABVN on RATRP of AN under MWI

Figure 3 shows the kinetics of RATRP of AN at the different initiator concentrations under MWI. The polymerizations were approximately first-order with respect to the initiator concentrations. The k_p^{app} values calculated from the kinetic plot were 12.5×10^{-5} , 10.8×10^{-5} , and $10.1 \times 10^{-5} s^{-1}$, corresponding to $[AN]/[ABVN]$ ratios of 300 : 2, 300 : 1, and 300 : 0.5. k_p^{app} increased with increasing ABVN concentration.

The variations of the molecular weights and molecular weight distributions with the monomer conversion are shown in Figures 4 and 5, respectively. Figure 4 indicates that the molecular weights of the resulting polymers measured by GPC increased linearly with conversion, and the molecular weights agreed reasonably well with M_{th} at conversions beyond 10%. The molecular weight at conversions less than 10% was higher, and this indicates the incomplete decomposition of ABVN at the beginning of the reaction resulting in a small amount of the polymer chain. When precipitation was used to

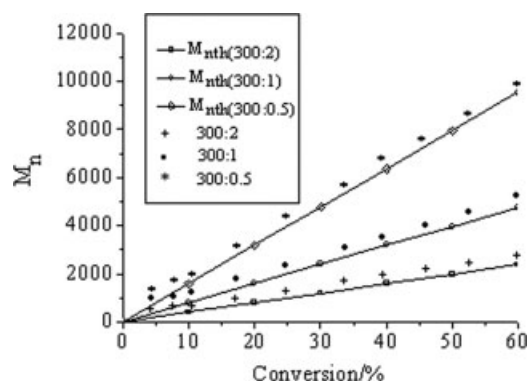


Figure 4 Dependence of M_n on the monomer conversion at various $[AN]/[ABVN]$ ratios under MWI for RATRP of AN with $[AN] = 7.0M$ and $[AN]/[FeCl_3]/[IA] = 300 : 1 : 2$.

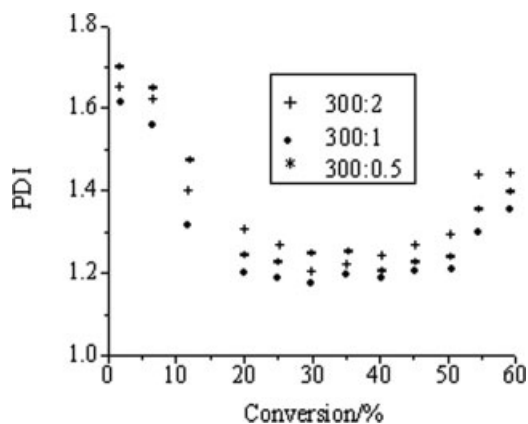


Figure 5 Dependence of PDI on the monomer conversion at various $[AN]/[ABVN]$ ratios under MWI for RATRP of AN with $[AN] = 7.0M$ and $[AN]/[FeCl_3]/[IA] = 300 : 1 : 2$.

collect the polymer, only polymer chains with a high molecular weight precipitated. That caused the high molecular weight at the early stage of polymerization. A similar phenomenon was observed by Chen and Qiu²¹ for RATRP of methyl methacrylate with the initiation system 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)/ $FeCl_3/PPH_3$.

It can be seen from Figure 5 that a broader PDI was obtained when the conversion was less than 20%. This suggests that the conventional radical polymerization took place during the initial polymerization in the reaction system. The PDI was as narrow as about 1.20 when the conversion went beyond 20%. In other words, the RATRP system set up as the conversion went beyond 20%. However, when the conversion went beyond 50%, the molecular weight distribution became broad, and the same trend could be seen at almost all ABVN concentrations.

Effect of the concentration of the catalyst on RATRP of AN under MWI

To further discuss the effects of catalysts on RATRP of AN, a series of experiments were carried out. The results have been compiled in Table I. As more

$FeCl_3/IA$ catalyst system was added (entries 1–4), slower polymerization rates and narrower molecular weight distributions were observed, and the initiation efficiency also increased from 0.81 to 0.91; this suggests that the concentration of $FeCl_3$ had a favorable influence on the activation and equilibrium of RATRP. With an increasing amount of IA in the catalyst system (entries 2, 5, 6, and 7), the rate of polymerization and initiation efficiency showed a trend of decreasing, whereas the molecular weight distribution of the polymers remained narrow. This illustrates that a large amount of IA not only poisoned the metal catalyst but also had 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 $[FeCl_3]/[IA]$ ratio was changed from 0.5 : 2 to 3 : 2 (entries 2, 8, 9, and 10), the initiation efficiency increased from 0.84 to 0.93, the molecular weight distribution of polymers remained narrow, but the rate of polymerization decreased prominently. This implies that $FeCl_3$ itself was an effective catalyst in RATRP.

Chain extension of polyacrylonitrile

An additional method for verifying the functionality of a polymer prepared by RATRP was using it as a macroinitiator for the same or other monomers.²² Therefore, the obtained polyacrylonitrile ($M_n = 4225$, PDI = 1.21) could act as a macroinitiator for the chain-extension polymerization. The chain-extension polymerization of the obtained polyacrylonitrile with AN under MWI was successfully carried out by ATRP in DMF at 85°C in the presence of the $FeCl_2/IA$ catalyst system. The AN polymer obtained had $M_n = 53,670$ and PDI = 1.30. This clearly demonstrates that the chain extension of polyacrylonitrile took place. However, the molecular weight distribution (1.30) was a little broader than that of the macroinitiator (1.21) because a part of the macroinitiator was not active. The chain extension of polyacrylonitrile further verified the active nature of the precursor chain end.

TABLE I
Data for RATRP of AN Catalyzed by $FeCl_3/IA$ Under MWI with $[AN] = 7.0M$ and $[AN]/[ABVN] = 300 : 1$

Entry	$[ABVN]/[FeCl_3]/[IA]$	Time (min)	Conversion (%)	M_{th}	M_n	PDI	$k_p^{app} \times 10^5 (s^{-1})$	Initiation efficiency
1	1 : 0.5 : 1	100	52.2	4150	5123	1.25	12.3	0.81
2	1 : 1 : 2		47.3	3760	4225	1.21	10.8	0.89
3	1 : 2 : 4		43.2	3434	3816	1.18	9.43	0.90
4	1 : 3 : 6		39.7	3156	3468	1.16	8.43	0.91
5	1 : 1 : 1		50.1	3983	4283	1.20	11.6	0.93
6	1 : 1 : 3		44.8	3562	4292	1.23	9.90	0.83
7	1 : 1 : 4		40.9	3252	4169	1.22	8.77	0.78
8	1 : 0.5 : 2		55.4	4404	5243	1.22	13.5	0.84
9	1 : 2 : 2		41.5	3299	3625	1.21	8.94	0.91
10	1 : 3 : 2		34.8	2767	2975	1.20	7.13	0.93

CONCLUSIONS

A new catalyst system, FeCl_3/IA , was successfully used in RATRP of AN under MWI. Well-defined polyacrylonitrile was synthesized when DMF was used as the solvent. The conversion under MWI was higher than that under CVH under the same experimental conditions. The polymerization not only showed the best control of the molecular weight and its distribution but also provided a rather rapid reaction rate with the $[\text{AN}]/[\text{ABVN}]/[\text{FeCl}_3]/[\text{IA}]$ ratio of 300 : 1 : 1 : 2. AN polymers with a molecular weight of 53,670 and a narrow polydispersity as low as 1.30 were successfully obtained with polyacrylonitrile as a macroinitiator.

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