Atom-Transfer Radical Polymerization of Acrylonitrile Under Microwave Irradiation

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ABSTRACT: A single-pot atom-transfer radical polymerization under microwave irradiation was first used to successfully synthesize polyacrylonitrile. This was achieved with $FeBr_2$/isophthalic acid as the catalyst and 2-bromopropionitrile as the initiator. With the same experimental conditions, the apparent rate constant under microwave irradiation was higher than that under conventional heating. An $FeBr_2$/isophthalic acid ratio of 1:2 not only gave the best control of molecular weight and its distribution but also provided a rather rapid reaction rate. The polymers obtained were end-functionalized by bromine atoms, and they were used as macroinitiators to proceed the chain extension polymerization. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1382–1385, 2007

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

INTRODUCTION

Atom-transfer radical polymerization (ATRP) has attracted much attention over the past decade because it provides a simple and robust route for synthesizing well-defined and low-molecular-weight distribution polymers.[1,2] The polymerization process involves a fast dynamic equilibrium between dormant species and active radical species to provide control.[3–5] Recent studies have been aimed at developing new ligands or additional measures to enhance the reactivity of this catalyst system.[6,7] Microwave irradiation (MWI) has been widely applied to enhance chemical reactions.[8–10] The main benefit of performing reactions under MWI is the significant rate enhancement; that is, it can enhance the reactivity of the reaction system.

Polyacrylonitrile (PAN) polymers with narrow polydispersity are essential precursors for the synthesis of high-performance PAN fibers.[11,12] Recently, ATRPs of acrylonitrile (AN) have almost all been studied with a conventional heating (CVH) method,[13,14] and so far, there have not been any reports about ATRP under MWI. For this reason, MWI was applied to ATRP of AN. Isophthalic acid (IA), which is nontoxic and commercially available, complexes with iron easily.[15] In this study, a new catalytic system based on iron complexes with IA was used. The living polymerization of AN with a new iron-based ATRP process under MWI is described first. The effects of the catalyst system on ATRP were investigated.

EXPERIMENTAL

Materials

AN [Shanghai Chemical Reagents Co., analytical reagent (AR) grade] was vacuum distilled from CaH_2 just before polymerization. $FeBr_2$ (Shanghai Chemical Reagents Co., AR grade) was washed with absolute ethanol and dried *in vacuo* at 60°C before use. IA (Shanghai Chemical Reagents Co., AR grade) was used as received. 2-Bromopropionitrile (BPN) was obtained from Aldrich and was used without further purification. *N,N*-dimethylformamide (DMF; Shanghai Dongyi Chemical Reagents Co.) was distilled at reduced pressure and stored over type 4 Å molecular sieves before use.

Apparatus

A domestic microwave oven (Samsung) was used. Its irradiation power was from 90 to 900 W. The polymerization temperature was controlled by the placement of the tubes in a refluxing solvent that was carefully selected with a boiling point at the desired reaction temperature. Dry and sealed glass tubes filled with
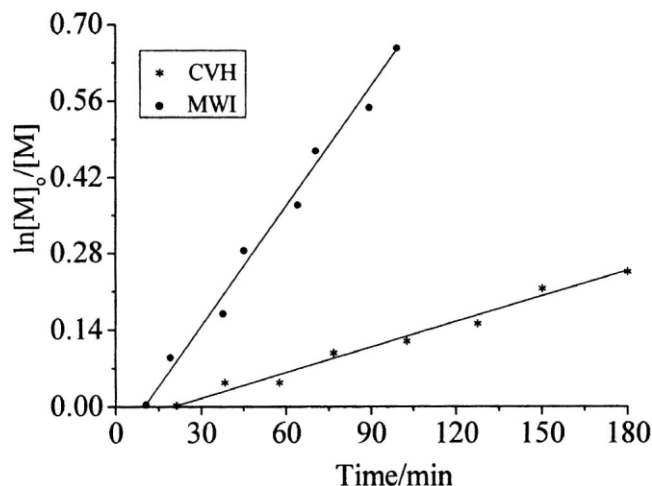
Figure 1 Kinetics of ATRP of AN under MWI and CVH with $[AN] = 6.0M$ and $[AN]/[BPN]/[FeBr_2]/[IA] = 400 : 1 : 1 : 2$.

FeBr$_2$, IA, BPN, and AN were placed in the refluxing solvent so that polymerization could take place.

General procedures of polymerization

A dry glass tube was filled with FeBr$_2$, IA, BPN, and AN. Three freeze–pump–thaw cycles were performed, and the tube was sealed *in vacuo* and placed in a self-improved microwave oven with a reflux of CCl$_4$ at the boiling point (76.8°C) for a certain time with MWI (MWI power = 450 W), whereas with CVH, the tube was placed in an oil bath. The polymerizations were stopped at the desired time by the cooling of the tubes in ice water. Afterward, the tubes were opened, and the contents were 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 conversion of the monomer was determined gravimetrically. The number-average 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 mL/min through a combination of Waters HR1, HR3, and HR4 Styragel columns. Poly(methyl methacrylate) strands 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.

To compare with the previous measurements of the molecular weight of AN (M_{wAN}) polymers, the theo-

retical molecular weight (M_{th}) was used. According to the characteristics of living polymerization, M_{th} could be calculated from the following equation:

$$M_{th} = \frac{[AN]}{[BPN]} \times M_{wAN} \times \text{Conversion}$$

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

RESULTS AND DISCUSSION

ATRP of AN

ATRP of AN catalyzed by FeBr$_2$/IA was carried out with both MWI and CVH processes. A change of color from light yellow to deep orange was observed during the polymerization. This corresponded to the decomposition of BPN and the establishment of the equilibrium between Fe^{3+} and Fe^{2+}. Figure 1 shows the kinetic plots of $\ln([M]_0/[M])$ versus time for ATRP of AN with different polymerization processes (MWI and CVH), where $[M]_0$ is AN concentration in the feed and $[M]$ is AN 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 indicated that in the polymerization process, the number of active species was constant, and the termination reactions could be neglected. These results reveal that the polymerization of AN with BPN/FeBr$_2$/IA initiating system was a controlled radical polymerization process. According to the slopes of the kinetic plots, the apparent rate constant (k_p^{app}) was calculated. The k_p^{app} under MWI (1.1×10^{-4} s^{-1}) was much higher than that under CVH
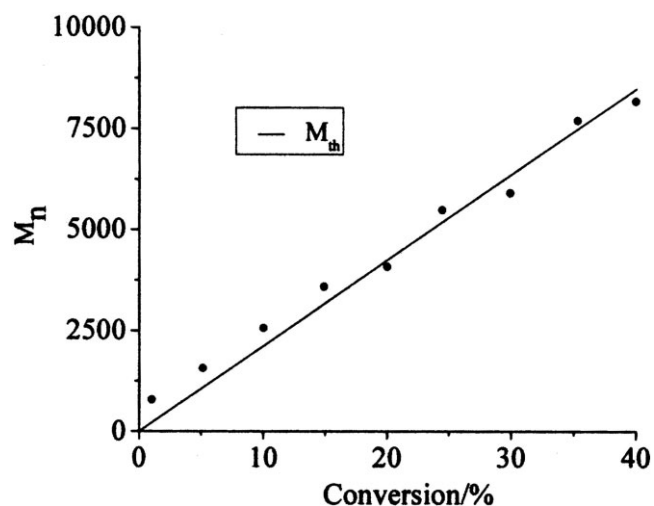

Figure 2 Dependence of M_n on the monomer conversion at various ratios of [FeBr$_2$]/[IA] under MWI for ATRP of AN with $[AN] = 6.0M$ and $[AN]/[BPN]/[FeBr_2]/[IA] = 400 : 1 : 1 : 2$.
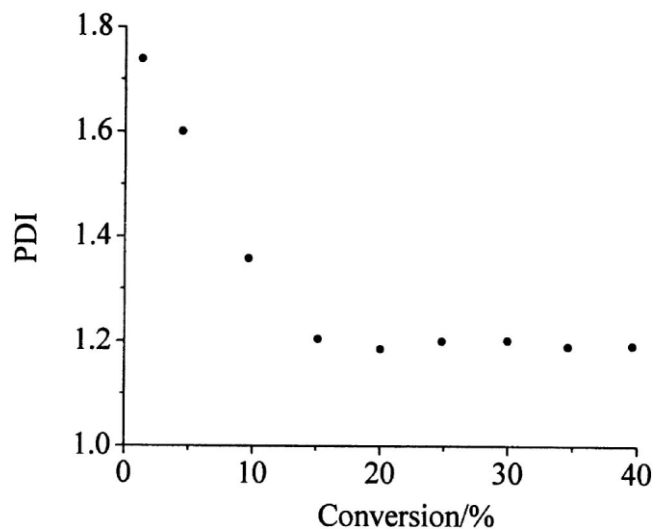
Figure 3 Dependence of PDI on the monomer conversion at various ratios of [FeBr$_2$]/[IA] for ATRP of AN under MWI with [AN] = 6.0M and [AN]/[BPN]/[FeBr$_2$]/[IA] = 400 : 1 : 1 : 2.

(2.3 × 10^{-5} s^{-1}), which indicated that the application of MWI could greatly enhance the rate of polymerization. As shown in Figure 1, ATRP of AN appeared to require an induction period. The induction period became shorter under MWI (10 min) than under CVH (20 min). The induction period was perhaps caused by two things: the presence of oxygen and impurities and the slow formation of the catalytic center.[16,17] A similar result was reported by Xiulin et al.[18] for the copper-mediated ATRP of methyl methacrylate under MWI. This suggests that MWI supplies the higher amount of energy in the system. Thus, applying MWI to polymerization can enhance the rate of polymerization.

Figure 2 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 conversion beyond 15%. The molecular weight at conversion less than 15% was higher. There were polymer chains with all different molecular weights in the system. When pre-

cipitation was used to collect the polymer, polymer chains with low molecular weight did not precipitate and were washed off. This caused the high molecular weight at the early stage of polymerization. A similar phenomenon has been observed earlier.[19]

The values of PDI of the AN polymers are shown in Figure 3. The PDI was as narrow as 1.19 when the conversion went beyond 15%, and a broader PDI was obtained when the conversion was less than 15%. This suggests that the conventional radical polymerization took place during the initial polymerization in the reaction system. In other words, the ATRP system set up as the conversion went beyond 15%.

Effect of the FeBr$_2$/IA catalyst system on ATRP of AN under MWI

It has been reported that a catalyst system might decrease initiator efficiency and lead to an increase in the observed molecular weight.[20] To further investigate the effects of a catalyst system, a series of experiments of ATRP of AN under MWI were carried out. The results are compiled in Table I. In this study, different conclusions were drawn. As more of the FeBr$_2$/IA catalyst system was added (entries 1, 2, 3, and 4), slower polymerization rates and narrower molecular weight distributions were observed, but the initiation efficiency ($f = M_{th}/M_n$) also increased from 0.87 to 0.94, which suggests that the concentration of FeBr$_2$ had a favorable influence on the activation and equilibrium of ATRP. With increasing IA in the catalyst system (entries 2, 5, 6, and 7), the rate of polymerization and f showed a trend of decreasing, whereas the molecular weight distribution of polymers remained narrow. This illustrates that a large amount of IA not only poisoned the metal catalyst, but it also had a role in producing a more significant side reaction, such as a reaction with active species.

Chain extension of PAN

An additional method toward verifying the functionality of a polymer prepared by ATRP is as a macro-

TABLE I
Data for ATRP of AN Catalyzed by FeBr$_2$/IA Under MWI

Entry	[BPN]/[FeBr$_2$]/[IA]	Time (min)	Conversion (%)	M_{th}	M_n	PDI	$k_p^{app} \times 10^4$ (s^{-1})	f
1	1 : 0.5 : 1		54.8	11,620	13,360	1.24	1.32	0.87
2	1 : 1 : 2		48.3	10,240	11,250	1.19	1.11	0.91
3	1 : 2 : 4		43.2	9,160	9,960	1.18	0.94	0.92
4	1 : 3 : 6	100	39.6	8,400	8,940	1.17	0.84	0.94
5	1 : 1 : 1		52.5	11,130	12,100	1.20	1.24	0.92
6	1 : 1 : 3		44.2	9,370	11,020	1.19	0.97	0.85
7	1 : 1 : 4		40.1	8,500	10,370	1.21	0.85	0.82

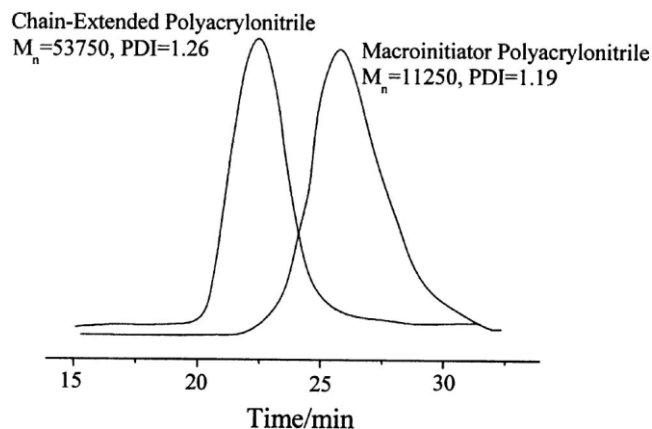[AN] = 6.0M; [AN]/[BPN] = 400 : 1.

Figure 4 GPC curves of PAN before and after a chain extension reaction.

initiator for the same or other monomers.[21] The chain extension polymerizatio n of AN with PAN (M_n = 11,250, PDI = 1.19) as the macroinitiator under MWI was performed. As shown in Figure 4, when [AN] = 7.0M, [AN]/[PAN]/[FeBr$_2$]/[IA] = 800 : 1 : 1 : 2, and time = 30 h, the conversion was greater than 90%. The PAN obtained was with M_n = 53,750 and PDI = 1.26. This clearly demonstrates the chain extension of PAN took place. The chain-extension polymerization further verified the active nature of the precursor chain end. Therefore, the obtained PAN could act as a macroinitiator for the extension polymerization.

CONCLUSIONS

A new catalyst system, FeBr$_2$/IA, was successfully used in ATRP of AN under MWI. k_p^{app} under MWI was higher than under CVH in the same experimental conditions. When the ratio of [AN]/[BPN]/[FeBr$_2$]/ [IA] was 400 : 1 : 1 : 2, the polymerization was best controlled. The PAN obtained was end-functionalized by chlorine atoms and could act as a macroinitiator for the extension polymerization.

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