

Synthesis of Polyacrylonitrile via ARGET ATRP Using CCl_4 as Initiator

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ABSTRACT: Activators regenerated by electron transfer (ARGET) for atom transfer radical polymerization (ATRP) of acrylonitrile (AN) was investigated using carbon tetrachloride (CCl_4) as initiator, ferric trichloride anhydrous (FeCl_3)/iminodiacetic acid (IDA) as catalyst system, L-ascorbic acid (VC) as reducing agent, and *N,N*-dimethylformamide (DMF) as solvent. Kinetic data of polymerization demonstrated the features of living/controlled free-radical polymerization. The conversion of AN increased with the increasing concentration of CCl_4 , $[\text{FeCl}_3]/[\text{IDA}]$ catalyst system and VC. The molecular weight decreased

with the increasing concentration of CCl_4 , $[\text{FeCl}_3]/[\text{IDA}]$ catalyst system and VC. The value of polydispersity index (PDI) increased with the increasing concentration of $[\text{FeCl}_3]/[\text{IDA}]$ catalyst system and VC, while the value of PDI decreased first and then increased with the increasing concentration of CCl_4 and IDA. $^1\text{H-NMR}$ spectra of PAN further verified the features of living/controlled free radical polymerization of AN. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3673–3677, 2010

Key words: ARGET ATRP; CCl_4 ; AN

INTRODUCTION

Polyacrylonitrile (PAN) is an important precursor for polymer materials because of its unique and well-known properties including hardness and rigidity, chemical resistance, compatibility with certain polar substances, and low gas permeability.¹ A narrower molecular weight distribution desired for PAN is important for the mentioned applications. However, PAN is usually prepared by normal radical polymerization without control molecular weight and polydispersity index (PDI) which affects the mechanical performance of PAN fibers. In recent years, more and more attention has been attracted to living/controlled radical polymerization (CRP), which allows for excellent control over molecular microstructure to produce specialty polymers.² In particular, atom transfer radical polymerization (ATRP)^{3,4}

has become one of the preferred methods for the preparation of well-defined polymeric materials. Scheme 1 shows the general mechanism of ATRP. It relies on involving a fast dynamic equilibrium between dormant species R-X and active radical species $\text{R}\cdot$ to provide control.^{4–10}

However, the toxicity of the halide species RX and the oxidation of the catalyst M_t^n/L_x by oxygen in air limit its widespread in industrial utilization. Reverse atom transfer radical polymerization (RATRP)^{11,12} and activators generated by electron transfer ATRP (AGET)^{13–15} are used to overcome these drawbacks. Although RATRP and AGET ATRP can solve some questions and obtain some results, they have some insufficiencies. Reverse ATRP rarely allows the synthesis of pure block copolymers since the products are always contaminated with homopolymers formed by direct initiation from the free radical initiator. In AGET ATRP, the oxidative stable metal catalyst, present at a considerably higher concentration (>0.1 mol % vs. monomer), was reduced with nearly stoichiometric amounts of reducing agents. So it is difficult to eliminate the color of the product. To overcome these drawbacks, Matyjaszewski et al. introduced the concept of activator regenerated by electron transfer (ARGET),¹⁶ which has allowed the polymerizations to be established at ppm level of catalysts concentration making this approach more attractive for commercial acceptance. The typical mechanism is shown in Scheme 2.

In the ARGET system, a tiny amount of metal catalyst is used together with a sufficiently large excess

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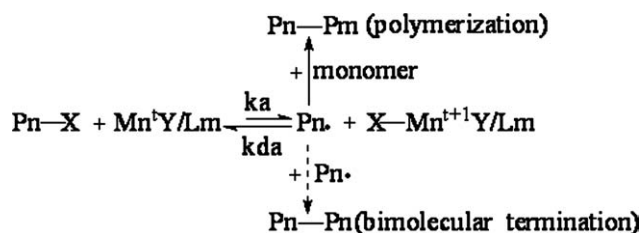
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Scheme 1 Proposed mechanism for atom transfer radical polymerization (ATRP).

of reducing agent, which not only reduces excess M_t^{n+1} deactivator formed in termination reactions to the original active M_t^n state but is also responsible for scavenging oxygen and suppressing side reactions between the chain end and the catalyst. Well-defined polymers of styrene^{17,18} or acrylate^{19,20} have been prepared by ARGET ATRP. ARGET ATRP of AN using $\text{CuCl}_2/\text{tris} [(2\text{-pyridyl})\text{methyl}]\text{amine}$ (TPMA) as the catalyst and tin(II) 2-ethylhexanoate $[\text{Sn}(\text{EH})_2]$ as the reducing agent in ethylene carbonate and dimethyl sulfoxide (DMSO) in the absence of oxygen has been reported by Matyjaszewski et al.²¹ Our group²² have reported that ARGET ATRP of AN using $\text{FeCl}_3/\text{isophthalic acid}$ (IA) as the catalyst and ascorbic acid (VC) as the reducing agent in *N,N*-dimethylformamide (DMF) in the presence of oxygen.

Traditionally, the initiator employed in ARGET ATRP includes ethyl 2-bromoisobutyrate (EBiB),^{17,19-23} methyl 2-chloropropionate (MCP),²⁴ methyl 2-bromopropionate (MBP),²⁴ and so on. These initiators might often be expensive, and add significantly to production costs. Carbon tetrachloride (CCl_4) has been used as initiator in redox-catalyzed radical addition and telomerization.²⁵ ATRP of MMA with CCl_4 as an efficient initiator has been reported.^{3,26-28} To the best of our knowledge, CCl_4 as initiator of the ARGET ATRP has not been reported. Also, Fe-catalyzed ARGET ATRP was rarely reported.

In this article, we report a novel ARGET ATRP system to prepare PAN with high molecular weight and narrow polydispersity. In this ARGET ATRP system, CCl_4 was selected to be initiator, and ferric trichloride anhydrous (FeCl_3)/iminodiacetic acid (IDA) were chosen to be catalyst system, ascorbic acid (VC) was served as the reducing agent, and DMF was used as the solvent. Effects of the amount of CCl_4 , the ratio of metal to ligand and the amount of VC were also investigated.

EXPERIMENTAL

Materials

Acrylonitrile (AN) (Tianjin FuChen Chemical Reagents, Tianjin, China) was distilled under normal

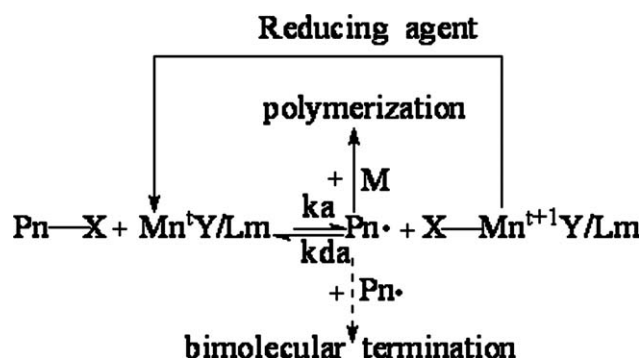
pressure and stored at 5°C. Carbon tetrachloride (CCl_4) (Tianjin Regent Chemical, Tianjin, China), ferric trichloride anhydrous (FeCl_3) (Sinopharm Chemical Reagent, Shanghai, China), IDA (Sinopharm Chemical Reagent, Shanghai, China), L-ascorbic acid (VC) (Tianjin Regent Chemical, Tianjin, China), and DMF (Tianjin FuChen Chemical Reagents, Tianjin, China) were used as received. All other chemical reagents were used as received.

ARGET ATRP polymerization procedure

In a typical experiment, AN (19.8 mL, 0.3 mol), CCl_4 (0.14 mL, 1.5 mmol), FeCl_3 (1.5×10^{-5} mol), IDA (1.5×10^{-4} mol) and VC (1.5×10^{-4} 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 with N_2 finally. The mixture was always colorless and the flask was then 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 was precipitated by methanol-water (V : V, 1 : 1). The production was dried 24 h under vacuum.

Characterization

Percentage conversion of AN was determined by gravimetry. 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 Waters HT3, HT4, and HT5 styragel columns. A Waters 2414 differential refractometer was used as the detector. Linear poly-(methyl methacrylate) standards was used for calibration. The analysis was undertaken at 35°C with purified chromatography-grade DMF as an eluent. The $^1\text{H-NMR}$ spectra were recorded at 25°C in DMSO-d_6 on a Bruker



Scheme 2 Proposed mechanism for activator regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP).

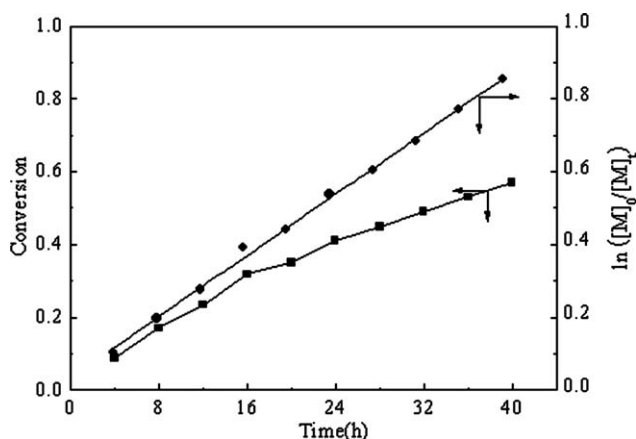


Figure 1 Kinetic plot for ARGET ATRP of AN at 65°C in DMF with [AN] = 6.0 M and [AN] : [CCl₄] : [FeCl₃] : [IDA] : [VC] = 200 : 1 : 0.01 : 0.1 : 0.1.

Avance DMX500 NMR instrument operating at 500 MHz for ¹H, and using the standard Bruker software. Chemical shifts are reported in ppm with respect to TMS as internal standard.

RESULTS AND DISCUSSION

Synthesis of PAN using ARGET ATRP

Well-defined PAN was synthesized using ARGET ATRP, which was initiated by CCl₄ and catalyzed by FeCl₃/IDA. Polymerizations were performed at 65°C in DMF with molar ratio of [AN] : [CCl₄] : [FeCl₃] : [IA] : [VC] at 200 : 1 : 0.01 : 0.1 : 0.1. Kinetic plot for ARGET ATRP of AN with 50 ppm of Fe versus monomer was shown in Figure 1. The monomer conversions increased with the reaction time and reached about 57% within 40 h. The linear kinetic plot of monomer conversion suggested that a constant radical concentration was maintained and the termination reactions could be neglected. According to the slopes of the kinetic plots, the apparent rate constant (k_p^{app}) was calculated to be $6.017 \times 10^{-6} \text{ s}^{-1}$.

Figure 2 indicates the values of molecular weights and PDI of the resulting polymers measured by GPC. From Figure 2 we can see that, the polymerization conversion reached 57% with almost linear

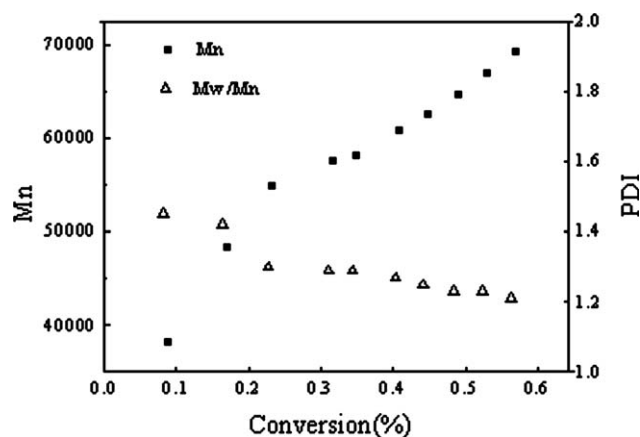


Figure 2 Dependence of M_n and PDI on monomer conversion for ARGET ATRP of AN at 65°C in DMF with [AN] = 6.0 M and [AN] : [CCl₄] : [FeCl₃] : [IDA] : [VC] = 200 : 1 : 0.01 : 0.1 : 0.1.

increase in M_n with total conversion. The value of PDI remained with the range of 1.45–1.20 as shown in Figure 2.

Effect of concentration of [CCl₄] on ARGET ATRP of AN

To clarify the role of CCl₄ in the ARGET ATRP system, the effect of different amounts of CCl₄ on the AN polymerizations was studied at 65°C in DMF with [AN] = 6.0 M and [AN] : [FeCl₃] : [IDA] : [VC] = 200 : 1 : 0.1 : 0.1. The results were shown in Table I. It was found that the conversion of AN increased with the increasing concentration of CCl₄, while the molecular weight decreased from 58,700 to 26,400. And the value of PDI decreased first and then increased with increasing concentration of CCl₄. When the ratio of [CCl₄] : [FeCl₃] : [VC] was 1 : 0.01 : 0.1, the features of living/controlled was better. The molecular weight was much higher than the theory molecular weight. These can be explained that the mechanism of initiating of ARGET ATRP is more difficult than the alkyl halides initiators, and a greater activity of chain ends would result in an incomplete initiation with higher molecular weight.²⁹ Sawamoto et al.²⁵ and Teyssie and coworkers²⁸ also

TABLE I
Effect of Concentration of [CCl₄] on ARGET ATRP of AN at 65°C in DMF with [AN] = 6.0 M and [AN] : [FeCl₃] : [IDA] : [VC] = 200 : 0.01 : 0.1 : 0.1

Entry	[CCl ₄] : [FeCl ₃] : [VC]	Fe [ppm]	Reaction time/h	Conversion/%	M_n	M_w/M_n
1	0.25 : 0.01 : 0.1			9.8	58,700	1.37
2	0.5 : 0.01 : 0.1			12.5	55,300	1.48
3	1 : 0.01 : 0.1	50	12	23.3	54,900	1.30
4	1.5 : 0.01 : 0.1			26.3	27,900	1.57
5	1.75 : 0.01 : 0.1			32.28	26,400	1.60

TABLE II
Effect of Concentration of L-Ascorbic Acid (VC) on ARGET ATRP of AN at 65°C in DMF with [AN] = 6.0 M and [AN] : [CCl₄] : [FeCl₃] : [IDA] = 200 : 1 : 0.01 : 0.1

Entry	[FeCl ₃] : [VC]	Fe [ppm]	Reaction Time/h	Conversion/%	<i>M_n</i>	<i>M_w</i> / <i>M_n</i>
1	0.01 : 0.05			4.98	66,600	1.22
2	0.01 : 0.075			20.15	60,100	1.28
3	0.01 : 0.1	50	12	23.30	54,900	1.30
4	0.01 : 0.125			24.25	50,200	1.48
5	0.01 : 0.15			33.45	48,200	1.50

used CCl₄ to initiate ATRP of Methyl Methacrylate. They all indicated the presence of an unexpected downward deviation from linearity of the molecular weight during ATRP process.

Effect of concentration of L-ascorbic acid (VC) on ARGET ATRP of AN

In an ARGET ATRP the added VC reduced the oxidative stable Fe(III)/ligand precursor to the active Fe(II)/ligand complex. Consequently, the concentration of VC added to the reaction mixture directly influences the ratio of Fe(II)/L_X activator to Fe(III)/L_X deactivator in the reaction mixture and ultimately the rate of polymerization as well as the molecular weight distribution of the polymer formed in an ATRP. To further discuss effects of reducing agent VC on ARGET ATRP of AN, a series of experiments were carried out. The results have been summarized in Table II. The conversions increased from 4.98% to 33.45% with the increasing concentration of VC. And the value of PDI increased from 1.22 to 1.50 with the increasing concentration of VC. The molecular weights decreased with the increasing VC concentration. Increasing the amount of VC resulted in the higher concentration of Fe(II)/IDA produced by the reduction of Fe(III)/IDA complex, and then increased concentrations of the propagating radicals in the polymerization system. According to the former article, increased concentration of propagating radicals gives higher termination rate. Thus the broader molecular weight distributions of PAN were observed.

Effect of [FeCl₃]/[IDA] catalyst system on ARGET ATRP of AN

Table III summarized a series of experiment results in which AN was polymerized in the presence of different ratio of [FeCl₃]/[IDA]. It was found that the molecular weights decreased with the increasing concentration of [FeCl₃]/[IDA] catalyst system, while the conversions of AN increased from 8.50 to 24.89%. The value of PDI increased from 1.22 to 1.50 with the increasing [FeCl₃]/[IDA] concentration (Table III, entry 1–4). In ARGET ATRP of AN, Fe(II)/IDA activator and stable Fe(III)/IDA precursor are in balance. Increasing the amount of stable Fe(III)/IDA precursor resulted in the higher concentration of Fe(II)/IDA, and then increased concentrations of the propagating radicals in the polymerization system. Thus the broader molecular weight distributions of PAN were observed (1.24–1.40). When the concentration of Fe was constant (50 ppm), the conversion and the molecular weights increased first and then decreased with the increasing concentration of ligand (Table III, entry 2, 5, 6), while the value of PDI decreased first and then increased. When the concentration of Fe was 50 ppm and the ratio of [FeCl₃]/[IDA] = 1 : 0.01 : 0.05, the conversion of AN, molecular weight and value of PDI was 31.34%, 69,900 and 1.22, respectively.

¹H-NMR spectra of PAN

The chain end of the PAN prepared via ARGET ATRP using CCl₄ as an initiator was analyzed by

TABLE III
Effect of [FeCl₃]/[IDA] Catalyst System on ARGET ATRP of an at 65°C in DMF with [AN] = 6.0M and [AN] : [CCl₄] : [VC] = 200 : 1 : 0.1

Entry	[CCl ₄] : [FeCl ₃] : [IDA]	Fe [ppm]	Reaction time/h	Conversion/%	<i>M_n</i>	<i>M_w</i> / <i>M_n</i>
1	1 : 0.0075 : 0.075	37.5		8.50	69,200	1.24
2	1 : 0.01 : 0.1	50		23.30	54,800	1.30
3	1 : 0.0125 : 0.125	62.5	12	23.14	53,300	1.32
4	1 : 0.015 : 0.15	75		24.89	51,300	1.40
5	1 : 0.01 : 0.05	50		31.34	69,900	1.22
6	1 : 0.01 : 0.075	50		22.21	68,200	1.23

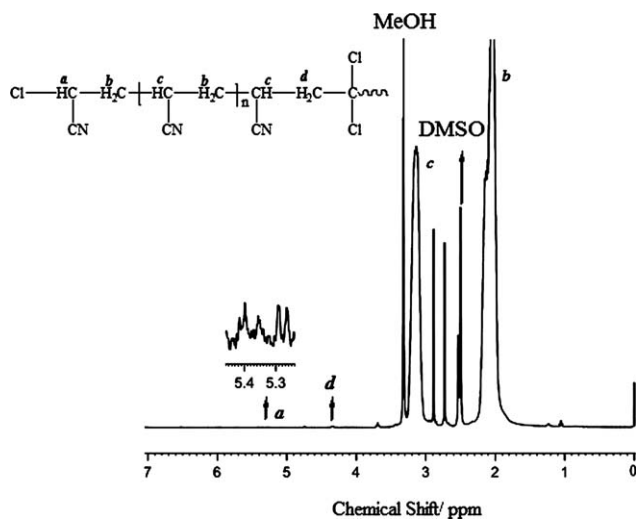


Figure 3 $^1\text{H-NMR}$ spectrum of CCl_4 initiated PAN imethylene carbonate at 44°C . $[\text{AN}] : [\text{CCl}_4] : [\text{FeCl}_3] : [\text{IDA}] : [\text{VC}] = 200 : 1 : 0.01 : 0.1 : 0.1$.

$^1\text{H-NMR}$ spectroscopy, as shown in Figure 3. $\text{CHCl}(\text{CN})$ proton from the end group at 5.2–5.4 ppm [Fig. 3(a)] in PAN were observed. The chemical shift $\delta = 4.3$ ppm [Fig. 3(d)] was attributed to the $\text{CH}_2\text{CH}_2\text{CCl}_2$. The chemical shift $\delta = 3.3$ ppm was corresponded to the $\text{CH}(\text{CN})$ [Fig. 3(c)]. The chemical shift $\delta = 2.0$ ppm [Fig. 3(b)] was attributed to the CH_2 . The $^1\text{H-NMR}$ spectra of PAN verified the features of controlled/living free-radical polymerization of AN.

CONCLUSIONS

A new method for conducting ARGET ATRP of AN mediated by FeCl_3/IDA , using CCl_4 as bifunctional initiator and VC as reducing agent, was firstly developed. The kinetic plot demonstrated the features of living/controlled free-radical polymerization such as the number-average molecular weights increasing linearly with monomer conversion and narrow molecular weight distributions. The living feature of the obtained polymer was further verified by the $^1\text{H-NMR}$ spectra of PAN. Experiments of effects of the amount of CCl_4 , the ratio of metal to ligand and the amount of VC suggest that the molecular weight decreased with the increasing concentration of CCl_4 , $[\text{FeCl}_3]/[\text{IDA}]$ catalyst system and VC. The value of PDI increased with the increasing concentration of $[\text{FeCl}_3]/[\text{IDA}]$ catalyst system and VC, while the

value of PDI decreased first and then increased with the increasing concentration of CCl_4 and IDA.

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