e-Polymers **2011**, no. 007

http://www.e-polymers.org
ISSN 1618-7229

Preparation of polyacrylonitrile via AGET ATRP initiated by CCl_4

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(Received: 06 June, 2010; published: 18 February, 2011)

Abstract: A commercially available alkyl halide carbon tetrachloride (CCl_4) was used as the initiator for activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) of acrylonitrile (AN) in N,N-dimethyl formamide (DMF). Environmentally benign ascorbic acid (VC) was chosen as the reducing agent and copper bromide ($CuBr_2$) as the catalyst precursor together with iminodiacetic acid (IDA) as the ligand. The polymerization proceeded in a controlled manner as evidenced by kinetic of AGET ATRP of AN, a linear increase of number-average molecular weight (M_n) with monomer conversion and low polydispersity index (PDI) throughout the reactions. The monomer (AN) conversion increased with the increase of VC and CCl_4. The value of PDI increased with the increase in concentration of VC. For an increase of CCl_4, the value of PDI decreased first and then increased. ^{1}H-NMR spectrum of PAN further confirmed the “living”/controlled feature of AGET ATRP of AN.

Introduction

PAN, which possess outstanding chemical and mechanical properties, has proved to be an important polymer precursor, such as the preparation of carbon fibers, nanometer carbon tubes, membrane materials, etc [1, 2]. High molecular weight and narrow polydispersity are the two essential requirements for synthesis of PAN to satisfy the requirements for high performance carbon-based materials [3]. Conventional radical polymerization is normally applied to the preparation of PAN, while the molecular dimension and structure of PAN synthesized via this technique are not well controlled [4]. As a result, atom transfer radical polymerization (ATRP), as one of the most attractively controlled/living radical polymerization (CRP) [5] technologies, is proposed by Wang and Matyjaszewski [6, 7] as an extension of atom transfer radical addition (ATRA) [8] in organic chemistry. Since there is a quick dynamic equilibrium between dormant species and active chains mediated by low-valent transition metal in ATRP, the side reactions of coupling termination of radicals and chain transfer are dramatically suppressed and the control over polymerization is implemented. A large number of polymers with predefined molecular weight and narrow polydispersity index have been successfully prepared using a wide range of monomers such as styrenics, [9] (meth)acrylates,[10-13] acrylonitrile, [14-17] and nanostructured materials [18].

Unfortunately, ATRP has its inherent drawbacks due to the sensitivity of low-valent catalyst to air and humidity. This problem can be partially solved by rigorous deoxygenation procedures. However, the procedure is time-consuming and uneconomic for substantial production [19-22]. Based on ATRP techniques, reverse atom transfer radical polymerization (RATRP), using oxidation state transition metal and normal radical initiator in place of reduction state transition metal and alkyl halide in ATRP, is put forward and this is more convenient. But the shortage also exists that pure block copolymers cannot be prepared because the concentration of catalyst cannot be changed independently of the initiator [23].

Activator generated by electron transfer for atom transfer radical polymerization (AGET ATRP) [24-28] can act as an alternative developed for the synthesis of polymer with controlled degree of polymerization, narrow polydispersity and well-defined architecture [29]. In AGET ATRP process, the active species is generated by the reduction of oxidation state transition metal complex via reducing agent, such as tin(II)-2-ethylhexanoate (Sn(EH)2) [30] or ascorbic acid (VC) [31, 32]. The presence of reducing agent can also compensate for the air or other radical traps in the system, so that the polymerization can perform in a controlled manner under aerobic conditions. It is similar to the process in activator generated by electron transfer for atom transfer radical polymerization (ARGET ATRP) [18, 29, 33-35].

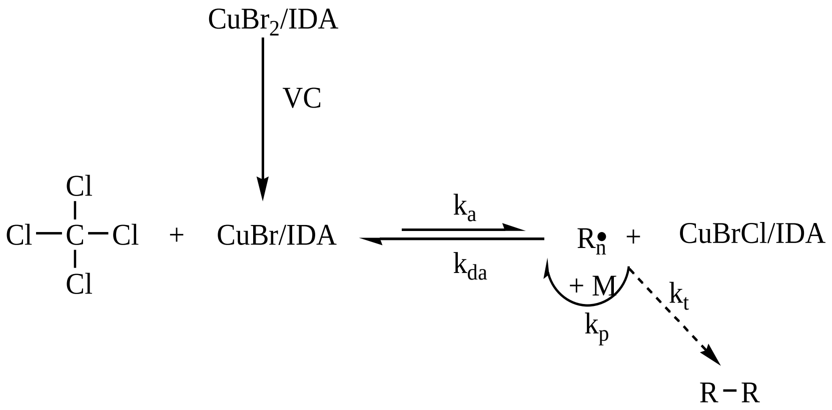
In ATRP, both low molecular weight and polymeric initiators has been used, such as ethyl 2-bromoisobutyrate (EBiB), [24] 1,3,5-(2'-bromo-2'-methylpropionato) benzene (BMPB) [36] and 1,1,1-tris(4-(2-bromoisobutyryloxy)-phenyl) ethane (TBiBPE) [37]. Carbon tetrachloride (CCl4), as a low-cost and commercially available initiator, has also been successfully used in ATRP of MMA and proves to be effective [38-40]. However, to the best of our knowledge, the use of CCl4 as the initiator in AGET ATRP of AN has never been reported. In view of this point, we first investigate the utilization of CCl4 as the initiator in AGET ATRP of AN.

In this paper, the method of activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) was applied to the synthesis of AN using CCl_4 as the initiator, $CuBr_2$ as the catalyst precursor and VC as reducing agent in DMF. Effects of the amount of VC and CCl_4 were also investigated.

Results and discussion

Preparation of PAN via AGET ATRP

A series of experiments were carried out with CCl_4 as initiator under the conditions of [AN]:[CCl_4]:[$CuBr_2$]:[IDA]:[VC] = 200:1:1:2:0.75 at 65 °C in DMF. The concentration of AN was set as 6 M. The kinetics curve has been presented in Figure 1.



Scheme 1. The proposed mechanism for AGET ATRP with CCl_4 as initiator.

The conversion of AN increased with the increase of reaction time and reached a 80% conversion within 60 h. The value of ln([M]$_0$/[M]) increased linearly with increasing time, demonstrating the polymerization was first-order to monomer concentration and the propagation radical concentration was constant in the whole process of polymerization. It can be concluded that the apparent rate constant (k_p^{app}) was 1.09×10^{-5} s^{-1} according to the slope of the kinetic plot. The proposed mechanism of AGET ATRP has been described in Scheme1.

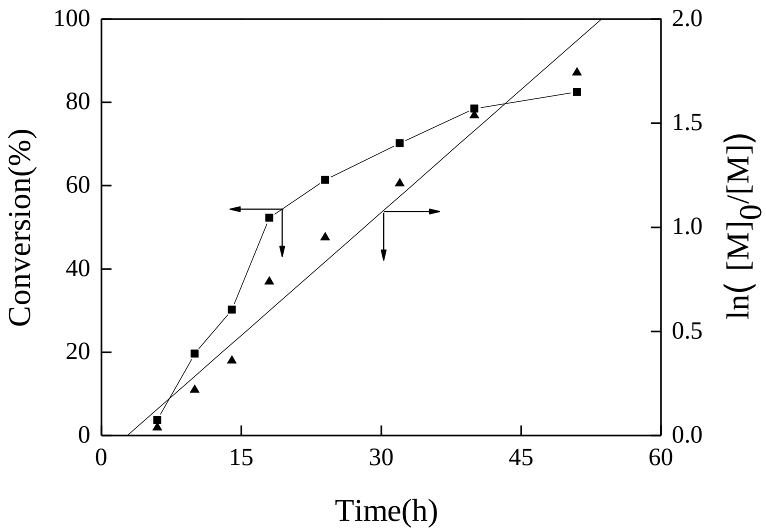


Fig. 1. First-order kinetics plot for AGET ATRP of AN at 65 °C in DMF with [AN] = 6.0 M and [AN]:[CCl_4]:[$CuBr_2$]:[IDA]:[VC]=200:1:1:2:0.75.

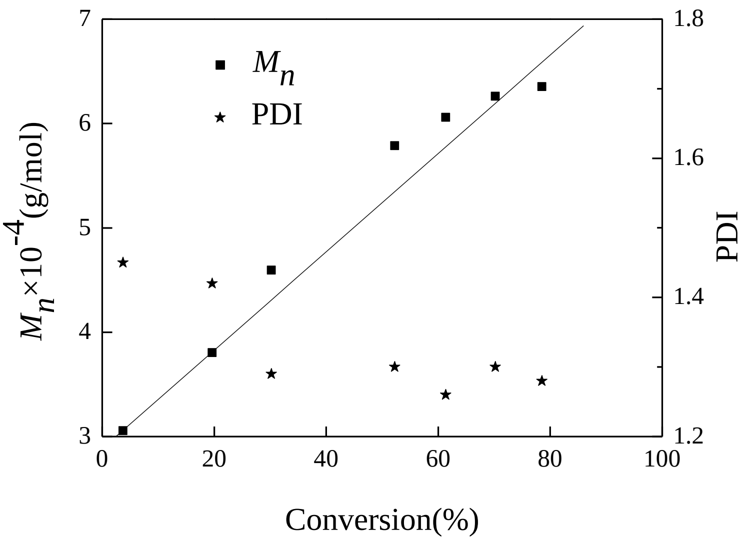


Fig. 2. Evolution of M_n and PDI versus monomer conversion for AGET ATRP of AN at 65 °C in DMF with CCl_4 as the initiator and [AN]:[CCl_4]:[$CuBr_2$]:[IDA]:[VC] = 200:1:1:2:0.75.

The evolution of M_n and PDI with the conversion of AN has been summarized in Figure 2. With the increasing monomer conversion, M_n increased almost linearly, indicating the number of propagation chains was almost constant. PDI was lower than 1.45 during the whole polymerization process.

Effect of VC concentration on AGET ATRP of AN

Active catalyst complex (CuBr/IDA) was generated by the in situ reduction of catalyst precursor ($CuBr_2$/IDA) with reducing agent VC for AGET ATRP of AN. To examine the effect of VC on the polymerization, experiments were conducted using different concentrations of VC with [AN]:[CCl_4]:[$CuBr_2$]:[IDA] = 200:1:1:2. Table 1 gives the conditions and results of AGET ATRP of AN at 65 °C in DMF for 14 h. AN conversion increased from 21.66% to 40.21% and the molecular weight distribution increased from 1.19 to 1.41 with the increase of VC concentration. The amount of VC added to the reaction mixture directly influenced the concentration of Cu(I) produced by the reduction of Cu(II), further changed the concentration of propagation radical. With the increase of VC concentration, the concentration of propagation radical increased, which enhanced the polymerization rate. As a result, the monomer conversion increased. The higher molecular weight polymers may also be formed by the termination reaction due to the higher propagation radical concentration. Also, broader molecular weight distribution was observed in Table 1.

Tab. 1. Data for AGET ATRP of AN with different ratios of [VC] to [$CuBr_2$].

Entry	[VC]:[$CuBr_2$]	Conversion%	M_n	*PDI*
1	0.6:1	21.66	41520	1.19
2	0.75:1	30.22	45940	1.27
3	0.9:1	36.20	46570	1.32
4	1.0:1	40.21	47390	1.41

[AN]:[CCl_4]:[$CuBr_2$]:[IDA]=200:1:1:2, [AN]=6 mol/L, T=65°C, t=14 h, in DMF

Effect of the feed ratio of [AN] to [CCl_4]

The effect of initiator on the polymerization of AN via AGET ATRP was investigated to define the conditions for better control on polymerization by conducting the experiments in the range of [AN]/[CCl_4] from 200:0.5 to 200:1.5 at fixed concentration of the other components at 65 °C in DMF for 14 h. Table 2 shows the results of the experiments. As expected, monomer conversion increased with increasing the concentration of initiator CCl_4, while M_n decreased correspondingly under the same conditions. PDI decreased first, but increased when the ratio of [AN] to [CCl_4] exceeded 200:1. As a result, as far as this study is concerned, the best feed ratio of [AN] to [CCl_4] was selected as 200:1.

Tab. 2. Results for AGET ATRP of AN with different feed ratios of AN to CCl_4.

Entry	[AN]:[CCl_4]	Conversion %	M_n	*PDI*
1	200:0.5	22.93	52030	1.29
2	200:0.75	26.89	47900	1.32
3	200:1	30.22	45940	1.27
4	200:1.25	35.28	43960	1.36
5	200:1.5	44.59	40830	1.47

[AN]:[$CuBr_2$]:[IDA]:[VC]=200:1:2:0.75, [AN]=6.0 mol/L, *T*=65°C, *t*=14 h, in DMF

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

The end-group of PAN synthesized via AGET ATRP with CCl_4 as initiator ([AN]:[CCl_4]:[$CuBr_2$]:[IDA]:[VC] at 200:1:1:2:0.75) was analyzed by ^{1}H-NMR spectroscopy, as shown in Figure 3. The peak at δ = 2.3 ppm (a in Figure 3) was attributed to the methylene protons of acrylonitrile unit of the resulting polymer. NMR signal enlarged at δ = 5.2-5.3 ppm (c in Figure 3) corresponded to methylidyne attached to the end of chain. It deviated from the chemical shift (δ = 3.0-3.3 ppm, b in Figure 3) of other methylidyne protons of acrylonitrile unit for the electronic-attracting function of Cl at the end of chain. The chemical shift at δ = 4.3 ppm (d in Figure 3) was attributed to the protons of CH_2CCl_2.

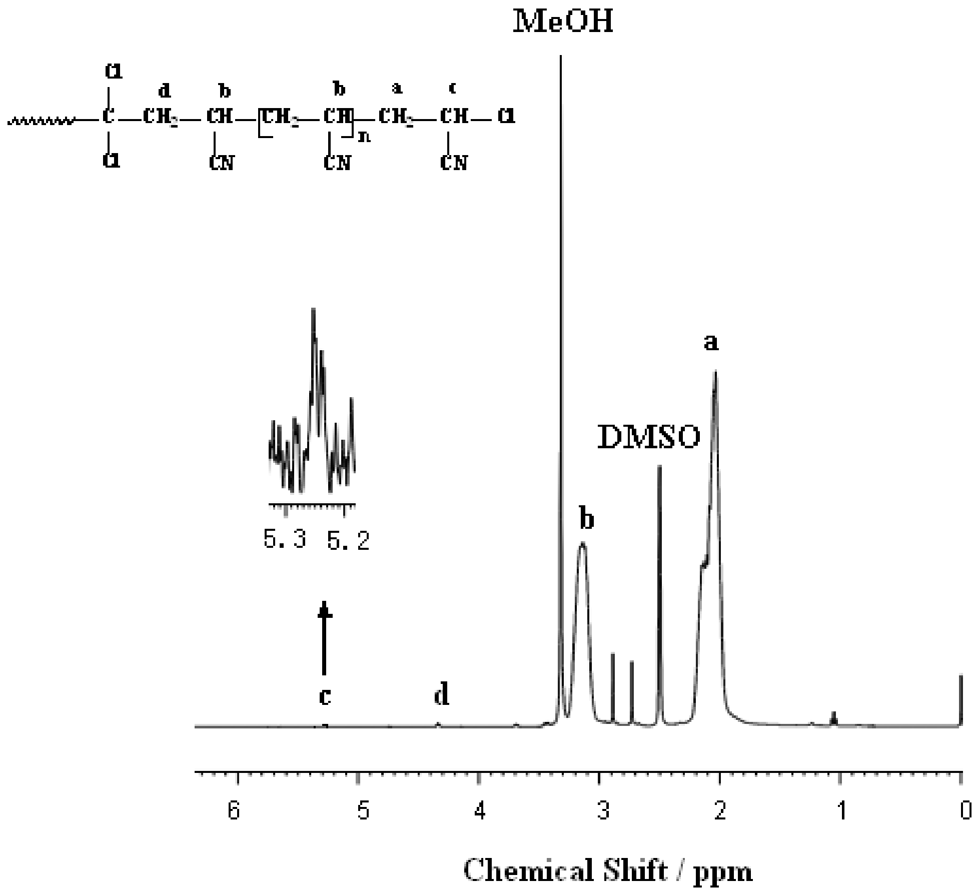


Fig. 3. ^{1}H-NMR spectrum of PAN with CCl_4 as the initiator and [AN]:[CCl_4]:[$CuBr_2$]:[IDA]:[VC] = 200:1:1:2:0.75 at 65 °C in DMF for 14 h.

From the results above, it could be concluded that polymerization proceeded according to the mechanism of “living”/controlled free radical polymerization.

Conclusions

In this paper, commercially available alkyl halide carbon tetrachloride (CCl_4) was successfully used as the initiator for AGET ATRP of AN. Water-soluble ascorbic acid (VC) was selected as the reducing agent for the activation of catalyst precursor $CuBr_2$/IDA complex. Narrow polydispersity PAN was successfully synthesized in the homogeneous reaction system with N,N-dimethyl formamide (DMF) as the solvent at 65 °C. The results studied above demonstrated the “living”/controlled characteristic of AGET ATRP of AN.

Experimental part

Materials

The monomer, AN (>98%), was purchased from Chengdu Chemical Reagents Co. It was purified under air distillation to get 76-78 °C distillation and stored in the refrigerator before use. Ascorbic acid (VC) (>99.7%) (Tianjin Chemical Reagents Co.) was used as received. Cupric bromide ($CuBr_2$) (>98.5%) and carbon tetrachloride (CCl_4) (>99.5%) were purchased from Tianjin Chemical Reagents Co. and used without further purification. Iminodiacetic acid (IDA) (>98%), methanol (>99.5%), hydrobromic acid (HBr) and N,N-dimethylformamide (DMF) were used as received.

Polymerization

General polymerization procedure was as follows: $CuBr_2$ (7.5×10^{-4} mol, 0.1675 g), IDA (1.5×10^{-3} mol, 0.1997 g), DMF (15 ml), AN (0.15 mol, 9.9 ml), CCl_4 (7.5×10^{-3} mol, 0.07 ml) and VC (5.6×10^{-4} mol, 0.0991 g) were added in that order to a dry two-neck flask immersed in an ice bath. The mixture was degassed in vacuum and charged with N_2 for three cycles to remove the oxygen in the system, before transferring the flask into the oil bath thermostated at 65 °C to initiate the polymerization. After predetermined time, the polymerization was stopped by opening the flask and exposing the catalyst to air. The resulting solution was first diluted into DMF, washed with a limited amount of HBr to remove the copper residual on the polymer, and then precipitated into an excess of aqueous solution of methanol (V:V, 1:1). Finally, the product was filtered and dried under vacuum for 24 h.

Characterization

The monomer conversion was measured gravimetrically. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n, PDI) were determined by Gel Permeation Chromatography (GPC). It 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 an eluent. A Waters 2414 differential refractometer was used as the detector. ^{1}H NMR spectra were recorded on a **Bruker** Avance 400 NMR spectrometer using DMSO-d6 as a solvent.

Acknowledgements

The authors are grateful for the financial support by the National Natural Scientific Foundation of China (Nos. 20904018, 51073075), the Youth Science Foundation of Shandong Province (No. 2007BS08027), the Natural Science Foundation of Shandong Province (No. Q2006F05), the Program for Science and Technology Development of Shandong Province (No. 2009GG10003012), and A Project of Shandong Province Higher Educational Science and Technology Program (No. J08LC03).

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