Atom Transfer Radical Polymerization of Acrylonitrile

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ABSTRACT: Iron(II) chloride coordinated by succinic acid was first used as the catalyst in 2-chloropropionitrile-initiated atom transfer radical polymerization (ATRP) of acrylonitrile. N,N-dimethylformamide was used as a solvent to improve the solubility of the ligand. An iron(II) chloride to succinic acid ratio of 0.5 not only gives the best control of molecular weight and its distribution but also provides rather rapid reaction rate. Effects of solvent on polymerization of acrylonitrile were also investigated. The induction period is shorter in N,N-dimethylformamide than in propylene carbonate and toluene and the rate of the polymerization in N,N-dimethylformamide is fastest. The molecular weight of polyacrylonitrile agrees reasonably well with the theoretical molecular weight of N,N-dimethylformamide. The rate of polymerization increases and the induction period becomes shorter with increasing polymerization temperature, and the apparent activation energy was calculated to be 56.5 kJ mol^{-1}. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1050–1054, 2006

Key words: atom transfer radical polymerization; living polymerization; kinetics

INTRODUCTION

It is well known that high molecular weight and narrow polydispersity are essential requirements for the synthesis of polyacrylonitrile (PAN) polymers, satisfying the requirements for high performance PAN fibers.[1,2] PAN is usually prepared by radical polymerization without control over molecular dimension and structure, while other methods exist for more controlled polymerization of acrylonitrile (AN), such as anionic polymerization, which often involves complex catalysis or side reactions with the nitrile groups.[3] Living/controlled free radical polymerization can be used as an alternative; atom transfer radical polymerization (ATRP) is one of the most widely used method, which involves a fast dynamic equilibrium between dormant species and active radical species to provide control.[4–6] PAN with predefined molecular weights and narrow polydispersity has been successfully synthesized by the use of ATRP.[7–9] Recent studies have been aimed at developing new ligands and new metals that increase the activity and selectivity of the catalyst. The choice of ligand is one of the key factors influencing the reactivity of the catalyst. Acids were 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 than with copper and may therefore act as a ligand in iron-mediated ATRP. A new catalytic system, based on iron complexes with succinic acid (SA), was first used in this study. This article reports this new catalytic system for controlled/living radical polymerization of AN. The polymerization was controlled over a broad range of molecular weights and produced polymers with relatively low polydispersity and rapid kinetics. The influence of the ratio of the metal to ligand and the solvent was also investigated.

EXPERIMENTAL

Materials

AN (Shanghai Chemical Reagents Co., A.R. grade) was vacuum distilled from CaH$_2$ just before polymerization. FeCl$_2$ (Shanghai Chemical Reagents Co., A.R. grade) was washed with absolute ethanol and dried under vacuum (at 60°C) before use. SA (Shanghai Chemical Reagents Co., A.R. grade) was used as received. 2-chloropropionitrile (CPN) was obtained from Aldrich and used without further purification. N,N-dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents Co.) was distilled at reduced pressure and stored until use. Propylene carbonate and toluene (Shanghai Chemical Reagents Co., A.R. grade) were used as received.

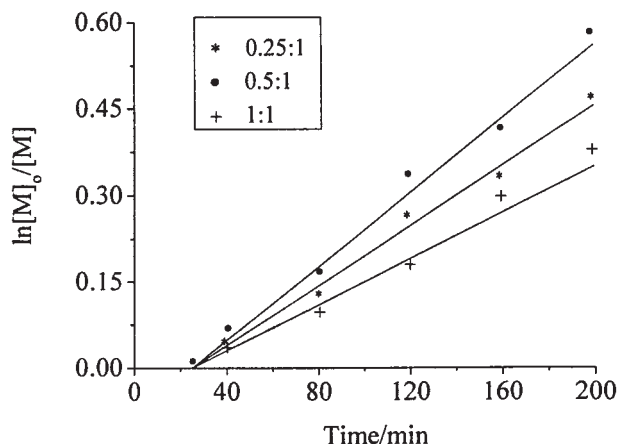**Figure 1** First-order kinetic plot of monomer consumption as a function of time in DMF at various ratios of $[FeCl_2]/[SA]$, during ATRP of AN with $[AN[RSQB] = 5M$ and $[AN]:[CPN]:[FeCl_2] = 800:1:1$ at 60°C.

Polymerization

A typical example of the general procedure was as follows: A dry flask was filled with $FeCl_2$, SA, DMF, CPN, and AN in the same order. It was degassed in vacuum and charged with N_2 (four times) and was sealed under N_2. The mixture was stirred at room temperature until the catalyst dissolved. The flask was then immersed in an oil bath and held at the desired temperature by a thermostat. After a definite time, the polymerization was terminated by cooling the flask in ice water. The polymerization product was dissolved in DMF. The resultant mixture was then poured into large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C under vacuum.

Characterization

The conversion of the monomer was determined gravimetrically. The 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 mL min^{-1} 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.

RESULTS AND DISCUSSION

Effect of the ratio of $FeCl_2/SA$ on ATRP of AN

A series of experiments of ATRP of AN in DMF were carried out with different $FeCl_2/SA$ ratios. Figure 1

shows kinetic plots of $\ln[M]_0/[M]$ *versus* time for ATRP of AN, catalyzed by $FeCl_2/SA$ and initiated by CPN. During the reaction, the white color of the $FeCl_2/SA$ complex changed to yellowish-red as the reaction proceeded, which indicates that Fe^{3+} compound was formed. The linearity of the plot indicates that the polymerization is approximately first order with respect to the monomer concentration. The slope of the kinetic plot indicates that during the polymerization process, the number of active species is constant, and the termination reactions can be neglected.

The monomer conversion reached about 36.5%, 42.9%, and 29.5% corresponding to 0.25, 0.5, and 1 of $[FeCl_2]/[SA]$ ratios within 200 min, respectively. The corresponding value of the apparent rate constant (k_p^{APP}) calculated from the kinetic plot is $5.33 \times 10^5 \text{ s}^{-1}$ at the $[FeCl_2]/[SA]$ ratio of 0.5. Comparing the apparent rate constants derived from the kinetic plots in Figure 1, the reaction rate corresponding to the ratio of 0.5 is the highest one (Fig. 2). Lower or higher concentrations of ligand result in low reaction rate. As shown in Figure 1, ATRP of AN seems to require an induction period. induction period is perhaps caused by two reasons: the presence of oxygen and impurities and the slow formation of the catalytic center.[10,11]

In Figures 3 and 4, the molecular weights of the resulting polymers measured by GPC increase linearly with conversion at all $[FeCl_2]/[SA]$ ratios with low polydispersity throughout the polymerization process. The molecular weights match the theoretical values very well and the PDI is 1.15 when the ratio of $[FeCl_2]/[SA]$ is 0.5. The plot of the molecular weight shows an obvious curvature and the PDI becomes higher corresponding to 0.25 and 1 of $[FeCl_2]/[SA]$ ratios, respectively. The reason may be that the catalyst system cannot efficiently turn the active species
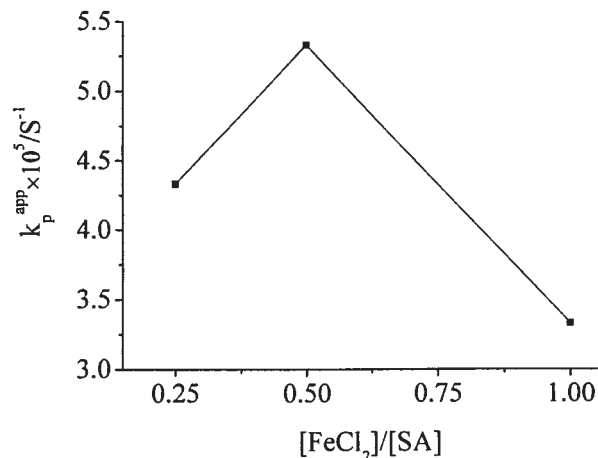

Figure 2 Dependence of the apparent rate constants on the ratio of $[FeCl_2]/[SA]$ for ATRP of AN with $[AN] = 5M$ and $[AN]:[CPN]:[FeCl_2] = 800:1:1$ at 60°C.
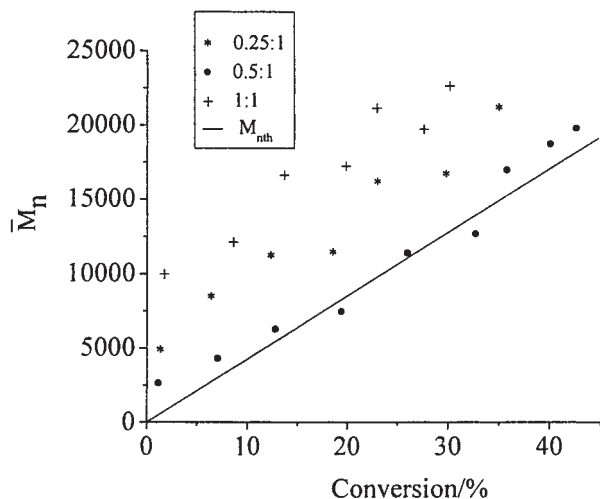
Figure 3 Dependence of M_n on the monomer conversion at various ratios of $[FeCl_2]/[SA]$ for ATRP of AN with $[AN] = 5M$ and $[AN]:[CPN]:[FeCl_2] = 800:1:1$ at 60°C.

Figure 5 First-order kinetic plot of monomer consumption as a function of time in different solvents, during ATRP of AN with $[AN] = 5M$ and $[AN]:[CPN]:[FeCl_2]:[SA] = 800:1:1:2$ at 60°C.

into a dormant species when the ratios of $[FeCl_2]/[SA]$ are 0.25 and 1, and many more side reactions occur.

In a summary, the $[FeCl_2]$ to $[SA]$ ratio of 0.5 not only gives the best control of molecular weight and its distribution but also provides rather rapid reaction rate in a controlled fashion.

Effect of solvent on the polymerization

To study the effect of solvent on ATRP of AN, DMF, propylene carbonate, and toluene were used as solvents, respectively. Figure 5 shows kinetic plots of $\ln[M]_0/[M]$ versus time for ATRP of AN in three different solvents. The polymerizations are approxi-
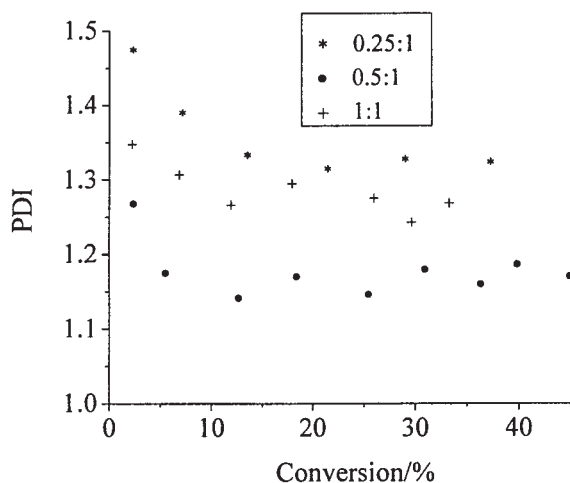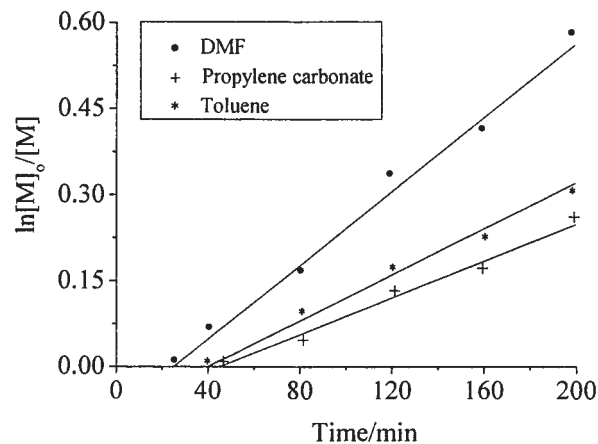
mately first order with respect to the monomer concentration. As shown in Figure 5, the induction period is shorter in DMF than in propylene carbonate and toluene, and the rate of the polymerization in DMF is unexpectedly faster than in propylene carbonate and toluene. A similar result was reported by Shenmin[12] for iron-mediated ATRP. The experimental data reported in this study are different from those reported by Pascual,[13] who used 2, 2′-bipyridine, and Ziegler,[14] who used monodentate amines as the ligands in copper-mediated systems. They concluded that DMF affects the living nature of ATRP. In our ATRP system, DMF has no significant effect on the living nature if there is sufficient ligand to complex the transition metal.
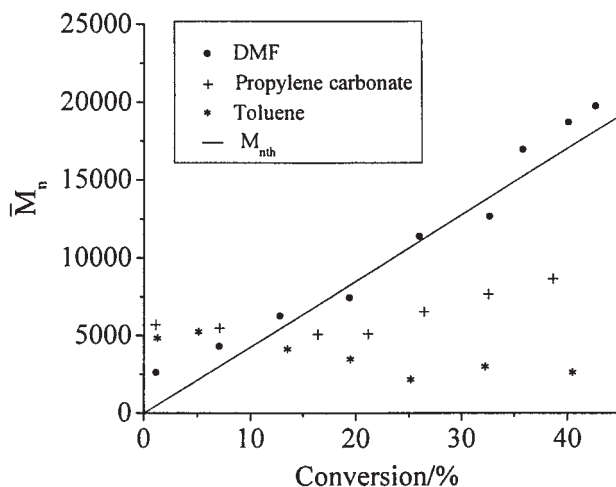

Figure 4 Dependence of PDI on the monomer conversion at various ratios of $[FeCl_2]/[SA]$ for ATRP of AN with $[AN] = 5M$ and $[AN]:[CPN]:[FeCl_2] = 800:1:1$ at 60°C.

Figure 6 Dependence of M_n on the monomer conversion in different solvents for ATRP of AN with $[AN] = 5M$ and $[AN]:[CPN]:[FeCl_2]:[SA] = 800:1:1:2$ at 60°C.
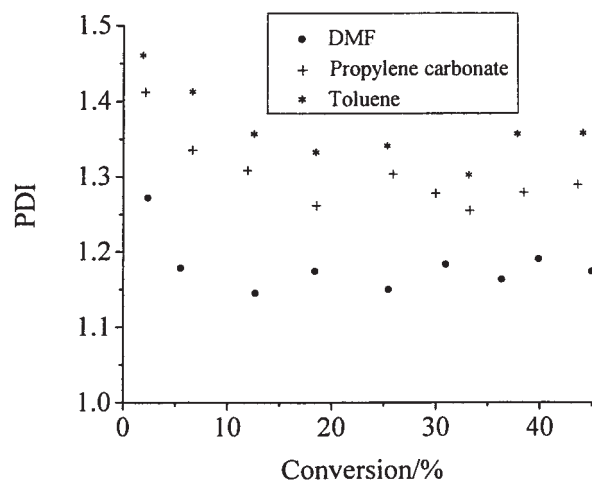
Figure 7 Dependence of PDI on the monomer conversion in different solvents for ATRP of AN with [AN] = 5M and [AN]:[CPN]:[FeCl$_2$]:[SA] = 800:1:1:2 at 60°C.

Figure 8 Effect of temperature on k_p^{app}.

Figure 6 indicates that the molecular weights agree reasonably well with the theoretical molecular weight when DMF was used as the solvent. When using propylene carbonate as the solvent, the plot of the molecular weight shows an obvious curvature. With toluene as the solvent, only AN oligomer was reached. The higher molecular weight at conversion less than 10% indicates that there is some termination or side reaction at the beginning of the reaction because the radicals are not immediately deactivated. It can be seen from Figure 7 that PDI of PAN decreases with increasing monomer conversion, reaching values of 1.15 at about 20% conversion for DMF systems.

The polymerization is quite sensitive to the polarity of the solvent. When using propylene carbonate and toluene as the solvent, the polymerizations were heterogeneous because of the limited solubility of FeCl$_2$ and SA in monomer. SA cannot complex with FeCl$_2$ sufficiently and fails to catalyze the polymerization. Addition of DMF increases the solubility of the catalyst in monomer and provides a homogeneous catalyst system. In addition, the polarity of the solvent can also affect the metal complex structure. In a polar solvent, such as DMF, Cl$^-$Fe^{2+}(SA)$_2$Cl$^-$ may exist, but in a less polar solvent (SA)FeCl$_3$Fe(SA) could exist.[15]

Thus, the DMF-based system provides the desired characteristics of high initiation efficiency, low polydispersity, and a fast polymerization rate.

Effect of the polymerization temperature on the polymerization

Effect of the polymerization temperature on ATRP of AN was investigated. The experimental results are given in Table I. The rate of polymerization increases and the induction period becomes shorter when the polymerization temperature increases. It means that the solubility of the catalyst increases obviously along with the temperature. The Arrhenius plot obtained from the experimental data, given in Table I, was given in Figure 8. The apparent activation energy was calculated to be 56.5 kJ mol^{-1}.

CONCLUSION

The new catalyst system, FeCl$_2$/SA, was successfully used in ATRP of AN. Well-defined PAN was synthesized when DMF was used as the solvent. When the ratio of FeCl$_2$/SA is 0.5, the polymerization was best controlled. Polymerizations of AN seem to require an induction period. The induction period is shorter in DMF than in propylene carbonate and toluene, and the rate of the polymerization in DMF is fastest. The molecular weight of PAN agrees reasonably well with the theoretical molecular weight of DMF. The rate of polymerization increases and the induction period becomes shorter with increasing polymerization temperature.

TABLE I
Kinetic Data for ATRP of AN at Different Temperatures, with [AN] = 5M and [AN]:[CPN]:[FeCl$_2$]:[SA] = 800:1:1:2

Temperature (°C)	k_p^{app} (10^5 s^{-1})	Induction period (min)
60	5.33	25
65	7.25	20
70	9.69	16

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