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Reverse ATRP of acrylonitrile with diethyl 2,3-dicyano-2,3-diphenyl succinate/$FeCl_3$/iminodiacetic acid

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Abstract

The reverse atom transfer radical polymerization (RATRP) technique using $FeCl_3$/iminodiacetic acid (IMA) complex as a catalyst was applied to the living radical polymerization of acrylonitrile (AN). A hexa-substituted ethane thermal initiator, diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), was firstly used as the initiator in this iron-based RATRP system. The polymerization in *N*,*N*-dimethylformamide not only shows the best control of molecular weight and its distribution but also provides rather rapid reaction rate with the ratio of [AN]:[DCDPS]:[$FeCl_3$]:[IMA] at 500:1:2:4. The rate of polymerization increases with increasing the polymerization temperature and the apparent activation energy was calculated to be 49.9 kJ mol^{-1}. The polymers obtained were end-functionalized by chlorine atom, and they were used as macroinitiators to proceed the chain extension polymerization in the presence of $FeCl_2$/IMA catalyst system via a conventional ATRP process. The resultant polyacrylonitrile fibers were obtained with the fineness at 1.16 dtex and the tenacity at 6.01cN dtex^{-1}.

Keywords: Reverse atom transfer radical polymerization; Living polymerization; Acrylonitrile

1. Introduction

High molecular weight and narrow polydispersity is an essential requirement for the synthesis of polyacrylonitrile (PAN) polymers satisfying the requirements for high performance PAN fibers [1]. PAN is usually prepared by radical polymerization without control over molecular dimension and structure [2,3], 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 [4–6]. Living/controlled free radical polymerization can be used as an alternative [7]. Several methods, such as atom transfer radical polymerization (ATRP) [8], reverse addition fragmentation chain transfer (RAFT) [9,10], etc. have been developed in the living radical polymerization process. ATRP is one of the most widely used methods, which involve a fast dynamic equilibrium between dormant species and active radical species to provide control [11–18], ATRP of AN has been studied systemically [19–25]. 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, have been reported and referred to as reverse ATRP (RATRP) by Matyjaszewski [26–28] and the other researchers [29–32]. It is important to find new initiators and new catalytic systems that are less toxic to human health for RATRP. In the past, only two kinds of initiators, such as azo- and peroxide compounds, were employed as the initiator in the RATRP system [33,34]. It is well known that the decomposition of conventional initiators is irreversible, which makes the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature. The development of new type initiators for RATRP, using carbon–carbon bond initiator instead of azo or peroxide ones, is of interest. This new type initiator could provide the initiation step of RATRP, in which the initiator reversibly decomposes to primary radicals, unlike other conventional initiators resulting in suitable amounts of primary radicals being generated. Qin [35] has introduced a carbon–carbon bond thermal initiator, diethyl

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2,3-dicyano-2,3-diphenylsuccinate (DCDPS), instead of AIBN into the iron-based RATRP system for styrene polymerization. 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 and may, therefore, act as a ligand. Shenmin has reported ATRP of styrene catalyzed by $FeCl_2$/succinic acid [36].

Given these concepts, this study was firstly to investigate the synthesis of polyacrylonitrile with high molecular weight and narrow polydispersity using RATRP of AN. A novel catalyst system based on iron complexes with iminodiacetic acid (IMA) and a new thermal initiator, DCDPS were used for the first time for AN polymerization using RATRP method. The first successful attempt of the well-controlled RATRP of AN in *N*,*N*-dimethylformamide was described. The main work was targeted on the catalytic activity of the catalyst system for the polymerization and chain growing with its own monomer using polyacrylonitrile as macroinitiator. Effects of temperature on the polymerization were also discussed and the overall activation energy for the polymerization system was calculated. In addition, the properties of the resultant fibers prepared by AN polymers were determined.

2. Experimental

2.1. Materials

Acrylonitrile (AN, Shanghai Chemical Reagents Co., A. R. grade) was vacuum distilled from CaH_2 just before polymerization. $FeCl_3$ (anhydrous) was prepared from $FeCl_3 \cdot 6H_2O$ (Shanghai Chemical Reagents Co., A. R. grade) treated with thionyl chloride according to reference procedure [37] and dried under vacuum at 60 °C before use. DCDPS was prepared according to the method reported previously [38]. Iminodiacetic acid (IMA, Shanghai Chemical Reagents Co., A. R. grade) was used as received without 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. Anisole, toluene and dimethylsulfoxide (Shanghai Chemical Reagents Co., A. R. grade) were used as received.

2.2. Polymerization

A typical example of the general procedure was as follows. $FeCl_3$, IMA and DMF were added to a dry tube under stirring, four cycles of vacuum nitrogen were applied to remove the oxygen. After the catalyst was dissolved, AN with DCDPS dissolved in advance was added via an argon-washed syringe. The tube was then sealed under nitrogen and immersed in an oil bath 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 a large amount of methanol for precipitation, washed with methanol several times and dried at 60 °C under vacuum.

2.3. Characterization

The conversion of the monomer was determined gravimetrically. The molecular weight (M_n) and polydispersity index (PDI) of AN polymers were measured by gel permeation chromatography (GPC) and many angle laser light scatter (MALLS) made by Wyatt Technology Corp.; the GPC-MALLS system involves a Styagel HWN 6E GPC column, a Wyatt OPTILAB RI detector, and a Wyatt MALLS detector (DAWN E). All samples was performed at a flow rate of $1.0\ \mathrm{mL\ min^{-1}}$. The analysis was undertaken at 30 °C with purified high-performance-liquid-chromatography-grade DMF as an eluent.

In order to compare with the above measurements of the molecular weight of AN polymers, the theoretical molecular weight (M_{th}) was used. According to the characteristics of living polymerization, M_{th} could be calculated from the following equation [39]

$$M_{\mathrm{th}} = \frac{[\mathrm{AN}]}{2[\mathrm{DCDTS}]} \times M_{\mathrm{wAN}} \times \mathrm{Conversion} \tag{1}$$

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

3. Results and discussion

3.1. Polymerization of AN with the DCDPS/$FeCl_3$/IMA initiating system

AN was polymerized catalyzed by $FeCl_3$/IMA with DCDPS as the initiator in the different solvents at 70 °C ([AN]:[DCDPS]:[$FeCl_3$]:[IMA] = 500:1:2:4). After heating, a change of color from deep orange to light yellow was observed as described by Moineau et al. [40]. This corresponds to the decomposition of DCDPS and the establishment of the equilibrium between Fe^{3+} and Fe^{2+}. Fig. 1 shows kinetic plots of $\ln[M]_0/[M]$ versus time. The linearity of the plot indicates that the polymerization is approximately first-order with respect to the monomer concentration. The slope of the kinetic plots indicates that in the polymerization process,

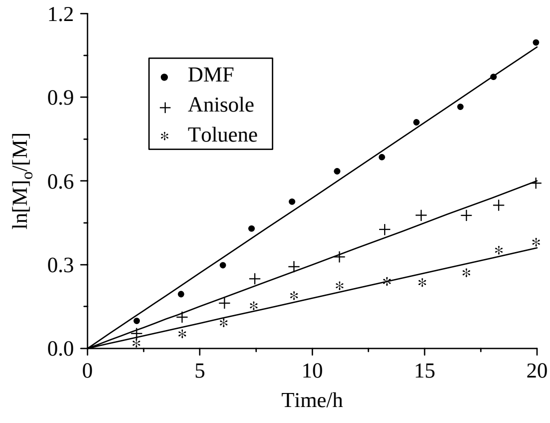


Fig. 1. First-order kinetic plot of monomer consumption as a function of time in different solvents during reverse ATRP of AN with [AN] = 8.0 M and [AN]:[DCDPS]:[$FeCl_3$]:[IMA] = 500:1:2:4 at 70 °C.

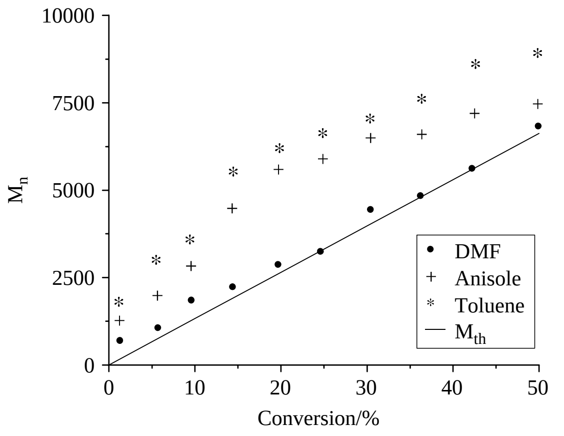
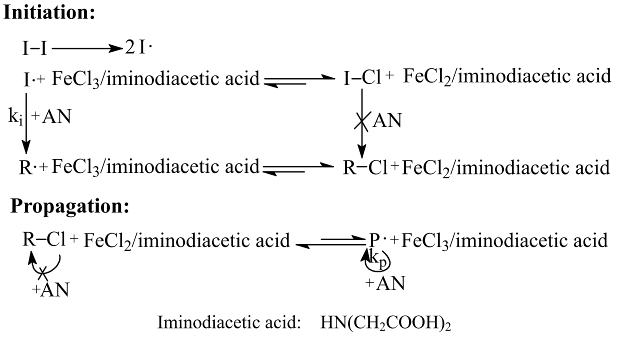


Fig. 2. Dependence of M_n on the monomer conversion in different solvents for reverse ATRP of AN with [AN] = 8.0 M and [AN]:[DCDPS]:[$FeCl_3$]:[IMA] = 500:1:2:4 at 70 °C.

the number of active species is constant. As shown in Fig. 1, the rate of polymerization in DMF is unexpectedly faster than in anisole and toluene. The monomer conversion in DMF reached about 66.3% within 20 h. The corresponding value of the apparent rate constant (k_p^{app}) calculated from the kinetic plot is $1.51 \times 10^{-5}\ s^{-1}$. A similar result was reported by Shenmin [41] for iron-mediated ATRP. The experimental data reported in this study are different from those reported by Pascual [42], who used 2,2′-bipyridine, and Ziegler [43], who used monodentate amines as the ligands in copper-mediated systems. They concluded that DMF affects the living nature of ATRP. In our RATRP system, DMF has no significant effect on the living nature if there is sufficient ligand to complex the transition metal.

Fig. 2 indicates that the molecular weights of the resulting polymers measured by GPC increase linearly with conversion when DMF was used as the solvent, and the molecular weights agree reasonably well with the theoretical molecular weight. The high molecular weight at conversion less than 10% indicates the incomplete decomposition of DCDPS at the beginning of the reaction resulting small amount of the polymer chain. A similar phenomenon has been observed [44]. The initiation efficiency f of DCDPS in DMF is calculated from $f = M_{th}/M_n$ to be 0.91 (conversion = 66.3%). These results reveal that the polymerization of AN with DCDPS/$FeCl_3$/IMA initiating system in DMF is a living/controlled radical polymerization process. A polymerization mechanism is proposed, as described in Scheme 1. In the initiation step, after the homolytic decomposition of one DCDPS (I–I) into two primary radicals (I$^\cdot$), these radicals can add to the monomer. Then, the activated monomer radicals (R$^\cdot$) react with $FeCl_3$/IMA through chlorine atom transfer and generate the lower oxidation state metal complex, $FeCl_2$/IMA. Finally, the polymer propagates via a conventional ATRP process.



Scheme 1. Polymerization mechanism of reverse ATRP of AN including the ligand structure.

The values of PDI of AN polymers are shown in Fig. 3. For DMF systems, the polydispersity is narrow (PDI = 1.19) when the conversion goes beyond 15%, and a broader polydispersity is obtained when the conversion is less than 15%. The slow rate of the primary radicals at 70 °C produced from the decomposition of DCDPS changing into dormant species is responsible for the broader polydispersity during the initial polymerization in the reaction system. In other words, the RATRP system will set up as the conversion goes beyond 15%.

The dielectric constants of the three solvents are in the following order: ε_{DMF} (37.6, 20 °C), $\varepsilon_{anisole}$ (4.33, 20 °C), $\varepsilon_{toluene}$ (2.39, 20 °C). The polymerization is quite sensitive to the solubility of the catalyst. When using anisole and toluene as the solvent, the polymerizations were heterogeneous due to the limited solubility of $FeCl_3$ and IMA in monomer. The thermal decomposition rates of DCDPS in anisole and toluene are not high, the RATRP processes have lower initiation efficiencies, and this may be the reason for the low amount of the polymer chains, which produces higher molecular weight than that of the theoretical value (Fig. 2). 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 DMF, $Cl^-Fe^{2+}(IMA)_2Cl^-$ may exist, but in a less polar solvent, $(IMA)FeCl_3Fe(IMA)$ could exist [45]. Thus, the DMF-based system provides the desired characteristics of higher initiation efficiency, low polydispersity, and a fast polymerization rate.

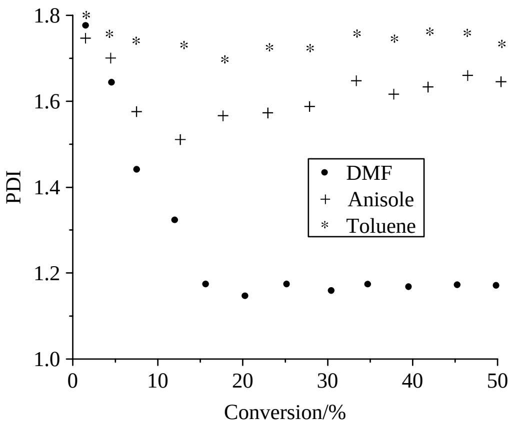


Fig. 3. Dependence of PDI on the monomer conversion in different solvents for reverse ATRP of AN with [AN] = 8.0 M and [AN]:[DCDPS]:[$FeCl_3$]:[IMA] = 500:1:2:4 at 70 °C.

Table 1
Data for RATRP of AN catalyzed by $FeCl_3$/IMA

Entry	[DCDPS]:[$FeCl_3$]:[IMA]	Time (h)	Conversion (%)	M_{th}	M_n	PDI	$k_p^{app} \times 10^5 (s^{-1})$	Initiation efficiency
1	1:1:2	20	73.5	9739	11730	1.25	1.84	0.83
2	1:2:4		66.3	8785	9650	1.19	1.51	0.91
3	1:3:6		51.6	6837	7430	1.17	1.01	0.92
4	1:4:8		44.5	5896	6270	1.15	0.82	0.94
5	1:2:2		64.8	8586	9540	1.18	1.45	0.90
6	1:2:5		51.7	6850	8150	1.20	1.01	0.84
7	1:2:6		45.7	6055	7570	1.21	0.85	0.80
8	1:1:4		71.5	9474	12300	1.26	1.74	0.77
9	1:4:4		49.1	6505	7070	1.14	0.94	0.92
10	1:5:4		38.9	5154	5540	1.13	0.68	0.93

[AN] = 8.0 M, [AN]:[DCDPS] = 500:1, t = 70 °C.

3.2. *Effect of $FeCl_3$/IMA catalyst system on RATRP of AN*

It has been reported that IMA might decrease the initiator efficiency, leading to an increase in the observed molecular weight [46]. To further investigate the effects of IMA, a series of experiments of RATRP of AN were carried out. The results have been compiled in Table 1. In this study, different conclusions are drawn. As more $FeCl_3$/IMA catalyst system was added (entries 1–4), slower polymerization rates and narrower molecular weight distributions were observed, and the initiation efficiency also increased from 0.83 to 0.94, which suggests that the concentration of $FeCl_3$ has a favorable influence on the activation as well as equilibrium of RATRP. With increasing the amount of IMA in the catalyst system (entries 2, 5–7), the rate of polymerization and initiation efficiency showed a trend of decrease while the molecular weight distribution of polymers remained narrow. This illustrates that a large amount of IMA not only poison the metal catalyst, but also it has 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 ratio of [$FeCl_3$]/[IMA] was changed from 1:4 to 5:4 (entries 2, 8–10), the molecular weight distribution of polymers decreased from 1.26 to 1.13, and the initiation efficiency increased from 0.77 to 0.93, but the rate of polymerization decreased prominently. This implies that $FeCl_3$ itself is an effective catalyst in RATRP.

3.3. *Effect of the polymerization temperature on the polymerization*

Effect of the polymerization temperature on RATRP of AN was investigated. The experimental results are given in Table 2. The apparent rate constant increases with increasing temperature. The Arrhenius plot obtained from the experimental data given in Table 2, was given in Fig. 4. The apparent activation energy was calculated to be 49.9 kJ mol^{-1}. According to Eq. (2) and $\Delta H_{prop} = 22.3$ kJ mol^{-1} [47]

$$\Delta H_{eq}^0 = \Delta H_{app} - \Delta H_{prop} \tag{2}$$

where ΔH_{eq}^0 is the enthalpy of the equilibrium, ΔH_{app} is the apparent enthalpy of activation, and ΔH_{prop} is the activation enthalpy of propagation. Then, $\Delta H_{eq}^0 = 27.6$ kJ mol^{-1} was calculated for RATRP of AN initiated by DCDPS/$FeCl_3$/IMA. This value is smaller than those for the polymerization of methyl methacrylate ($\Delta H_{eq}^0 = 43.9$ kJ mol^{-1}) [48] for the $FeCl_3$/isophthalic acid system and is bigger than those for the polymerization of styrene ($\Delta H_{eq}^0 = 26.5$ kJ mol^{-1}) for the Cl-mediated system and 20.2 kJ mol^{-1} for the Br-mediated system [49].

3.4. *Chain extension of PAN*

According to the initiation mechanism of DCDPS [35] and the mechanism polymerization of RATRP using DCDPS/$FeCl_3$/IMA system, the well-defined polyacrylonitrile with an ω-chlorine atom end groups will be obtained in the polymerization of AN using DCDPS/$FeCl_3$/IMA system. Therefore, the obtained PAN can act as a macroinitiator for the extension polymerization. It is reported that the limited solubilty of PAN, even in its own monomer-acrylonitrile, prevented the formation of high polymer using ATRP [50,51]. Thus, in this study, DMF was used as the solvent to enable the formation of high molar mass PAN. The extension polymerization of the obtained PAN (M_n = 9650, PDI = 1.19) with AN was carried out in DMF at 80 °C in the presence of the $FeCl_2$/IMA catalyst system. As shown in Fig. 5, when [AN] = 8.0 M, [AN]:[PAN]:[$FeCl_2$]:[IMA] = 500:1:2:4, t = 40 h, the conversion was 95%. It clearly demonstrates the chain extension of polyacrylonitrile takes place. The theoretical value of the molecular weight of polyacrylonitrile is calculated from $M_{th} = 9650 + 53 \times ([AN]/[PAN] \times \text{conversion})$ to be 34825. In this case, polyacrylonitrile obtained was with M_n = 35,600,

Table 2
Kinetic data for RATRP of AN at different temperature with [AN] = 8.0 M and [AN]:[DCDPS]:[$FeCl_3$]:[IMA] = 500:1:2:4

Temperature (°C)	$k_p^{app} \times 10^5 (s^{-1})$
60	0.89
65	1.15
70	1.51
72	1.67
75	1.94
80	2.47
85	3.14

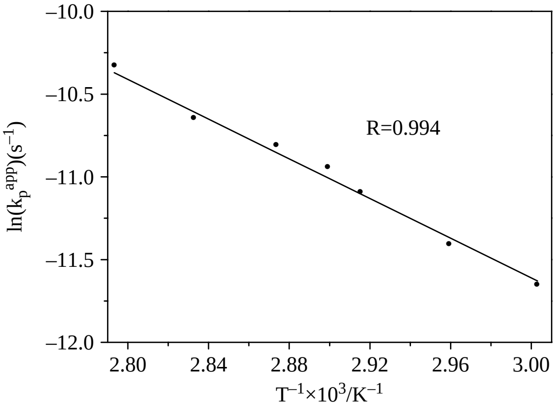


Fig. 4. Effect of temperature on k_p^{app}.

PDI = 1.27, which suggests the coupling of high molecular chains.

3.5. Properties of the fibers prepared by AN polymers

In order to obtain high performance PAN fibers, the extension polymerization of the obtained PAN ($M_n = 9650$, PDI = 1.19) with AN was carried out in DMF at 80 °C in the presence of the $FeCl_2$/IMA catalyst system. When [AN] = 8.0 M, [AN]:[PAN]:[$FeCl_2$]:[IMA] = 1500:1:2:4, $t = 40$ h, the conversion was 90%. Polyacrylonitrile obtained was with $M_n = 83{,}250$, PDI = 1.28. Davis [52] and Shipp [53] also draw the same conclusion and reported there is reduced termination with initiator dilution experiments. AN polymers with $M_n = 83{,}250$, PDI = 1.28 prepared by RATRP were washed with methanol several times and dissolved in dimethylsulfoxide after drying under vacuum to get a clear dope. The obtained dope was deaerated, filtered, and then pumped through a spinneret to a coagulation bath. After a definite time, the coagulated protofibers were obtained. The wet-spun protofibers were washed and drawn in three steps in a water bath, and the filaments were then dried to collapse them, further drawn in steam, set, dried, and wound to fibers. The overall draw ratio was 12.5. The fibers were obtained with the fineness at 1.16 dtex and the tenacity at 6.01cN dtex^{-1}. The fibers satisfy the requirements for high performance PAN fibers and can be used to prepare carbon fibers.

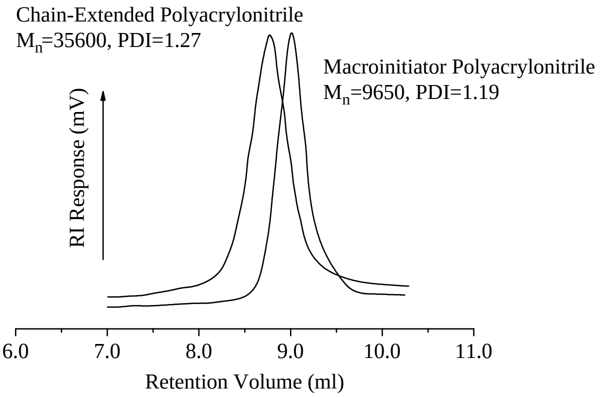


Fig. 5. GPC curves of polyacrylonitrile before and after a chain extension reaction.

4. Conclusions

The new catalyst system, DCDPS/$FeCl_3$/IMA, was successfully used in the RATRP of AN in DMF. When the ratio of [AN]:[DCDPS]:[$FeCl_3$]:[IMA] equals 500:1:2:4, the polymerization was best controlled. Increasing the dosage of the catalyst system would decrease the rate of polymerization and enhanced the degree of the controlled polymerization. The rate of polymerization increases with increasing the polymerization temperature and the apparent activation energy was calculated to be 49.9 kJ mol^{-1}. Polyacrylonitrile obtained were end-functionalized by chlorine atoms and can act as a macroinitiator for the extension polymerization. The resultant fibers obtained from AN polymers satisfy the requirements for high performance PAN fibers and can be used to prepare carbon fibers.

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