

Reverse Atom Transfer Radical Polymerization of Acrylonitrile

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ABSTRACT: FeCl₃ coordinated by succinic acid was used as the catalyst for the first time in azobisisobutyronitrile-initiated reverse atom transfer radical polymerization of acrylonitrile (AN). *N,N*-dimethylformamide (DMF) was used as a solvent to improve the solubility of the ligand. A FeCl₃ 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 different solvents on polymerization of AN were also investigated. The rate of the polymerization in DMF is faster than that in

propylene carbonate and toluene. The molecular weight of polyacrylonitrile agrees reasonably well with the theoretical molecular weight in DMF. The rate of polymerization increases with increasing the polymerization temperature, and the apparent activation energy was calculated to be 64.8 kJ mol⁻¹. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 32–36, 2006

Key words: reverse atom transfer radical polymerization; living polymerization; acrylonitrile

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 methods, which involve 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 use of ATRP.^{7–9} 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, such as azobisisobutyronitrile (AIBN) in the presence of complexes of transition metals in their higher oxidation state, have been re-

ported and referred to as “reverse” or “alternative” ATRP by Matyjaszewski and coworkers^{10,11} and Teyssie et al.¹² Reverse ATRP differs from the conventional ATRP in the initiation step, in which the initiating active species or propagating active species can abstract a halogen atom from the oxidized transition-metal complex to form the dormant species and the reduced transition-metal species. Recent studies have been aimed at developing new ligands and new metals that influence the reactivity of the catalyst. Acids were generally believed to deactivate the metal organometallic 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. Zhu has reported ATRP of styrene catalyzed by FeCl₂/succinic acid.¹³ In this study, a new catalytic system based on iron complexes with succinic acid was firstly used. This paper reports the well-controlled reverse ATRP of AN in *N,N*-dimethylformamide with a conventional radical initiator, AIBN, and FeCl₃ complexed with succinic acid as a catalyst. Effects of the ratio of metal to ligand and the solvents were also investigated.

EXPERIMENTAL

Materials

Acrylonitrile (AN, Shanghai Chemical Reagents Co., AR grade) was vacuum distilled from CaH₂ just before

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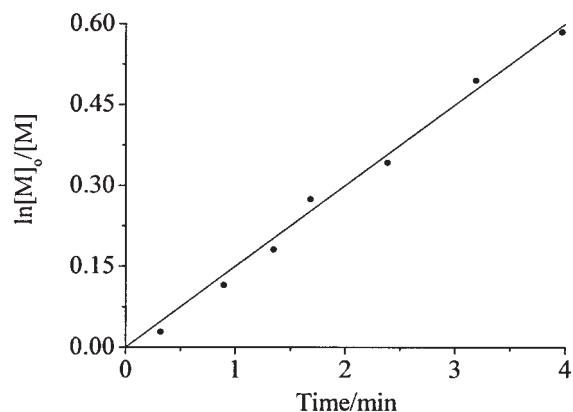


Figure 1 First-order kinetic plot of monomer consumption as a function of time in DMF during reverse ATRP of AN with $[AN] = 5.0M$ and $[AN] : [AIBN] : [FeCl_3] : [SA] = 800 : 1 : 1 : 2$ at $60^\circ C$.

polymerization. $FeCl_3$ (Shanghai Chemical Reagents Co., AR grade) was washed with the absolute ethanol and dried under vacuum at $60^\circ C$ before use. Succinic acid (SA, Shanghai Chemical Reagents Co., AR grade) was used as-received. AIBN was used as an initiator and was recrystallized from ethanol and dried in a desiccator. 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., AR grade) were used as-received.

Polymerization

A typical example of the general procedure was as follows. A dry flask was filled with $FeCl_3$, SA, DMF, AIBN, and AN in that order. It was degassed in vacuum and charged with N_2 (4 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 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 $60^\circ C$ under vacuum.

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). GPC was performed with a Waters model 515 solvent delivery system (Milford, MA) at a flow rate of $1.0 mL min^{-1}$ through a combination of Waters HR1, HR3,

and HR4 styragel columns. The analysis was undertaken at $30^\circ C$ 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 above measurements of M_n , the molecular weight (\bar{M}_n) of AN polymers was determined by the intrinsic viscosity measurements. The intrinsic viscosity $[\eta]$ of AN polymers was measured at $30^\circ C$ in DMF using an Ubbelohde viscometer,¹⁴ and the molecular weight was calculated from the following equation

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75} \quad (1)$$

RESULTS AND DISCUSSION

Polymerization of AN with the AIBN/ $FeCl_3$ /SA initiating system

Reverse ATRP of AN in DMF were carried out with AIBN/ $FeCl_3$ /SA initiating system at $60^\circ C$. Figure 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, the number of active species is constant, and the termination reactions can be neglected. The monomer conversion reached about 45% within 4 h. The corresponding value of the apparent rate constant (k_p^{app}) calculated from the kinetic plot is $3.13 \times 10^{-5} s^{-1}$.

Figure 2 represents M_n and \bar{M}_n of the resulting polymers increases linearly with conversion. The high molecular weight at conversion less than 15% indicates that there is some termination or side reaction at the beginning of the reaction because the radicals are

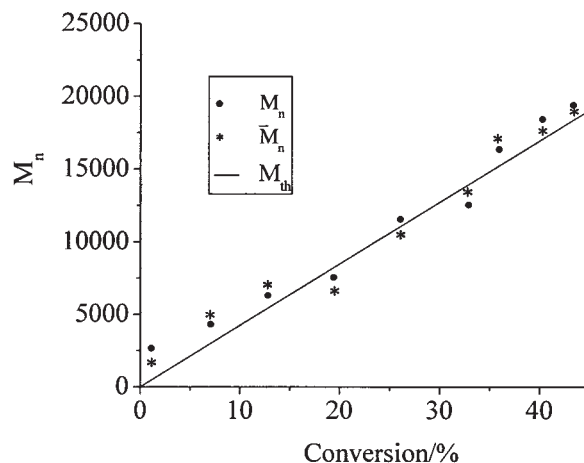
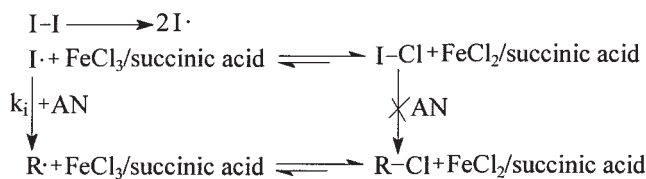
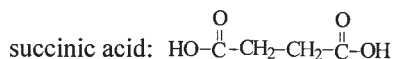
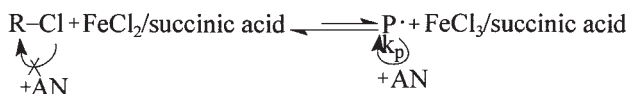


Figure 2 Dependence of M_n on the monomer conversion in DMF for reverse ATRP of AN with $[AN] = 5.0M$ and $[AN] : [AIBN] : [FeCl_3] : [SA] = 800 : 1 : 1 : 2$ at $60^\circ C$.

Initiation:



Propagation:



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

not immediately deactivated. The values of M_n determined by GPC agree well with those of M_n determined by the intrinsic viscosity. Both M_n and M_w agree reasonably well with the theoretical molecular weight (M_{th}). These results reveal that the polymerization of AN with AIBN/ FeCl_3 /SA initiating system 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 AIBN (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 /succinic acid through chlorine atom transfer and generate the lower oxidation state metal complex, FeCl_2 /succinic acid. Finally, the polymerization propagates via a conventional ATRP process.

The values of PDI of AN polymers are shown in Figure 3. The polydispersity values are narrow (PDI = 1.17) when the conversion is from 20% to 45%. A broader polydispersity is obtained when the conversion is less than 20%. This suggests that the conventional radical polymerization takes place during the initial polymerization in the reaction system. In other words, the reverse ATRP system will set up as the conversion goes beyond 20%.

Effect of the ratio of FeCl_3 /SA on reverse ATRP of AN

A series of experiments of reverse ATRP of AN in DMF were carried out at various ratios of $[\text{FeCl}_3]/[\text{SA}]$ at 60°C. Figure 4 reveals kinetic plots of $\ln[M]_0/[M]$ versus time. The monomer conversion reached about 33%, 45%, 38% corresponding to 0.25, 0.5, 1 of $[\text{FeCl}_3]$ to $[\text{SA}]$ ratio within 4 h, respectively. Comparing the apparent rate constants derived from the kinetic plots, the reaction rate corresponding to the ratio of 0.5 is the highest one.

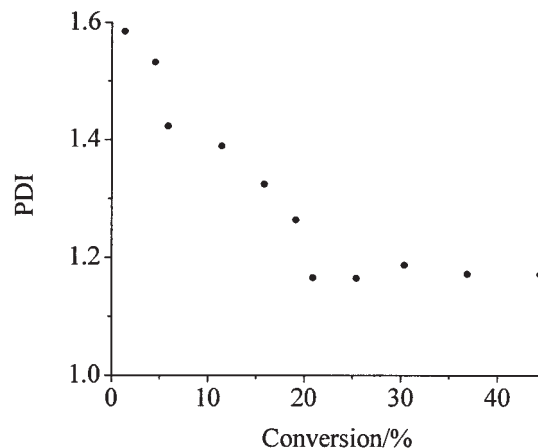


Figure 3 Dependence of PDI on the monomer conversion in DMF for reverse ATRP of AN with $[\text{AN}] = 5.0\text{M}$ and $[\text{AN}] : [\text{AIBN}] : [\text{FeCl}_3] : [\text{SA}] = 800 : 1 : 1 : 2$ at 60°C.

Lower or higher concentrations of ligand will result in low reaction rate. In Figure 5, the molecular weights of the resulting polymers measured by GPC increases with conversion are shown. The plot of the molecular weight shows an obvious curvature at the $[\text{FeCl}_3]/[\text{SA}]$ ratios of 0.25 and 1. As shown in Figure 6, a broader polydispersity is obtained at the $[\text{FeCl}_3]/[\text{SA}]$ ratios of 0.25 and 1 throughout the polymerization. In a summary, a $[\text{FeCl}_3]$ to $[\text{SA}]$ 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 effect of solvents on reverse ATRP of AN, DMF, propylene carbonate, and toluene were used as solvents, respectively. Figure 7 shows kinetic plots of $\ln[M]_0/[M]$ versus time for reverse ATRP of AN in

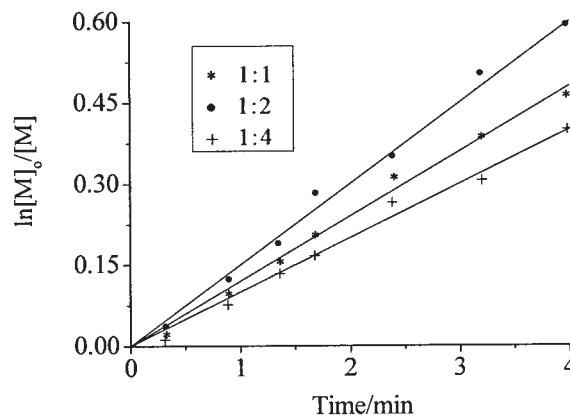


Figure 4 First-order kinetic plot of monomer consumption as a function of time in DMF at various ratios of $[\text{FeCl}_3]/[\text{SA}]$ for reverse ATRP of AN with $[\text{AN}] = 5.0\text{M}$ and $[\text{AN}] : [\text{AIBN}] : [\text{FeCl}_3] = 800 : 1 : 1$ at 60°C.

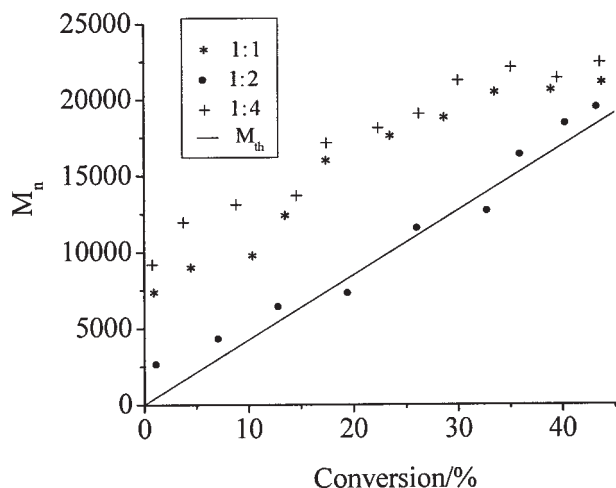


Figure 5 Dependence of M_n on the monomer conversion in DMF at various ratios of $[\text{FeCl}_3]/[\text{SA}]$ for reverse ATRP of AN with $[\text{AN}] = 5.0\text{M}$ and $[\text{AN}] : [\text{AIBN}] : [\text{FeCl}_3] = 800 : 1 : 1$ at 60°C .

three different solvents. The polymerizations are approximately first-order with respect to the monomer concentration. As shown in Figure 7, the rate of polymerization in DMF is unexpectedly faster than in propylene carbonate and toluene. A similar result was reported by Shenmin¹⁵ for iron-mediated ATRP. The experimental data reported in this study are different from those reported by Pascual,¹⁶ who used 2,2'-bipyridine, and Ziegler,¹⁷ 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 8 indicates that the molecular weights measured by GPC agree rea-

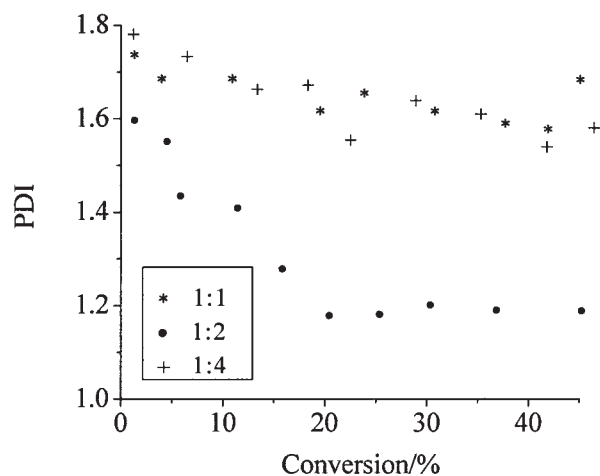


Figure 6 Dependence of PDI on the monomer conversion in DMF at various ratios of $[\text{FeCl}_3]/[\text{SA}]$ for reverse ATRP of AN with $[\text{AN}] = 5.0\text{M}$ and $[\text{AN}] : [\text{AIBN}] : [\text{FeCl}_3] = 800 : 1 : 1$ at 60°C .

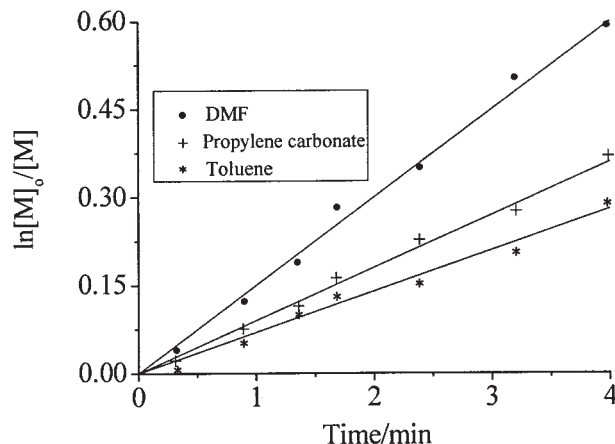


Figure 7 First-order kinetic plot of monomer consumption as a function of time in different solvents during reverse ATRP of AN with $[\text{AN}] = 5.0\text{M}$ and $[\text{AN}] : [\text{AIBN}] : [\text{FeCl}_3] : [\text{SA}] = 800 : 1 : 1 : 2$ at 60°C .

sonably well with the theoretical molecular weight when DMF is used as the solvent. When using propylene carbonate as the solvent, the plot of the molecular weight shows an obvious curvature. When using toluene as the solvent, only AN oligomer was reached. It can be seen from Figure 9 that PDI of PAN decreases with increasing monomer conversion, reaching values of 1.17 at about 20% conversion for DMF systems.

The polymerization is quite sensitive to the polarity of the solvent. When using propylene carbonate or toluene as solvent, the polymerizations were heterogeneous because of the limited solubility of FeCl_3 and SA in monomer. SA cannot complex with FeCl_3 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

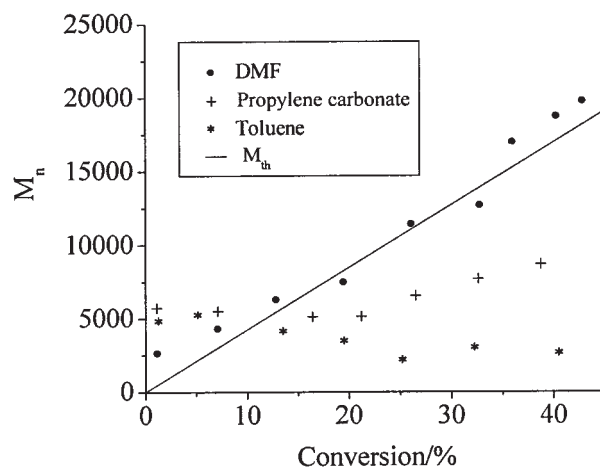


Figure 8 Dependence of M_n on the monomer conversion in different solvents for reverse ATRP of AN with $[\text{AN}] = 5.0\text{M}$ and $[\text{AN}] : [\text{AIBN}] : [\text{FeCl}_3] : [\text{SA}] = 800 : 1 : 1 : 2$ at 60°C .

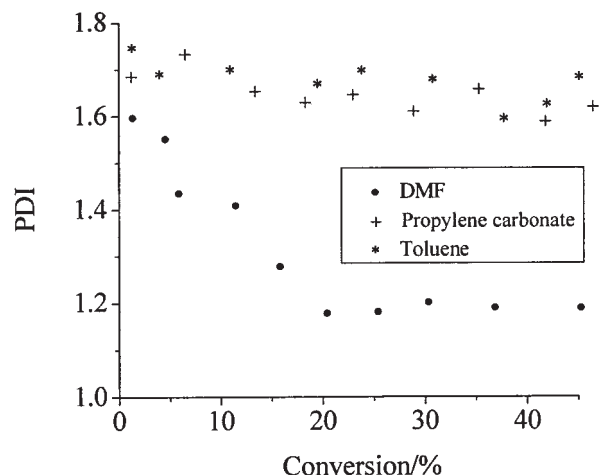


Figure 9 Dependence of PDI on the monomer conversion in different solvents for reverse ATRP of AN with $[AN] = 5.0M$ and $[AN] : [AIBN] : [FeCl_3] : [SA] = 800 : 1 : 1 : 2$ at $60^\circ C$.

affect the metal complex structure. In a polar solvent DMF, $Cl^-Fe^{2+}(SA)_2Cl^-$ may exist, but in a less polar solvent, $(SA)FeCl_3Fe(SA)$ could exist.¹⁸ 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 reverse ATRP of AN was investigated. The experimental results are given in Table I. The apparent rate constant increases with increasing temperature. The Arrhenius plot obtained from the experimental data given in Table I was given in Figure 10. The apparent activation energy was calculated to be 64.8 kJ mol^{-1} . According to eq. 2 and $\Delta H_{prop} = 22.3 \text{ kJ mol}^{-1}$,¹⁹

$$\Delta H_{eq}^0 = \Delta H_{app} - \Delta H_{prop} \quad (2)$$

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. $\Delta H_{eq}^0 = 42.5 \text{ kJ mol}^{-1}$ was calculated for reverse ATRP of AN catalyzed by $FeCl_3/succinic$ acid.

TABLE I
Kinetic Data for Reverse ATRP of AN at Different Temperatures in DMF with $[AN] = 5.0 M$ and $[AN] : [AIBN] : [FeCl_3] : [SA] = 800 : 1 : 1 : 2$

Temperature ($^\circ C$)	$k_p^{app} (\times 10^5 \text{ s}^{-1})$
60	3.13
65	4.45
68	5.41
70	6.23

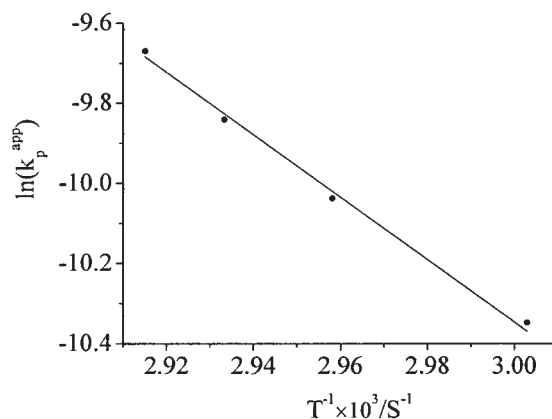


Figure 10 Effect of temperature on k_p^{app} .

CONCLUSIONS

The new catalyst system, $FeCl_3/SA$, was successfully used in the reverse ATRP of AN. Well-defined PAN was synthesized when DMF was used as the solvent. When the ratio of $FeCl_3/SA$ equals 0.5, the polymerization was best controlled. The rate of the polymerization in DMF is fastest. The molecular weight of PAN agrees reasonably well with the theoretical molecular weight in DMF. The rate of polymerization increases with increasing the polymerization temperature and the apparent activation energy was calculated to be 64.8 kJ mol^{-1} .

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