

Copolymerization Kinetics of Poly(acrylonitrile-ran-2-ethenyl-pyridine) and Its Degradation Apparent Activation Energy

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ABSTRACT: 2-Ethenyl-pyridine (EPD) was first used to successfully copolymerize with acrylonitrile (AN) in a H₂O/dimethyl formamide (DMF) mixture by using azobisisobutyronitrile as the initiator. Kinetics of copolymerization and degradation of poly(AN-ran-EPD) were discussed. The kinetic equation of copolymerization and the apparent activation energy of degradation of poly(AN-ran-EPD) were obtained. In H₂O-rich reaction medium, copolymerization followed the suspension polymerization more, but in DMF-rich reaction medium, copolymerization followed the solu-

tion polymerization more. Increase in DMF concentration in the solvent mixture lead to a rapid increase in the degradation apparent activation energy. The apparent activation energy decreased quickly with an increase in EPD concentration, and such a change became less prominent as the molar ratio of EPD/AN went beyond 3/100. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2651–2655, 2008

Key words: apparent activation energy; degradation; kinetics

INTRODUCTION

It is important to select a suitable comonomer and optimize the conditions of polymerization for the synthesis of acrylic polymers satisfying the requirements for high-tenacity acrylic fibers.^{1,2} Solution and aqueous suspension are the most common useful techniques.^{3–5} The solvent–water suspension method is a new and promising technique. It cleverly combines the advantages of solution and those of aqueous suspension. Various carboxylic acids are used as comonomers to copolymerize with acrylonitrile (AN) to obtain specialty fibers for various applications.^{6,7} Considerable information exists in the literature on the degradation behavior of AN polymers, and several reaction mechanisms have been proposed.^{8,9} In the published studies, the authors only presented the results obtained intermittently in nitrogen. It is very difficult to instantaneously track the small changes of polymer structure and property along

with the tiny changes of experimental conditions. There are a great many differences between the reported experimental conditions and the true environments of AN polymers degradation in air.

To our knowledge, there are fewer reports on 2-ethenyl-pyridine (EPD) as a comonomer, and there is almost no report on copolymerization kinetics of AN with EPD. In this study, copolymerization kinetics of AN with EPD were studied in H₂O/dimethyl formamide (DMF) mixture systems between 50 and 70°C under N₂ atmosphere. For estimating polymerization kinetics, copolymerization experiments were terminated at less than 10% conversion.¹⁰ Suitable kinetic schemes were proposed. This study was thus undertaken to carry out degradation of AN/EPD copolymers by use of differential scanning calorimetry (DSC) performed in air. The apparent activation energy of degradation of AN/EPD copolymers was calculated using Kissinger method.¹¹ Effects of different copolymerization conditions on the apparent activation energy of AN/EPD copolymers were discussed in contrast.

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EXPERIMENTAL

Materials

AN (A.R. grade Shanghai Chemical Reagents, Shanghai, China) was vacuum-distilled from CaH₂ just before polymerization. EPD was supplied as analytical-reagent grade by Zibo Zhangdian Oriental Chem-

ical (Zibo, China). Azobisisobutyronitrile (AIBN) was used as the initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) (polymerization degree = 1800) was obtained from Shanghai Chemical Resin Industry (Shanghai, China) and used as the suspending agent. Deionized water (H₂O) and DMF were adopted as the polymerization medium.

Copolymerization

Polymerizations were carried out in a 250-mL three-necked flask equipped with a gas supply, a Liebig condenser and a stirrer (double-bladed, Teflon). A typical example of the general procedure was as follows. Required amounts of AN, EPD, PVA, AIBN, deionized water, and DMF were placed in a flask, which was continuously flushed with ultrapure nitrogen. The flask was wholly immersed in a temperature-controlled water bath and shaken from time to time. All the experimental conditions have been provided in the following tables. For estimating polymerization rates, copolymerization experiments were terminated at <10% conversion by cooling the flask in the ice water after the polymerization was carried out under stirring for 20 min. The resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, dried at 60°C in vacuum until the constant weight, and then weighed.

Characterization

Conversion and the rate of polymerization were calculated from the weight of polymer obtained. The molecular weight (M_w) of the purified polymers was determined by viscosity measurements. Intrinsic viscosity (η) of the polymers were measured at 25°C in DMF using an Ubbelohde viscometer,¹² and the molecular weight was calculated from the following equation¹³:

$$[\eta] = 3.92 \times 10^{-2} M_w^{0.75} \quad (1)$$

The triad tacticities [(*mm*), (*mr*), (*rr*); *m* and *r* mean *meso* and *racemo* diad sequences, respectively] of AN/EPD copolymers were determined, on the basis of the Schaefer's assignment,¹⁴ from the ratio of intensities for the three nitrile carbon peaks in the ¹³C NMR spectra. ¹³C NMR spectra were recorded on a Bruker-DPX300 spectrometer (Germany) operating at 75 MHz.

Differential scanning calorimetry (DSC) spectra of AN/EPD copolymers were determined on a DSC 204 F1 Phoenix thermal analyzer in air. Particular care was taken to ensure that the heating rate was the same as that of the precursor thermal stabilization process used in carbon fibers production in the

TABLE I
Effect of AIBN Concentration on Copolymerization

AIBN concentration (10 ³ /mol L ⁻¹)	Conversion (%)	M_w (10 ⁴)
4.0	4.53	43.2
5.0	5.28	36.8
6.0	6.02	29.8
8.0	7.33	21.2

Conditions: $C_{AN} = 5.0$ mol L⁻¹; $C_{EPD} = 0.05$ mol L⁻¹; $C_{PVA} = 0.20$ g L⁻¹; H₂O/DMF (w/w) = 100/0; $T = 60^\circ\text{C}$; $t = 18$ min.

temperature range from 50 to 350°C. The apparent activation energy of degradation of the copolymers was calculated by Kissinger method from the following equation:

$$-\frac{\Delta E_a}{R} = \frac{d \ln(\phi/T_m^2)}{d(1/T_m)} \quad (2)$$

where ΔE_a is the apparent activation energy of degradation, ϕ is the heating rate, T_m is the highest temperature of exothermic peak, and R is the gas constant. ΔE_a was determined from the slope of a linear plot of $\ln(\phi/T_m^2)$ versus $1/T_m$.

RESULTS AND DISCUSSION

Kinetic equation of different copolymerization system

According to the radical polymerization, AN/EPD copolymers prepared in this study was random copolymers, which could be described as poly(AN-ran-EPD). To study the effects of AIBN on the copolymerization of AN with EPD, aqueous suspension technique was used. Variation in the percentage conversion and the molecular weight as a function of AIBN concentration were shown in Table I. It showed that the conversion increases and M_w reduced quickly as AIBN concentration increased. The rate of polymerization (R_p) was also calculated. Figure 1 was a logarithmic plot of R_p versus [AIBN]. The reaction order of AIBN for the copolymerization could be estimated from the line slope in Figure 1, and the reaction order of AIBN was 0.695.

Effects of AN and EPD concentrations on R_p were also studied. The reaction orders were 1.89 and 1.41, respectively. The overall rate of copolymerization is $R_p \propto [\text{AIBN}]^{0.695}[\text{AN}]^{1.89}[\text{EPD}]^{1.41}$. This was different from the reaction order reported. Pan¹⁵ revealed that the reaction orders of initiator and monomer were 0.5 and 1 when the solution technique was used to synthesize polyacrylonitrile. Zou et al.¹⁶ also studied the kinetics of polymerization of AN initiated by the redox system using the aqueous suspension

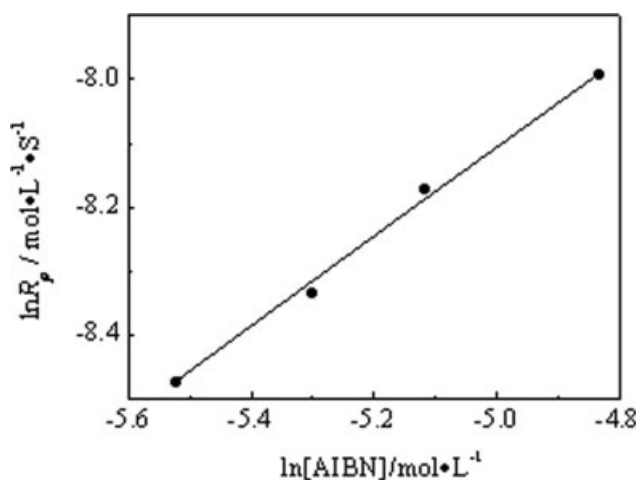


Figure 1 Relationship between $\ln R_p$ and $\ln [AIBN]$.

technique and a kinetic equation $R_p \propto [\text{initiator}]^{0.7}[\text{AN}]^2$ was proposed.

Effects of H₂O/DMF mixture on the copolymerization kinetic equation were shown in Table II. In general, AIBN could not dissolve in H₂O easily. When AN copolymers were prepared using H₂O/solvent suspension technique, oligomeric radicals might form quickly in the initial stages of polymerization. The oligomeric polymers precipitated out at the different critical molecular weight depending on the solvent/H₂O ratio and then acted as primary particles.^{17,18} In H₂O-rich reaction medium (H₂O/DMF > 70/30), propagation of the oligomeric polymers was more likely to follow the way of suspension polymerization because of the insoluble primary radicals. The chain termination was mainly resulted from the one-radical reaction, so that the reaction order of initiator tended to be 1. The rate of initiation was influenced by monomer concentration, so that the reaction order of monomer was larger than 1, and solubility and reactivity of EPD was greater than AN in DMF, and so the departure from 1 of the

TABLE II
Effect of Ratio of H₂O/DMF on the Kinetic Equation

H ₂ O/DMF(w/w)	R_p (mol L ⁻¹ s ⁻¹)
100/0	$R_p \propto [AIBN]^{0.695}[AN]^{1.89}[EPD]^{1.41}$
90/10	$R_p \propto [AIBN]^{0.688}[AN]^{1.82}[EPD]^{1.37}$
80/20	$R_p \propto [AIBN]^{0.675}[AN]^{1.76}[EPD]^{1.33}$
70/30	$R_p \propto [AIBN]^{0.662}[AN]^{1.71}[EPD]^{1.28}$
60/40	$R_p \propto [AIBN]^{0.648}[AN]^{1.64}[EPD]^{1.21}$
50/50	$R_p \propto [AIBN]^{0.636}[AN]^{1.52}[EPD]^{1.15}$
40/60	$R_p \propto [AIBN]^{0.621}[AN]^{1.41}[EPD]^{1.13}$
30/70	$R_p \propto [AIBN]^{0.615}[AN]^{1.35}[EPD]^{1.09}$
20/80	$R_p \propto [AIBN]^{0.589}[AN]^{1.28}[EPD]^{1.06}$
10/90	$R_p \propto [AIBN]^{0.574}[AN]^{1.21}[EPD]^{1.03}$
0/100	$R_p \propto [AIBN]^{0.542}[AN]^{1.15}[EPD]^{1.02}$

Conditions: $T = 60^\circ\text{C}$; $t = 18$ min.

reaction order was smaller. In DMF-rich reaction medium (DMF/H₂O > 70/30), there was no oligomeric polymers precipitating out and the copolymerization followed the way of solution polymerization. The kinetic equation of was $R_p \propto [AIBN]^{0.542}[AN]^{1.15} \times [EPD]^{1.02}$ when the ratio of H₂O/DMF is 0/100 (Table II). The extent of active free radicals embedded became less prominent. The chain termination mainly resulted from the two-radical reaction, so that the reaction order of initiator was close to 0.5. Efficiency of initiator increased and almost all the radicals were used to initiate the monomers. The reaction order of monomers tended to be 1.

Effect of H₂O/DMF mixture on the apparent activation energy of degradation of poly(AN-ran-EPD)

The thermal degradation behavior of poly(AN-ran-EPD) was studied by means of DSC in the temperature range from 50 to 350°C, and the heating rate was the same as that of the precursor thermal stabilization process used in carbon fibers production. Table III showed DSC parameters and polymerization conditions of poly(AN-ran-EPD) prepared by aqueous suspension polymerization technique at the different heating rate. The value of apparent activation energy of degradation, calculated from linear plot was 84.8 kJ mol⁻¹ (Fig. 2), which was a criterion to judge other results.

ΔE_a of poly(AN-ran-EPD) prepared by H₂O/DMF suspension polymerization technique was also calculated using Kissinger method. The experimental results were listed in Table IV. The value of ΔE_a of the copolymer synthesized in DMF solution, which was the largest, was 138.6 kJ mol⁻¹. With an increase of DMF concentration in the reaction media, the apparent activation energy of degradation increased rapidly. The degradation apparent activation energy was determined by the energy needed to initiate intramolecular cyclization of poly(AN-ran-EPD). There were a number of factors that appear to limit the extent of cyclization reaction of AN units, the most important of which were tacticity, sequence

TABLE III
DSC Parameters of Copolymers Synthesized by the Aqueous Suspension Technique

ϕ (k min ⁻¹)	T_m (K)	$\ln(\phi/T_m^2)$	$10^3 \times 1/T_m$ (K ⁻¹)
3	516	-11.39	1.938
5	529	-10.93	1.890
7	536	-10.62	1.866
8	541	-10.51	1.848

Condition: $C_{AN} = 5.0$ mol L⁻¹; $C_{EPD} = 0.05$ mol L⁻¹; $C_{AIBN} = 0.006$ mol L⁻¹; $C_{PVA} = 0.20$ g L⁻¹; H₂O/DMF (w/w) = 100/0; $T = 60^\circ\text{C}$; $t = 18$ min.

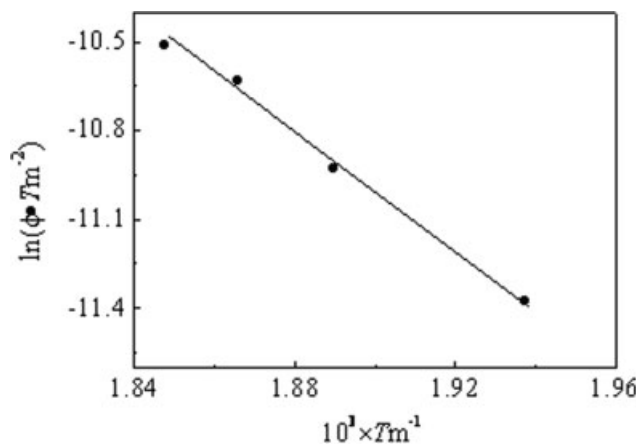


Figure 2 Plot of $\ln(\phi/T_m^2)$ versus $1/T_m$.

distribution, stereochemistry of AN and EPD units in the copolymer chain, and spacial considerations.¹⁹ Initiation by EPD units of cyclization reaction of adjacent isotactic AN units was a relatively rapid reaction, as was the propagation of the cyclization of subsequent isotactic AN units down the chain, so the value of ΔE_a was small.²⁰

When poly(AN-ran-EPD) was synthesized by H₂O/DMF suspension technique, in H₂O-rich reaction media (H₂O/DMF > 70/30), copolymerization followed the suspension polymerization technique more. Propagation would mostly occur in oligomeric radicals phase. AN units were more easily absorbed by polymer radicals than EPD units. The value of ΔE_a was small. In DMF-rich reaction media (DMF/H₂O > 70/30), copolymerization followed the solution polymerization technique more. The extent of chain transfer reaction was growing. The value of the high-chain transfer coefficient of DMF was 2.8×10^{-4} at 50°C.²¹ The impacting opportunities between EPD units and polymer radicals were increasing, which lead to the random array of EPD units in the copolymer chain. The extent of tacticity of AN units

TABLE IV
Values of ΔE_a of Copolymer Synthesized in H₂O/DMF Solvent Mixture

H ₂ O/DMF (w/w)	ΔE_a (kJ mol ⁻¹)	Triad isotacticity (mm)
100/0	84.8	0.374
90/10	91.2	0.369
80/20	96.9	0.362
60/40	102.8	0.358
50/50	110.5	0.349
40/60	117.3	0.343
20/80	124.7	0.338
10/90	131.2	0.331
0/100	138.6	0.325

Condition: $C_{AN} = 5.0$ mol L⁻¹; $C_{EPD} = 0.05$ mol L⁻¹; $C_{AIBN} = 0.006$ mol L⁻¹; $C_{PVA} = 0.20$ g L⁻¹; $T = 60^\circ\text{C}$; $t = 18$ min.

TABLE V
Effect of Monomer Ratio on ΔE_a of Degradation

EPD/AN (mol/mol)	ΔE_a (kJ mol ⁻¹)	Triad isotacticity (mm)
0/100	99.7	0.387
1/100	84.8	0.374
2/100	79.3	0.368
3/100	74.6	0.364
4/100	73.8	0.361
5/100	72.9	0.359

Condition: $C_{AN} = 5.0$ mol L⁻¹; $C_{AIBN} = 0.006$ mol L⁻¹; $C_{PVA} = 0.20$ g L⁻¹; H₂O/DMF (w/w) = 100/0; $T = 60^\circ\text{C}$; $t = 18$ min.

in copolymer decreased (Table IV), thus ΔE_a showed a trend of increase with an increase in the DMF concentration.

Effect of EPD on the apparent activation energy of degradation of poly(AN-ran-EPD)

To study the effect of EPD on ΔE_a , poly(AN-ran-EPD) with different monomer ratios were synthesized, which was given in Table V. ΔE_a decreased quickly with EPD concentration increasing, when the molar ratio went beyond 3/100, changes of ΔE_a became less prominent. This means EPD could directly initiate and accelerate intramolecular cyclization of poly(AN-ran-EPD). Bajaj et al.²² also reported that the activation energy of AN/itaconic acid copolymers showed a trend of decrease with the addition of itaconic acid. When the weight ratio of EPD/AN was higher than 3/100, the extent of isotacticity of AN units in copolymer was affected and began to decrease (Table V). The changes of the apparent activation energy then became correspondingly less. The theory that the extent of tacticity of AN units in the copolymer chains played a major role in controlling the apparent activation energy of degradation of poly(AN-ran-EPD) was confirmed.

CONCLUSIONS

Laboratory kinetic studies of different copolymerization systems reveal that AIBN successfully initiates copolymerization of AN with EDP in H₂O/DMF mixture systems. The kinetic equations were obtained. The apparent activation energy of degradation of poly(AN-ran-EPD) were also determined. With an increase of DMF concentration in the reaction media, the apparent activation energy of degradation of poly(AN-ran-EPD) increased rapidly. EPD could directly initiate and accelerate intramolecular cyclization of poly(AN-ran-EPD), and the apparent activation energy of degradation decreases quickly with an increase of EPD concentration. When the molar ratio of EPD/AN went beyond 3/100, the

changes of the apparent activation energy of degradation become less prominent.

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