Aqueous Deposited Copolymerization of Acrylonitrile and Itaconic Acid

Yaqi Zhao, Chengguo Wang, Yanxiang Wang, Bo Zhu

Carbon Fiber Center, Institute of Polymer Materials, School of Materials Science and Engineering,
Key Lab for Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University,
Jinan Shandong 250061, People's Republic of China

ABSTRACT: Aqueous deposited copolymerization reactions of acrylonitrile (AN) with itaconic acid (IA) were carried out in deionized water at 60°C with a single water-soluble initiator. High-molecular-weight polyacrylonitrile (PAN) copolymers were acquired by adjustment of technical polymerization parameters. When the amount of IA in the feed reached 2 wt %, the conversion of the polymerization reaction, intrinsic viscosity, and viscosity-average molecular weight all achieved their maximum values, whereas the molecular weight distribution achieved its minimum value. The AN/IA reactivity ratios, calculated with Q–e schemes (where Q and e are measures of the reactivity and polarity, respectively), agreed well with those determined with the Fineman–Ross and Kelen–Tüdõs methods. The thermal properties and structural characteristics of the PAN polymers were measured with differential scanning calorimetry and Fourier transform infrared spectroscopy. The introduction of IA into the polymerization system was found to be propitious for the preoxidation of the PAN polymers, and the characteristic absorption bands of $C{\equiv}N$, $C{=}O$, or $O{-}H$ existed in the polymer main chains. With an increase in the required amount of IA in the polymerization system, the exothermic figure of the exotherms became broader, and the intensity of the $C{=}O$ and $O{-}H$ absorption bands became stronger. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 3163–3169, 2009

Key words: acrylonitrile; itaconic acid; aqueous deposit copolymerization; water-soluble initiator

INTRODUCTION

Polyacrylonitrile (PAN)-based precursors are widely used for making carbon fibers. PAN homopolymer as a precursor results in carbon fibers of poorer quality than a copolymer of PAN with a low percentage of a comonomer. Many suitable comonomers, such as itaconic acid (IA), acrylic acid, and methacrylic acid, which improve the hygroscopicity of PAN polymers and facilitate the cyclization of the nitrile group to form a ladder structure during thermooxidation, have been reported to copolymerize with acrylonitrile (AN) to produce special high-performance acrylic fibers for manufacturing good-quality carbon fibers.[1–5] The most common methods for synthesizing PAN include solution polymerization, aqueous suspension polymerization, and mixed-solvent deposited polymerization. Among the various polymerization techniques used in the production of AN polymers, there are some advantages of aqueous deposited polymerization over the other techniques. First, aqueous deposited copolymerization is solution polymerization using deionized water as the reaction medium, which is inhomogeneous phase solution polymerization.[6] Because of the zero chain-transfer coefficient of water, PAN copolymers synthesized with this polymerization technique have a high molecular weight, which is very important for producing high-performance carbon fibers. As a new and advanced spinning method, dry-jet spinning also needs high-molecular-weight PAN copolymers to provide the appropriate spinning dope. Second, there are no complicated computational relationships or extra impurities in an aqueous deposited copolymerization system. Therefore, it is becoming more noticeable during the production of carbon fibers. By now, there have been many reports about copolymerizations or terpolymerizations of AN and other vinyl monomers with this polymerization technique.[4–10] In these studies, many complex initiators containing alkali metal ions were used to initiate the polymerizations of AN and vinyl comonomers,[7–11] and they could reduce the mechanical properties of the resultant carbon fibers.

Although AN and IA are very common comonomers, there are very few reports about the aqueous

deposited copolymerization of AN and IA, the reaction medium of which is entirely deionized water instead of a mixed solvent. In this study, IA was copolymerized with AN in an aqueous deposited copolymerization system. A single water-soluble initiator that did not contain alkali metal ions was first used to synthesize AN/IA copolymers. The initiator contained only one kind of substance and was not a complex initiation system; this is different from many other aqueous deposited polymerizations of AN and vinyl monomers. The reactivity ratios for this system were investigated. Also, the thermal properties and structural characteristics of AN/IA copolymers obtained with different monomer ratios in the feed were examined.

EXPERIMENTAL

Materials

AN was purified by alkali washing followed by distillation between 76 and 78°C. IA was recrystallized twice from water. The initiator was also refined before polymerization. Deionized water was adopted as the polymerization medium.

Polymerization

The copolymerization of AN and different weight fractions of IA in the feed was carried out in a three-necked flask at 60°C under a nitrogen atmosphere with deionized water as a reaction medium. In the reaction system, the total monomer concentration was 22 wt %, and the concentration of the initiator was 0.8 wt % (on the basis of the total monomers). Good agitation was used in the polymerization process to throw off the reaction heat instantaneously. The reaction was stopped after 2 h. The precipitate mixture was isolated by filtration, washed successively with water and methanol, and dried *in vacuo* at 50°C.

Similar polymerization conditions were used to prepare the copolymers for determining the reactivity ratios. The weight fraction of the comonomer in the copolymerization system varied from 1 to 10 wt %, and the copolymerization was terminated at a low conversion of $\leq 10\%$.

Characterization

The carbon, nitrogen, hydrogen, and oxygen contents of the PAN polymers were determined with an Elementar Vario EL III elemental analyzer (Germany). The reactivity ratios of the monomers were calculated from the elemental analysis results.

The molecular weight of IA was 130, and the molecular weight of AN was 53. According to the mechanism of radical copolymerization, with the end-group effects on copolymers ignored, the IA concentration (mol/mol) in the formed copolymers was calculated with the following equation:

$$[IA] = \frac{\frac{C_O}{4 \times 16}}{\frac{1 - \frac{C_O}{4 \times 16} \times 130}{53} + \frac{C_O}{4 \times 16}} = \frac{53 C_O}{64 - 77 C_O}$$

where C_O is the oxygen content in the copolymers. Therefore, the ratios of the molar fractions of the monomers in the feed and in the obtained copolymers could be calculated from the molar weights of the monomers.

On the basis of the elemental analysis results for the oxygen content, the AN/IA reactivity ratios could be calculated with different methods. The most ordinary methods include the Kelen–Tüdõs[12] and Fineman–Ross[13] methods. The advantages of the Kelen–Tüdõs method over the Fineman–Ross method and some conventional methods have already been emphasized.[14,15]

The copolymer composition equation deduced by Mayo and Lewis[16] using the dynamic method is as follows:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

where $[M_1]$ and $[M_2]$ are the initial molar fractions in the feed, $d[M_1]$ and $d[M_2]$ are the final molar fractions in the copolymer formed, and r_1 and r_2 represent the monomer reactivity ratios in the binary copolymerization.

TABLE I
Parameters for Aqueous Deposited Copolymerization of AN/IA Under Low Conversions

AN/IA (w/w)	X (mol/mol)	Conversion (%)	O content in the copolymers (wt %)	Y (mol/mol)
99/1	242.830	6.2	0.798	148.869
98/2	120.189	6.3	1.553	75.303
96/4	58.868	6.5	3.196	35.330
90/10	22.075	6.1	7.825	12.979
85/15	13.899	6.0	10.223	9.359

TABLE II
Q and e Values of AN and IA Used To Calculate the
Monomer Reactivity Ratios

Monomer	Q	e	r_1 (AN)	r_2 (IA)
AN	0.48	1.23	—	—
IA	0.75	0.107	0.505	1.928

According to the Mayo–Lewis equation, the Fineman–Ross method, used to calculate the reactivity ratios, is expressed as follows:

$$G = r_1 H - r_2$$

G and H are represented by

$$G = \frac{X(Y-1)}{Y}$$

$$H = \frac{X^2}{Y}$$

X and Y are the ratios of the molar fractions of the monomers in the feed and in the copolymer formed:

$$X = [M_1]/[M_2]$$

$$Y = d[M_1]/d[M_2]$$

The plot of G versus H gives a straight line with the slope as r_1 and the intercept of the y axis as r_2.

The linear relationship equations used to calculate the monomer reactivity ratios and proposed by Kelen and Tüdõs are as follows:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$$

$$\eta = \frac{G}{\alpha + H}$$

$$\xi = \frac{H}{\alpha + H}$$

$$\frac{G}{\alpha + H} = \left(r_1 + \frac{r_2}{\alpha}\right)\frac{H}{\alpha + H} - \frac{r_2}{\alpha}$$

α is an arbitrary constant ($\alpha > 0$):

$$\alpha = (H_m H_M)^{-1/2}$$

where H_m and H_M represent the highest and lowest values calculated from the series of measurements made during copolymerization. The plot of η versus ξ gives a straight line. The extrapolation of the line to $\xi = 1$ gives r_1 and to $\xi = 0$ gives r_2/α.

The third method for calculating the monomer reactivity ratios is the use of Q–e schemes (where Q and e are measures of the reactivity and polarity, respectively); this is the simplest and the most immediate method for evaluating monomer reactivity ratios. On the assumption that the e values of the monomer and its radical are identical, the relationships between Q and e deduced by Alfrey and Price are well known:

$$r_1 = \frac{Q_1}{Q_2}\exp[-e_1(e_1 - e_2)]$$

$$r_2 = \frac{Q_2}{Q_1}\exp[-e_2(e_2 - e_1)]$$

The intrinsic viscosity ([η]) of the PAN polymers was measured in a dimethyl sulfoxide (DMSO) solution with the Ubbelohde viscometer method in a constant-temperature water bath at $50 \pm 0.5°C$. The viscosity-average molecular weight (M_η) of the polymer was determined via the Mark–Houwink equation:[17]

$$[\eta] = KM_n{}^a$$

where K is 2.83×10^{-4} and a is 0.758.

The polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] denotes the molecular weight distribution of PAN polymers, which was determined with a Waters GPC/ALC 150C (Japan) with dimethylformamide (DMF)-soluble polystyrene standards for calibration.

Fourier transform infrared (FTIR) spectra of the PAN polymers were recorded on a Thermo Nicolet Avatar 370 FTIR spectrophotometer (USA). The transmission mode was used on finely powdered samples prepared as KBr pellets. The thermal properties of the PAN polymers were investigated

TABLE III
Reactivity Ratios Calculated with Different Methods
in Aqueous Deposited Polymerization

	Q	e	r_1	r_2	Method	r_1	r_2
AN	0.48	1.23	—	—	Kelen–Tüdõs	0.64	1.37
IA	0.75	0.107	0.505	1.928	Fineman–Ross	0.61	1.47

TABLE IV
Reactivity Ratios for AN and IA in Different Polymerization Systems

Method of polymerization	Kelen–Tüdõs method		Fineman–Ross method	
	r_1 (AN)	r_2 (IA)	r_1 (AN)	r_2 (IA)
Aqueous deposited polymerization	0.64	1.37	0.61	1.47
Aqueous suspension polymerization	0.84	6.73	0.87	2.52
Solution polymerization in DMF	0.575	2.05	0.624	2.3

with a Netzsch 404 thermal analyzer (Germany) at a heating rate of 5°C/min from room temperature to 400°C under air and argon atmospheres.

RESULTS AND DISCUSSION

Reactivity ratio studies

The parameters for the aqueous deposited copolymerization of AN and IA and Q and e values of AN and IA are shown in Tables I and II, respectively. On the basis of these two tables, the reactivity ratios of AN and IA calculated with the Q–e scheme and with both methods are shown in Table III. The three pairs of reactivity ratios showed good agreement.

The reactivity ratios of AN and IA synthesized with different methods have also been reported. Bajaj and coworkers[5,8] reported the reactivity ratios of AN and IA for copolymers prepared by aqueous suspension polymerization and solution polymerization in DMF; these are shown in Table IV.

According to the experimental results in Tables III and IV, it is obvious that the reactivity ratios of AN and IA in different polymerization systems are greatly different. However, the values of the reactivity ratios for AN calculated with the methods are less than unity in different polymerization systems, and this implies that the growing radical ~~~ AN· prefers to combine with the IA unit. On the other hand, the reactivity ratio for IA is greater than unity, thereby suggesting that the growing comonomer radical ~~~ IA· has greater affinity toward its own monomer unit. Hence, both growing radicals, that is, ~~~ AN· and ~~~ IA·, have a preference for an acidic monomer. In this case, the propagation reac-

tions ~~~ M_2M_2· and ~~~ M_1M_2· will be preferred over ~~~ M_2M_1· and ~~~ M_1M_1·; therefore, the probability of M_2 (IA) entering the copolymer chain is higher than that of M_1 (AN). The copolymer that is formed will therefore be richer in M_2 (IA), which is propitious for the preoxidation process of PAN-based precursors.[5]

In other words, the reactivity of monomers in a polymerization system depends on the method of polymerization and the medium and temperature of the polymerization reaction. However, regardless of the method of polymerization, the IA comonomer is more reactive than AN.[5]

Molecular weight and elemental analysis studies

The changes in the [η], molecular weight, and molecular weight distribution values during the aqueous deposited copolymerization of AN and IA with the increase in the comonomer amount in the feed are shown in Table V. The changes in the elemental contents of the polymers are shown in Figure 1.

As revealed in Table V, high-molecular-weight PAN polymers can be obtained by aqueous deposited polymerization. According to the aforementioned experimental results for the reactivity ratios, the reactivity ratio of IA is greater than the reactivity ratio of AN, and this suggests that IA has greater reactivity

TABLE V
Aqueous Deposited Polymerization of AN/IA with Different Monomer Ratios

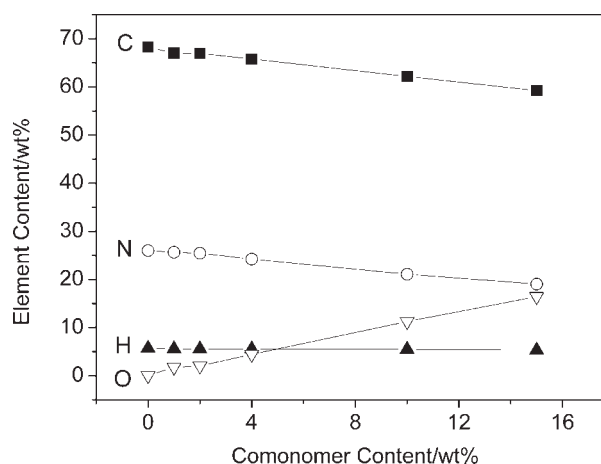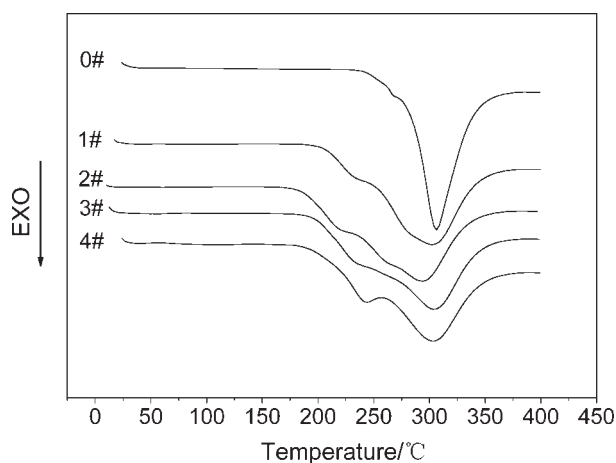| AN/IA (w/w)	Conversion (%)	[η]	M_n	M_w/M_n
100/0	60.2	9.66	95.6	2.08
99/1	75.3	11.49	120.2	1.94
98/2	80.1	12.15	129.4	1.87
96/4	49.4	9.20	89.7	2.36
90/10	30.9	7.10	63.7	2.59
85/15	25.6	6.10	52.1	3.02

Figure 1 Elemental analysis results for different PAN polymers.

Figure 2 DSC curves for PAN polymers measured under an air atmosphere.

than AN. Therefore, when the amount of IA in the feed is less than 2 wt %, a small quantity of IA in the polymerization system is advantageous for increasing the conversion of copolymerization and the kinetic chain length of PAN polymers. The molecular weight distribution has a tendency to become narrow. When the amount of IA in the feed reached 2 wt %, both the conversion of the polymerization reaction and the [η] value of the final copolymer achieved their maximum. At the same time, M_n achieved its maximum, whereas M_w/M_n achieved its minimum. After this, the molecular weight distribution became wide. The probable reason is that when the amount of IA in the feed is more than 2 wt %, the molecular volume of IA in the PAN polymer main chains is large enough to counteract the growth of the polymer chains. Hence, the kinetic chain length of the PAN polymers cannot become homogeneous.

The changes in the elements, including carbon, nitrogen, hydrogen, and oxygen, are due to the amounts of IA in the feed. Obviously, the oxygen element in the copolymers is mainly provided by IA. Therefore, with an increase in the amount of IA in the feed, the carbon, nitrogen, and hydrogen contents in the obtained copolymers were reduced, whereas the oxygen content increased.

Differential scanning calorimetry (DSC) studies

DSC exotherms of the PAN homopolymer and copolymers with various IA contents measured under an air atmosphere are shown in Figure 2. The various parameters obtained from these exotherms, including the temperature of initiation (T_i), the temperature of termination, that is, the final temperature (T_f), their difference ($\Delta T = T_f - T_i$), the peak temperature (T_p), the evolved heat (ΔH), and the velocity of evolving heat ($\Delta H/\Delta T$), are listed in Table VI.

DSC exotherms of the PAN homopolymer and copolymers are attributed to the oxidative reactions and cyclization reactions occurring in the temperature range. Oxidative reactions involve a group of reactions (i.e., dehydrogenation and other elimination reactions) that cause the conversion of the C—C structure to the C=C structure and generate oxygen-containing groups such as —OH and C=O. Cyclization reactions lead to the development of ladder structures by the oligomerization of nitrile (C≡N) groups. In the PAN homopolymer, the cyclization initiates through a radical mechanism, whereas in AN/IA copolymers, it follows an ionic mechanism. A cyclization reaction initiated through a radical mechanism is faster than cyclization initiated through an ionic mechanism.[9]

The T_i values for all the AN/IA copolymers are much lower than those of the PAN homopolymer, and this suggests greater ease of initiation of the exothermic process in the presence of IA in the feed. Furthermore, T_i becomes lower with an increase in the amount of IA in the feed, which is believed to play an important part in initiating the exothermic reaction. However, T_p and T_f show few changes with the required amount of IA in the polymerization system. This indicates that T_p and T_f are not affected by the increase in the IA comonomer.

In addition to this, the IA comonomer slows the rate of the exothermic reaction, as evidenced from the broader (higher ΔT) and smoother (lower $\Delta H/\Delta T$) exotherm in the copolymer versus the homopolymer.

The difference in the exotherms between the PAN homopolymer and copolymers in air and in argon is shown in Figure 3. The parameters of the exotherms are listed in Table VII. Under an argon atmosphere,

TABLE VI
Parameters for DSC Curves of PAN Polymers Measured Under an Air Atmosphere

Sample	AN/IA (w/w)	T_i (°C)	T_p (°C)	T_f (°C)	ΔT (°C)	ΔH (J/g)	$\Delta H/\Delta T$ (J g^{-1} °C^{-1})
0	100/0	241.7	306.2	344.1	102.4	4505	43.994
1	99/1	206.2	302.7	347.3	141.1	5160	36.570
2	98/2	199.4	302.1	342.9	143.5	5178	36.084
3	96/4	195.3	303.9	351.7	156.4	5286	33.798
4	90/10	192.7	243.5, 303.5	351.1	158.4	5038	31.806
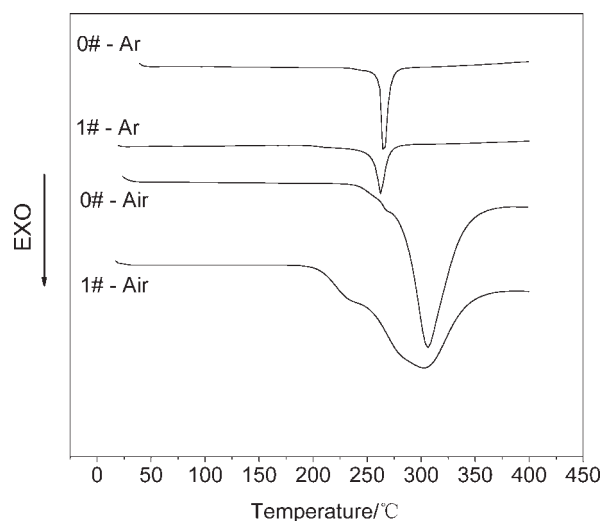
Figure 3 DSC curves for PAN polymers measured under different atmospheres.

exothermic reactions of the PAN homopolymer and copolymers are due only to a cyclization reaction because there is no oxygen in the reaction atmosphere. In the presence of oxygen, the T_i values for the PAN polymers under an air atmosphere are lower than those under an argon atmosphere, whereas ΔT and ΔH under an air atmosphere are much greater than those under an argon atmosphere. This indicates that the exothermic reactions of the PAN polymers under an argon atmosphere and of the PAN homopolymer under different atmospheres are all concentrative, and this is not advantageous for the making of preoxidative fibers.

From the DSC curves of the PAN homopolymer and copolymers under different atmospheres, it is shown that the introduction of a vinyl comonomer (IA) into the polymerization system is favorable for broadening the exotherms and lowering the reaction rate of the exothermic reaction, and this is better for preoxidation. With the increase in the required amounts of IA in the feed, the figure of the exotherms under an air atmosphere becomes more complex. The doublet peak phenomenon becomes more obvious.

FTIR studies

A comparison of FTIR spectra of the PAN homopolymer and copolymers obtained with different mono-

mer ratios is shown in Figure 4. The broad and weak band in the range of 3600–3100 cm^{-1} with its maximum at 3500 or 3250 cm^{-1} in the PAN copolymers is attributed to the O—H stretching, which is absent in the PAN homopolymer. It is IA containing O—H that makes the FTIR spectra of the PAN copolymers have the O—H stretching absorption bands. The strong band in the range of 1750–1700 cm^{-1} is present in the PAN copolymers because of the C=O stretching.[18] From the FTIR spectra, it is shown that the intensity of the C=O and O—H absorption bands becomes stronger with the increase in the required amounts of IA in the copolymerization.

The broad band in the range of 3100–2700 cm^{-1} with its maximum at 2940 cm^{-1} is attributed to C—H stretching in CH, CH$_2$, and CH$_3$ (including symmetrical and unsymmetrical stretching).[19] The position of the C≡N absorption band at 2240 cm^{-1}, which is the strongest absorption band in the polymers, remains invariable in all the PAN polymers, indicating the presence of long uninterrupted sequences of AN units in all the copolymers.[20] A shoulder-like appearance at 2190 cm^{-1} near the characteristic absorption for C≡N (at 2240 cm^{-1}) can be attributed to the stretching vibration of C=NH formed during polymerization.[21,22]

The bands in the regions of 1460–1440, 1370–1350, and 1270–1220 cm^{-1} have been assigned to the C—H vibrations of different modes.[21] Minagawa et al.[23] reported that the absorption bands at 1250 and 1230 cm^{-1} are stereospecific and appear because of the wagging mode of the C—H group coupled with the rocking mode of the CH$_2$ group. With respect to the assignment of the band at 1075 cm^{-1}, there is some confusion. Generally, it is due to the C—H mode mixed with some other mode whose vibration energy is not localized in the CH bending motion. In the finger zone, the weak absorption band at 538 cm^{-1} belongs to C—C≡N.[5]

CONCLUSIONS

The AN/IA reactivity ratios in the aqueous deposited copolymerization system initiated by the water-soluble initiator at 60°C are 0.64 for AN and 1.37 for IA according to the Kelen–Tüdõs method and 0.61 for AN and 1.47 for IA according to the Fineman–

TABLE VII
Parameters for DSC Curves of PAN Polymers Under Different Atmospheres

Sample	Atmosphere	T_i (°C)	T_p (°C)	T_f (°C)	ΔT (°C)	ΔH (J/g)	$\Delta H/\Delta T$ (J g^{-1} °C^{-1})
0	Ar	263.0	265.1	270.3	7.3	543.4	74.438
1	Ar	250.2	262.6	274.0	23.8	547.3	22.996
0	Air	241.7	306.2	344.1	102.4	4505	43.994
1	Air	206.2	302.7	347.3	141.1	5160	36.570
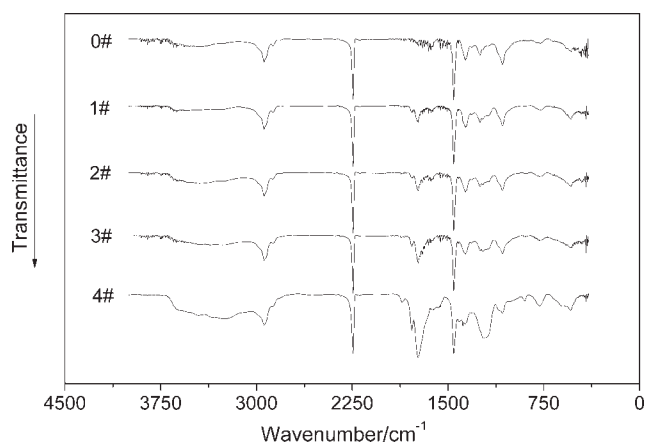
Figure 4 FTIR spectra of different PAN polymers.

Ross method. The AN/IA monomer reactivity ratios calculated from Q–e schemes are 0.505 for AN and 1.928 for IA. The three pairs of monomer reactivity ratios are in good agreement. High-molecular-weight PAN copolymers can be acquired by the adjustment of the polymerization technical parameters. The oxygen content in the polymers increased with the increase in the required amount of the comonomer (IA) in the feed. When the amount of IA in the feed reached 2 wt %, the conversion of the polymerization reaction, [η] of the final copolymer, and M_η all achieved their maximum values, whereas M_w/M_n achieved its minimum. From the DSC curves of the PAN polymers, it can be concluded that the introduction of IA into the polymerization system is helpful for preoxidation. With the increase in the required amount of IA in the copolymerization system, the exothermic figure of the exotherms becomes broader, and the intensity of the C=O and O—H absorption bands in the FTIR spectra becomes stronger.

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