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The effect of the distribution of composition among chains on the properties of polyacrylonitrile precursor for carbon fibre

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Co-monomers were introduced at a controlled rate into the reaction vessel in order to control the distribution of composition among the polymeric chains. When acrylate co-monomer, such as methyl acrylate or 2-ethyl hexyl acrylate was slowly fed into the reactor, the reaction time required for copolymerization to reach a fixed conversion was not affected, and the cycling temperature (or the temperature at the onset of the exotherm) during oxidation for polyacrylonitrile (PAN) precursor was slightly shifted to a higher temperature. On the other hand, as itaconic acid (IA) co-monomer was slowly fed into the reactor, the reaction rate of copolymerization was increased, and the cycling temperature could be depressed to a lower temperature due to the IA co-monomer being able to initiate the cycling of the CN groups. The structures (such as crystallinity, crystal size, orientation) and mechanical properties for PAN precursor and its resulting carbon fibre were influenced by the distribution of composition among the chains.

1. Introduction

Polyacrylonitrile (PAN) precursor is one of the most widely used materials for making high-performance carbon fibre, and the most commercial PAN precursors are copolymers. The introduction of suitable co-monomers into PAN precursor can depress the cycling temperature during stabilization [1–4], which lowers the production cost of the carbon fibre, and increases the solubility of PAN polymer [5–7] due to the disruption of the gelling tendency of the acrylonitrile groups, which is available in making a spinning solution. In general, the addition of co-monomers considerably affects mechanical properties of PAN fibre [8], and suitable co-monomer compositions can provide better mechanical properties for its resulting carbon fibre [9].

From our previous research [9], it was suspected that the distribution of composition among the polymer chains would largely affect the thermal properties of PAN precursor. Therefore, we investigated in detail how the properties of PAN precursor were affected by the co-monomers introduced at a controlled rate into the reactor.

2. Experimental procedure

The introduction of co-monomer into the reactor during copolymerization was controlled at a controlled rate by a meter pump, and copolymerization was carried out in the mixed solvent of acetone and dimethyl sulphoxide at 60 °C with α,α′-azo*bis*(isobutyronitrile) as initiator under an inert atmosphere of N_2. The resulting polymerization solution was directly spun through a 10% DMSO coagulation bath at 5 °C to form PAN precursor using a spinneret (1500 holes, 0.06 mm/hole, $L/d = 1$), then stretched in boiling water and dried. PAN precursor was stabilized at 250 °C for 30 min, then at 270 °C for 1 h in air, under 0.15 g/den tension. The oxidized PAN fibre was carbonized to 1200 °C under a high-purity N_2 atmosphere.

The average molecular weight and distribution ($\bar{M}_w/\bar{M}_n$) were determined using Water model 440 gel-permeation chromatography (eluting solvent DMF containing 0.5 LiBr wt %; column μ-Bondagel E-Linear). The molecular weights of various PAN precursors are shown in Table I.

The ^{13}C-NMR spectra were obtained using a Bruker AM-300 WB-FT-NMR Spectrometer. The polymers were dissolved in a deuterated solvent (DMSO-d_6) at 313 K.

The dependence of dynamic modulus, E', and tan δ on temperature were measured using a Rheovibron DDV-IIC under the following conditions: frequency, f, 11 Hz, heating rate 2 °C min^{-1}. Thermograms of PAN precursors were obtained using a Perkin–Elmer system 7/4 differential scanning calorimeter. Samples were heated under an air purge at a heating rate of 20 °C min^{-1}.

A Rigaku X-ray diffractometer, using Ni-filtered CuK_α radiation, was used to measure the crystalline related properties of the sample. Crystal size, L_c, was

TABLE I The composition and molecular weight of PAN precursors

Feed composition (mol %)	Sample number	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_w/\bar{M}_n$
AN:2-EHA:IA	PEI-1	3.7	1.9
98:1.5:0.5	PEI-2	3.6	1.9
	PEI-3	3.6	1.9
AN:MA	PM-1	3.3	1.9
96:4	PM-2	3.2	1.8
	PM-3	3.2	1.8
AN:2-EHA	PEH-1	2.7	1.6
98.5:1.5	PEH-2	3.0	1.6
	PEH-3	2.9	1.6

calculated from

$$L_c = K\lambda/(B \cos\theta) \quad (1)$$

where $\lambda = 1.54$, K is the apparatus constant (0.89), and B is the half-width (rad) of the X-ray diffraction intensity, I, versus 2θ curve.

The crystal orientation for the fibres was determined by an X-ray diffractometer combined with a fibre specimen attachment. The precursors and carbon fibres were located at around 17° (2θ) and 24°–25°, respectively, and the 360° azimuthal circle, used to permit the fibre axis to be rotated 360° about the vertical orientation was calculated from

$$\text{O\%} = [(360\text{-}H)/360] \times 100\% \quad (2)$$

where H is the half-width (deg) of the curve of intensity, I, versus azimuthal angle.

The "aromatization index", AI, value, described by Uchida *et al.* [10], was calculated from

$$\text{AI} = I_a/(I_p + I_a) \quad (3)$$

where I_a is the diffraction intensity of the aromatic structure at $2\theta = 25°$, and I_p is the diffraction intensity of the PAN crystal at $2\theta = 17°$.

The mechanical properties of the fibres were determined using the Microcomputer Universal Material Tester Type 8104 (Hung Ta Co., Ltd) with a crosshead speed of 10 mm min^{-1}, load cell 30 g, and 2 cm testing gauge.

3. Results and discussion

3.1. Reaction time of copolymerization

Table II shows that the reaction time of acrylonitrile–methyl acrylate (AN–MA) copolymerization was virtually unaffected by changing the feed rate of MA co-monomer into the reactor. The effect of the feed method of 2-ethyl hexyl acrylate (2-EHA) co-monomer on the reaction time of AN–2-EHA copolymerization is similar to that of AN–MA copolymerization. In AN–2-EHA–IA copolymerization, the feed method of itaconic acid (IA) co-monomer markedly influenced the reaction time. When IA co-monomer was slowly fed into the reactor during copolymerization, the reaction time required for copolymerization was considerably shortened (the rate of copolymerization became fast), which is attributed to a decrease in the content of IA co-monomer in the reactor by using a slow rate of feed. The reaction time of copolymerization is affected by the content of IA co-monomer in the reactor: as the IA co-monomer content was increased the reaction time was increased.

TABLE II The effect of feed rate of co-monomer during copolymerization on reaction time

Sample number	Feed rate of co-monomer	Reaction time (h)	Bulk viscosity at 60 °C (cP[a])
PM-1	0.94 mol/at one time	4	8200
PM-2	0.94 mol/2 h	4	8000
PM-3	0.94 mol/3 h	4	8100
PEH-1	0.23 mol/at one time	5	8200
PEH-2	0.23 mol/h	5	8200
PEH-3	0.23 mol/2 h	5	8100
PEI-1	0.56 mol 2-EHA/at one time 0.18 mol IA/at one time	7.3	8150
PEI-2	0.56 mol 2-EHA/h 0.18 mol IA/h	6.5	8100
PEI-3	0.56 mol 2-EHA/3 h 0.18 mol IA/3 h	4.8	8150

[a] 1cP = 10^{-3} Pa s.

3.2. Thermal properties

In Figs 1–3, the appearance of tan δ peaks is due to molecular motions, and these peak temperatures correspond to the glass transition temperature, T_g, of their individual copolymers. When the co-monomer was slowly fed into the reactor during copolymerization, the tan δ peak for PAN precursor fibre was shifted to a lower temperature, i.e. a decrease in T_g. This is because of the more dispersed distribution of co-monomers in polymeric chains, which resulted in a decrease of crystallinity. Gray and McCrum [11] used the decrease in damping as a measure of the crystalline content and expressed the relation as

$$\tan\delta = (1 - W_c)\tan\delta(a) \quad (4)$$

where tan $\delta(a)$ is the damping for a completely amorphous phase and W_c is the fraction of crystallinity. When the co-monomer was slowly fed into the reactor, the crystalline content for PAN fibre was decreased so that tan δ value increased, as shown in Figs 1–3.

The ^{13}C-NMR spectra are used to discuss the results in terms of the distribution of composition among the polymeric chains. Fig. 4 shows the nitrile resonance for the series of AN–2-EHA–IA copolymers. The line at 120 p.p.m. is assigned to nitrile carbon resonance, and the line from 177–179 p.p.m. is assigned to carbonyl carbon resonance. As the 2-EHA and IA co-monomers were slowly fed into the reactor during copolymerization, the more dispersed distribution of co-monomers among polymeric chains could be obtained, therefore, ^{13}C-NMR spectra exhibit the downfiled lines at 128.3 and 130.9 p.p.m. (see Fig. 4c), which are assigned to the AN co-monomer unit. From

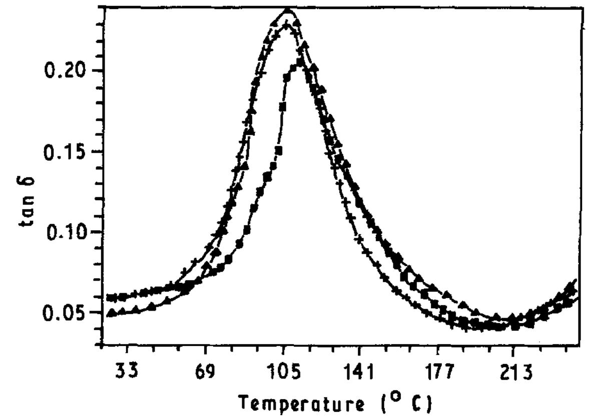

Figure 1 Temperature dependence of loss tangent for PAN precursors: (▲) sample PEI-3, (+) sample PEI-2, (■) sample PEI-1.

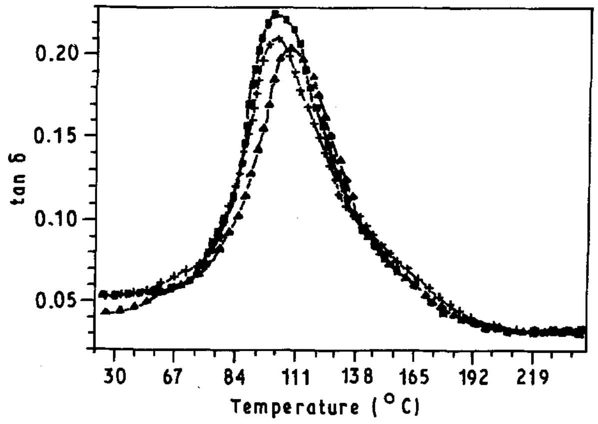

Figure 2 Temperature dependence of loss tangent for PAN precursors: (■) sample PM-3, (+) sample PM-2, (▲) sample PM-1.

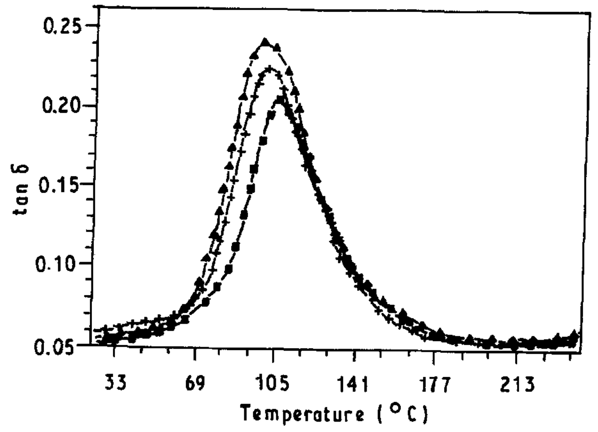

Figure 3 Temperature dependence of loss tangent for PAN precursors: (▲) sample PEH-3, (+) sample PEH-2, (■) sample PEH-1.

the ^{13}C-NMR spectra, it is apparent that the feed method of the co-monomer for copolymerization can control the distribution of composition among all polymeric chains.

The thermal properties of AN–MA and AN–2-EHA copolymers were slightly affected by the feed method of the co-monomer into the reactor (Table III). The decrease in the feed rate of the co-monomer resulted in the cycling temperature and peak temperature for PAN fibre being slightly shifted to higher temperatures. This is because MA and 2-EHA co-monomers prevented cycled propagation of CN groups. AN–MA and AN–2-EHA precursors were heated to 270 °C for 30 min and their AI values were measured using wide-angle X-ray diffraction. The AI values of samples PM3 and PEH3 were lower due to higher cycling temperatures.

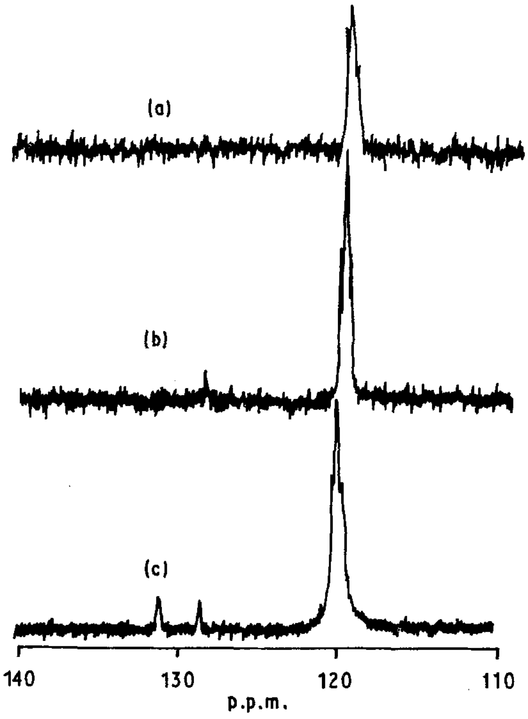

Figure 4 The ^{13}C-NMR nitrile region for AN–2-EHA–IA copolymers: (a) PEI-1, (b) PEI-2, (c) PEI-3.

TABLE III The DSC characterization and AI value of PAN precursors

Sample number	Onset of exotherm (°C)	Peak temperature (°C)	Heat of exotherm (cal g^{-1})	AI value (%)
PM-1	258	326	− 294	58.8
PM-2	259	328	− 315	58.7
PM-3	261	329	− 331	58.6
PEH-1	244	324	− 191	56.3
PEH-2	246	321	− 216	56.3
PEH-3	246	325	− 192	55.2

The thermal properties of AN–2-EHA–IA copolymers were considerably influenced by the feed method of co-monomers into the reactor (Table IV). When the co-monomers were slowly introduced into the reactor, the cycling temperature for PAN fibre during oxidation was decreased, which is attributed to IA co-monomer being able to initiate the cycling of the CN group.

All AN–2-EHA–IA precursors were heated to 250 °C for 30 min and their AI values were measured. It was evident that PAN precursor with a lower cycling temperature had a higher AI value. In Fig. 5, the dynamic storage modulus, E', for PAN fibre was slightly and gradually increased after sharply decreasing, and the increase in storage modulus indicates the formation of a ladder polymer (cycling of CN groups).

TABLE IV The DSC characterization and AI value of PAN precursors

Sample number	Onset of exotherm (°C)	Peak temperature (°C)	Heat of exotherm ($\mathrm{cal\,g^{-1}}$)	AI value (%)
PEI-1	200	283	− 129	50.0
PEI-2	191	285	− 132	52.4
PEI-3	167	286	− 137	54.6

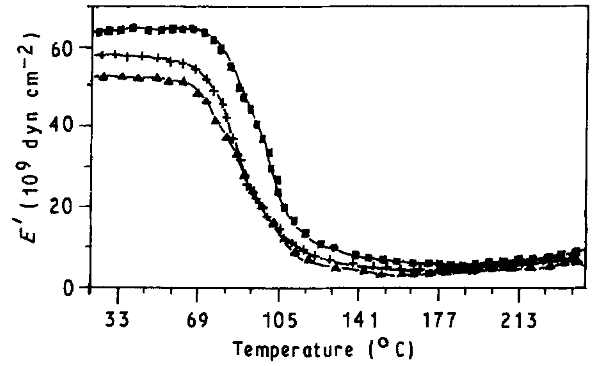

Figure 5 Storage modulus, E', as function of temperature: (■) sample PEI-1, (+) sample PEI-2, (▲) sample PEI-3. 1 dyn cm^{-2} = 10^{-1} Pa.

The storage modulus for sample PEI-3 was initially increased at a lower temperature due to a lower cycling temperature.

3.3. Mechanical properties

As the co-monomer was slowly fed into the reactor, the decrease in the orientation, crystallinity, and crystalline size was accompanied by a decrease in tensile strength for PAN precursor fibre, which is shown in Table V. The resulting carbon fibre made by a PAN precursor with more dispersed distribution of co-monomers among its chains gives a lower orientation and smaller crystalline size, which result in a decrease of tensile strength. This is shown in Table VI. Because the more dispersed distribution of co-monomer in polymeric chains might affect the length of the ring sequence (aromatic ring), the latter determines the crystalline size in the final carbon fibres and decides the ultimate mechanical properties of the carbon fibres.

4. Conclusions

In AN–MA and AN–2-EHA copolymerizations, the reaction time was not affected by the feed method of the co-monomer into the reactor. In AN–2-EHA–IA copolymerization, when the IA co-monomer was fed slowly into the reactor, the rate of copolymerization became faster.

As the co-monomers were more dispersed among the polymeric chains for AN–MA and AN–2-EHA

TABLE V The crystal and mechanical properties of PAN precursors

Sample number	Crystalline size, L_c (nm)	Crystallinity index	Orientation (%)	Tensile strength (g/den)[a]	Elongation (%)
PM-1	3.53	0.75	84	4.6	19.6
PM-2	3.06	0.74	81	4.3	17.8
PM-3	2.93	0.71	79	4.1	18.4
PEH-1	3.31	0.73	82	4.3	16.2
PEH-2	3.05	0.72	80	4.3	16.3
PEH-3	2.84	0.70	81	3.7	15.4
PEI-1	3.30	0.74	80	4.5	20.9
PEI-2	3.15	0.69	79	4.3	21.1
PEI-3	3.06	0.67	76	4.1	19.5

[a] g/den = $1.28 \times \rho \times 10^4$ p.s.i. = $8.8335 \times \rho \times 10^2$ GPa, where ρ is the density of fibre, 1.18 and 1.8 for PAN fibre and carbon fibre, respectively.

TABLE VI The crystal and mechanical properties of resulting carbon fibres

Sample number	Crystalline size, L_c (nm)	Orientation (%)	Tensile strength (g/den)	Elongation (%)
PM-1	1.18	76.3	13.7	1.18
PM-2	1.09	75.5	13.2	1.18
PM-3	1.08	74.6	12.6	1.09
PEH-1	1.07	75.2	12.1	1.07
PEH-2	1.02	74.0	11.9	1.02
PEH-3	0.98	72.8	10.2	0.96
PEI-1	1.18	75.0	14.6	1.22
PEI-2	1.11	75.4	14.7	1.21
PEI-3	1.11	74.3	13.5	1.19

copolymers, the cycling temperature for PAN precursor was slightly shifted to a higher temperature. The cycling temperature for AN–2-EHA–IA copolymer was largely depressed by more dispersed IA co-monomer among the chains due to IA co-monomer being able to initiate the cycling of CN groups at a lower temperature.

PAN precursor with more dispersed co-monomers among polymeric chains and its resulting carbon fibre showed lower crystallinity, orientation and tensile strength as well as smaller crystalline size.

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