



## EFFECT OF AN/IA RATIO ON THE STRUCTURE AND PROPERTIES OF ULTRA-HIGH MOLECULAR WEIGHT POLYACRYLONITRILE (UHMWPAN) SYNTHESIZED BY AQUEOUS SUSPENSION POLYMERIZATION

Huiyu Jiang<sup>\*1</sup> Ding Pan<sup>2</sup> Meihua Zhou<sup>3</sup>

<sup>\*1</sup>Key Laboratory of High Performance Fibers & Products Ministry of Education, Donghua University Shanghai, P.R.China 201620.

**KEYWORDS:** UHMWPAN; Aqueous suspension polymerization; AN/IA ratio; Structure and properties.

### ABSTRACT

Ultra-high molecular weight polyacrylonitrile (UHMWPAN) powders were synthesized by aqueous suspension polymerization with different AN/IA ratios using  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN) as initiator and Polyvinyl alcohol (PVA) as the disperser at 70°C for 2h. The thermal properties, structural characteristics, element component analysis and aggregation structure studies of the UHMWPAN samples were measured by thermal analyzer, differential scanning calorimeter, Fourier transform infrared spectrometer, element analyzer and X-ray diffractometer. The addition of IA was found to be favorable to retard the concentrated heat release and improve the carbon yield in the process of peroxidation of the precursor. The main absorption peaks corresponding to  $C\equiv N$ ,  $C=O$ ,  $-CH_2-$ ,  $-OH$ , and etc. were observed in FI-IR spectra of the copolymers. As the content of IA increased, the intensity of the absorption peak at 1735 $cm^{-1}$  corresponding to  $C=O$  increased; the content of oxygenium in the copolymer increased first and then leveled off; the former crystal structure of PAN was destroyed which meant the decline of the degree of crystallinity and the decrease of the grain size.

### INTRODUCTION

Polymerization is the initial period for preparing the carbon fibers with high performance for the reason that it could determine the molecular weight and molecular weight distribution of the precursors. As is seen from the homogeneity of the structure and carbon yield, PAN Homopolymer seems to be the optimal choice. But the homopolymer has the phenomenon of concentrated heat release during the preoxidation process which can easily result in the break wire. Therefore, small amount of comonomer should be added into the polymerization system to improve the properties of the precursors [1, 2]. The most common comonomers for copolymerizing with AN include acrylic acid (AA), methyl acrylate (MA), itaconic acid (IA), ammonium itaconate (AIA) and so on. And these comonomers can lower the activation energy of the copolymerization, be beneficial to promote the cyclization and crosslinking reaction of the molecular chain, reduce the concentrated exothermic phenomenon in the oxidation process, improve the compactness and homogeneity of the fibers, decrease the probabilities of break wire, and improve the strength of carbon fibers [3]. Certainly, there must be an appropriate polymerization process used to provide an ideal polymerization environment. The aqueous suspension polymerization is an admirable polymerization method for preparing high molecular weight polymers due to that the chain-transfer coefficient of the reaction medium (water) is zero and the water can help accelerating the exchanges of heat in the reaction system.

At present, the spinning dope with high molecular weight and molecular weight distribution is always the research emphasis. Owing to the addition of ultra-high molecular weight polyacrylonitrile (UHMWPAN), the tensile viscosity of spinning dope, the spinnability, the ability of stretching improve; the phenomena of break wire reduce whether by wet spinning or dry-jet wet spinning method; the strength of resultant fibers increase[4]. So it is meaningful to study the structure and properties of UHMWPAN with different contents of IA by aqueous suspension polymerization.

The structure and properties of PAN have been investigated by many researchers. Burkanudeen, A. et al. [5] had studied the effect of stereoregularity on the thermal behavior of I-PAN and A-PAN. And the thermal cyclization reactions of atactic polyacrylonitrile (A-PAN) with low isotactic content (26.4-29.7%) occurred at a lower temperature than that of isotactic polyacrylonitrile (I-PAN) with higher content (48.7-51.6%). The percentage of mass loss observed in I-PAN was less as compared to A-PAN. Sun, Tongqing et al. [6] studied the structure evolution of PAN fibers during thermal stabilization by mass spectrum (MS), differential scanning calorimetry (DSC) and thermogravimetry (TG), Fourier transform infrared (FTIR) spectroscopy. Yusof, N. et al. [7] discovered the properties and structure evolution of polyacrylonitrile/acrylamide-based carbon fibers during stabilization and carbonization prepared using a solvent-free coagulation process.



In this paper, IA was used as the comonomer to improve the structure and properties of PAN polymers by aqueous suspension polymerization. And the resultant UHMWPAN powders prepared with different AN/IA ratios were measured by TGA, DSC, FT-IR, EA and XRD to find out the effect of the increased content of IA in the total comonomers.

## EXPERIMENTAL

### Materials

Acrylonitrile (AN) [Shanghai Guanghua Technology Co., Ltd, Shanghai, China, analytical reagent (AR) grade] was vacuum-distilled to remove the inhibitor and stored under refrigeration until used. Itaconic acid (IA) [Sinopharm Chemical Reagent Co., Ltd, Shanghai, China, analytical reagent (AR) grade] and polyvinyl alcohol (PVA) [Sinopharm Chemical Reagent Co., Ltd, Shanghai, China, alcoholysis degree: 98.0~99.8mol%] were used as received.  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN) [Shanghai Shenbo Chemical Co., Ltd, Shanghai, China] was recrystallized from ethyl alcohol. The water used in this study was deionized.

### Methods

#### *Aqueous suspension polymerization*

Polymerizations were conducted in a three-neck, round-bottom flask with a motor-driven stirrer, a thermometer and N<sub>2</sub> inlet and outlet tubes. The comonomers AN and IA, 21wt%), the initiator (AIBN, 0.01wt%) and the disperser (PVA, 0.1wt%) were added in proportion and mixed evenly, followed by the deionized water being added to the reaction system, the system heated to 70°C by water bath heating for 2h. The nitrogen protection and the mechanical agitation were adopted in the whole process. After polymerization, the resultant polymer slurry was recovered by filtration, washed adequately with the deionized water and then dried fully at 50~60°C in the vacuum drying oven.

#### *Thermo gravimetric analyzer measurements*

The thermo gravimetric analysis (TGA) data of UHMWPAN with different monomer ratios were recorded on a TG209 (Netzsch, Germany) thermal analyzer under an air purge from 50°C up to 450°C at a heating rate of 10°C/min.

#### *Differential Scanning Calorimeter measurements*

Differential Scanning Calorimeter Diamond DSC (Perkin-Elmer, USA) was used to measure the thermal properties of UHMWPAN with different monomer ratios at a heating rate of 10°C/min under an air purge. The temperature range of the DSC tests was from 25 to 400°C.

#### *Fourier infrared spectrometer measurements*

FT-IR spectra were evaluated using a Tensor 27 IR spectrometer (Bruker, Germany). Typical conditions were as follows: the KBr disc technique; wavenumber, 400~4,000cm<sup>-1</sup> and scanning, 16 counts.

#### *Elemental analyzer measurements*

Elemental analysis was carried out using Vario Micro cube elemental analysis instrument (Elementar, Germany) to determine the carbon, hydrogen and nitrogen content of UHMWPAN samples. The oxygen in the molecular chain of the polymer was primarily supplied by itaconic acid, therefore, the monomeric unit content of IA in the polymer can be approximately evaluated by the calculated oxygen content. The relationship between the oxygen content and the monomeric unit content of IA can be expressed as follows:

$$\%IA = \frac{O}{13.0} \times 130.0 \quad (1)$$

#### *X-ray diffractometer measurements*

XRD patterns were obtained by Advanced D8 X-ray diffractometer (Bruker, Germany) with Cu K radiation (0.15406 nm), in order to determine the changes of UHMWPAN with different AN/IA ratios in the crystal structure. Test conditions: CuK radiation (0.15406 nm), tube voltage (40.0kV), tube electric current (30.0 mA), scanning speed (6°/min), and scan range from 5° to 60°, scanning step (0.0200°).



## Results and Discussion

### TGA

Three major reactions (the dehydrogenation reaction, the cyclization reaction and the oxidation reaction) accompanying with the changes of the weight of the copolymer will happen during the preoxidation process of the polyacrylonitrile fiber. Figure 1 and Table 1 showed the TG curves and data of UHMWPN with different AN/IA ratios. According to the difference of the slope of the curves in the figure, the weightlessness of PAN could be divided into three stages: the stage of trace weightlessness, the stage of fierce weightlessness and the stage of slow weightlessness. As shown in both the figure and the table, before 242°C, the weight loss ratios of all the samples were small which means only a portion of the dehydrogenation reaction happened. This stage belonged to the stage of trace weightlessness. During the temperature between 242~263°C, all of the samples had a severe weight loss, which indicated that the polymers had the drastic cyclization reaction and gave off heat tempestuously in a short time. This stage belonged to the stage of fierce weightlessness. After 263°C, the weightlessness had entered the stage of slow weightlessness. The rate of the weight loss decreased slightly with the appearance of the oxidation decomposition reaction.

It could also be seen in the table that the initial weight loss temperature was the highest. But as the content of IA increased, the initial temperature was getting lower and lower. In the stage of fierce weightlessness, the homopolymer had a fast and violent weight loss while the copolymers' weightlessness was slow and mild relatively. Then turning into the stage of slow weightlessness until the end, the homopolymer had larger weight loss than the copolymers. And the weightlessness ratio increased as the content of IA increased. These were due to the fact that the increased concentration of IA made the initial weight loss temperature lower continuously and the reaction time longer unceasingly [8]. Thus, IA has the function of avoiding concentrated heat release and reducing the oxidative cracking reaction.

Actually, the weight loss process of preliminary heat treatment in oxidizing of PAN in the air included two parallel processes: the thermal weight loss and the thermal weight gain. On one hand, the polymer had dehydrogenating, cyclizing, crosslinking, and oxidizing reactions with small-molecule gases giving up. On the other hand, the oxygen in the air combined with the carbon in the polymer chain to form the carbonyl or the oxygen entered into the ring structure to form the ether bond or the oxygen combined with the hydrogen in the polymer and the structure was dehydrogenated in the high temperature to form the double bond. The comprehensive effect of the two aspects was still characterized by the weightlessness.

In the actual production, the carbon yield of the carbon fiber is relevant to the weight loss in the process of preoxidation. As is analyzed above, the control of the content of IA must satisfy two requirements: one is to relieve the concentrated heat release, and another is to obtain considerable carbon yield.

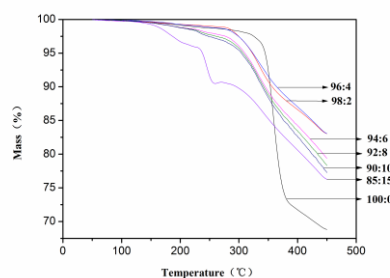


Figure 1 The thermogravimetric curves of polymers polymerized by different AN/IA ratios

Table 1 The thermogravimetric data of polymers polymerized by different AN/IA ratios

AN/IA ratios	Initial point	Inflection point	Terminal point	Residual ratio
100:0	349.0	351.2	362.5	68.59%
98:2	299.7	331.5	358.5	82.08%
96:4	295.7	335.2	360.9	82.16%
94:6	295.0	332.0	356.9	78.42%
92:8	294.1	332.2	357.8	78.30%
90:10	290.6	332.6	361.1	76.78%
85:15	242.1	244.9	249.0	75.09%

### DSC analysis

DSC plot of UHMWPAN with different AN/IA ratios was presented in Figure 2. As we could see from the figure, all of the curves had two or three peaks as a result of that the polymer had gone through the dehydrogenation reaction, the cyclization reaction and the oxidation reaction in air [9]. And we found that the peak shape of the homopolymer was sharper than the others, the initial exothermic temperature was the highest and the polymerization of the homopolymer was terribly drastic in a short time. Nevertheless, as the proportion of IA increased, the width of exothermic peak got longer and longer and the initial exothermic temperature became constantly lower. Accordingly, the addition of IA could lower the initial exothermic temperature effectively, relieve the phenomenon of the concentrated heat evolution, and make the preoxidation process controlled.

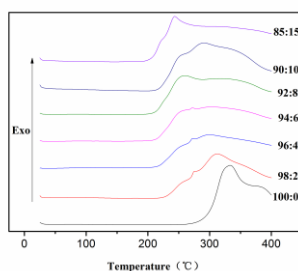


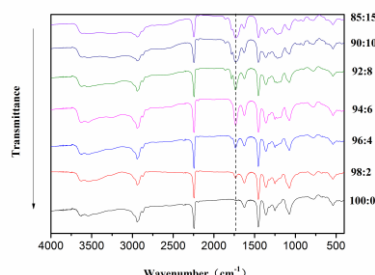
Figure 2 The DSC curves of polymers polymerized by different AN/IA ratios

### FT-IR analysis

Fourier transform infrared spectra of UHMWPAN with different monomer ratios was shown in Figure 3. The weak and broad peaks in the range of  $3700\sim 3200\text{cm}^{-1}$  corresponded to the stretching vibration of the hydroxide radical ( $-\text{OH}$ ) of the copolymers and the stretching vibration and frequency doubling absorption peaks of the  $\text{N}-\text{H}$  of all the samples in the high wave-number area which was generated by the hydrolyzation of the  $\text{C}\equiv\text{N}$  in the polymerization process due to the heat release. The absorption peaks at  $2940\text{cm}^{-1}$  corresponded to the stretching vibration of the methylene ( $-\text{CH}_2-$ ) and the methyne ( $-\text{CH}-$ ) of all the samples [10]. The absorption peaks at  $2243\text{cm}^{-1}$  which was the strongest among all the absorption peaks corresponded to the characteristic absorption peak of  $\text{C}\equiv\text{N}$  of all the PAN polymers, illustrating the existence of the long and successional AN monomeric unit in the polymers [11].

However, there was a difference at  $1735\text{cm}^{-1}$  between the curves owing to the wave number corresponded to the stretching vibration of  $\text{C}=\text{O}$  which was related to the content of IA monomeric unit in the copolymer [12]. We could see from the figure that the intensity of the absorption peak at  $1735\text{cm}^{-1}$  increased first and then decreased slightly as the content of IA increased. And the peaks got broaden when the IA ratio was larger than 8% of the total monomer concentration. Three factors contributed to the variation: first, the proportion of IA monomeric unit increased as the concentration of IA in the polymerization solution increased; second, as the fact that IA was hard to dissolve in the oil phase, the redundant IA could not be involved in the polymerization reaction when the content of IA was out of the solubility of IA in the oil phase (when the IA ratio was larger than 8% of the total monomer concentration, the proportion of IA monomeric unit in the copolymer no longer increased); third,  $\text{C}=\text{N}$  could be generated by the hydrolyzation of  $\text{C}\equiv\text{N}$  in the polymerization process because of the solvation, resulting in the strong absorption peak of bending vibration at  $1625\text{cm}^{-1}$ . When the content of IA was at a high level, the peaks at  $1625\text{cm}^{-1}$  would be overlapped mightily with the stretching vibration of  $\text{C}=\text{O}$  which caused the peaks getting broader. Nevertheless, the homopolymer also had a terribly weak stretching vibration peak at  $1735\text{cm}^{-1}$ , arising from  $\text{C}=\text{O}$  generated by the hydrolyzation of  $\text{C}\equiv\text{N}$  and  $-\text{NH}_2$ .

The peaks in the range of  $1280\text{-}1200\text{cm}^{-1}$ ,  $1380\text{-}1320\text{cm}^{-1}$  and  $1490\text{-}1410\text{cm}^{-1}$  corresponded to the bending vibration of  $\text{C}-\text{H}$  in different parts of the polymer respectively [13]. Their intensity depended on the stereo regularity of the PAN polymer. The peaks at  $1074\text{cm}^{-1}$  corresponded to the mixture vibration (the stretching vibration and the bending vibration) of  $-\text{CH}_2-$  and  $\text{C}-\text{CN}$  and the skeletal vibration of  $\text{C}-\text{C}$ . The peaks at  $778\text{cm}^{-1}$  corresponded to the bending vibration of  $-\text{CH}_2-$  and the mixture vibration (the stretching vibration and the bending vibration) of  $\text{C}-\text{CN}$ . The peaks at  $537\text{cm}^{-1}$  corresponded to the bending vibration of  $\text{C}-\text{CN}$ .

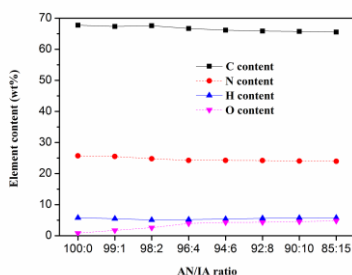


**Figure 3** The FT-IR curves of polymers polymerized by different AN/IA ratios

#### EA

The elemental analyzer was used to measure the content of C, H, O and N in the polymer synthesized with different AN/IA ratios. The results were shown in Figure 4.

The content of O and S which were introduced by the initiator and the disperser could be neglected due to the fact that the viscosity average molecular weight of UHMWPN prepared by aqueous suspension polymerization was tremendous. Oxygen in the polymer could be regarded as being completely introduced by IA. In the figure, the content of O in the polymer significantly increased first and then leveled off. The former accounted for that the proportion of the chain element of IA in the molecular chain increased while the later resultant from that IA was hard to dissolve in the oil phase. When the content of IA was more than the solubility of IA in the oil phase, the redundant IA dissolved in the water couldn't be involved in the reaction. As a result, blindly increasing the quantity of IA was meaningless. But the addition of IA could effectively ease the concentrated heat evolution in the process of preoxidation. So it is allimportant to determine the content of IA. As a general rule, the ratio of AN/IA is 98:2.



**Figure 4** The EA curves of polymers polymerized by different AN/IA ratios

#### XRD analysis

Figure 5 and Table 2 showed the XRD patterns and the calculated XRD structure parameters of polymers polymerized by different AN/IA ratios.

At present, most of the researchers considered that PAN polymer and precursor had two phase structure, which were crystalline region and amorphous region. And XRD is the widely used measurement to study the crystal structure and its evolution of PAN. From the figure, we could see clearly that PAN had two obvious characteristic diffraction peaks. The former ( $2\theta=17^\circ$ ) was strong and sharp while the latter ( $2\theta=29^\circ$ ) was weak and wide [14], corresponding to crystal face (100) and (110) of the hexagonal structure [15], respectively.

As the content of IA increased, both of the crystal size and the degree of crystallinity decreased on account of that the monomeric unit of IA destroyed the ordered arrangement of AN units in the crystalline region and the crystallization properties of the polymer decreased, followed by the declined intensity of the peaks and enlargement in the amorphous region[16].

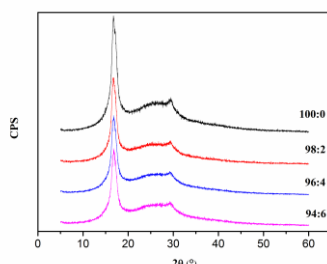


Figure 5 The XRD patterns of polymers polymerized by different AN/IA ratios

Table 2 The XRD structure parameters of polymers polymerized by different AN/IA ratios

AN/IA ratios	2θ (°)	L <sub>c</sub> (nm)	X <sub>c</sub> (%)
100:0	16.66	6.256	43.5
98:2	16.72	6.122	41.9
96:4	16.73	6.077	40.2
94:6	16.74	5.981	36.4

## CONCLUSIONS

With different AN/IA ratios, the ultra-high molecular weight polyacrylonitrile (UHMWPAN) samples were measured by TGA, DSC, FI-IR, EA, and XRD. The results were drawn as follows:

The addition of IA could effectively slow down the concentrated heat release of the precursor in the process of preoxidation and reduce the weight loss due to the oxidative chemical degradation to improve the carbon yield. From FI-IR analysis, it could be concluded that the intensity of the absorption peak at  $1735\text{cm}^{-1}$  increased as the content of IA increased as a result of the stretching vibration of C=O. And the strongest absorption peak at  $2243\text{cm}^{-1}$  corresponded to the characteristic peak of C≡N indicating the existence of the long and successional AN monomeric unit in the polymers. The content of oxygenium in the copolymer increased first and then leveled off as the addition of IA increased. By XRD analysis results, the increase concentration of IA could destroy the former crystal structure of PAN which caused the decline of the degree of crystallinity and the decrease of the grain size.

## ACKNOWLEDGEMENTS

The project in Hubei province department of education; Project number: Q20121708.

## REFERENCES

- Gupta, A.K., D.K. Paliwal, and P. Bajaj, *Effect of the nature and mole fraction of acidic comonomer on the stabilization of polyacrylonitrile*. Journal of Applied Polymer Science, 1996. **59**(12): p. 1819-1826.
- Gupta, D.C., J.P. Agrawal, and R.C. Sharma, *Effect of comonomers on thermal degradation of polyacrylonitrile*. Journal of Applied Polymer Science, 1989. **38**(2): p. 265-270.
- Zhang, W.X. and J. Liu, *Comparative study on preparing carbon fibers based on PAN precursors with different comonomers*. Journal of Wuhan University of Technology-Materials Science Edition, 2006. **21**(1): p. 26-28.
- Tan, L., J. Pan, and A. Wan, *Shear and extensional rheology of polyacrylonitrile solution: effect of ultrahigh molecular weight polyacrylonitrile*. Colloid and Polymer Science, 2011. **290**(4): p. 289-295.
- Burkanudeen, A., G.S. Krishnan, and N. Murali, *Thermal behavior of carbon fiber precursor polymers with different stereoregularities*. Journal of Thermal Analysis and Calorimetry, 2013. **112**(3): p. 1261-1268.
- Sun, T., Y. Hou, and H. Wang, *Mass DSC/TG and IR ascertained structure and color change of polyacrylonitrile fibers in air/nitrogen during thermal stabilization*. Journal of Applied Polymer Science, 2010. **118**(1): p. 462-468.
- Yusof, N. and A.F. Ismail, *Polyacrylonitrile/acrylamide-based carbon fibers prepared using a solvent-free coagulation process: Fiber properties and its structure evolution during stabilization and carbonization*. Polymer Engineering & Science, 2012. **52**(2): p. 360-366.
- Xiao, S., et al., *Mechanism and kinetics of oxidation during the thermal stabilization of polyacrylonitrile fibers*. Journal of Applied Polymer Science, 2013. **127**(4): p. 3198-3203.





9. Chang, S.H., *Thermal analysis of acrylonitrile copolymers containing methyl acrylate*. Journal of applied polymer science, 1994. **54**(3): p. 405-407.
10. Mittal, J., et al., IR studies of PAN fibres thermally stabilized at elevated temperatures. Carbon, 1994. **32**(6): p. 1133-1136.
11. Minagawa, M., et al., Infrared characteristic absorption bands of highly isotactic poly (acrylonitrile). Macromolecules, 1988. **21**(8): p. 2387-2391.
12. Yavorskii, I.A. and A.P. Barinova, Infrared spectroscopic study of thermal transformations of polyacrylonitrile in gas media. Fibre Chemistry, 1989. **21**(2): p. 121-125.
13. Varma, S., B. Lal, and N. Srivastava, *IR studies on preoxidized PAN fibres*. Carbon, 1976. **14**(4): p. 207-209.
14. Tse-Hao, K., Y. Ching-Chyuan, and C. Wen-Tong, *The effect of stabilization on the properties of PAN-based carbon films*. Carbon, 1993. **31**(4): p. 583-590.
15. Bohn, C., J. Schaeffgen, and W. Statton, *Laterally ordered polymers: Polyacrylonitrile and poly (vinyl trifluoroacetate)*. Journal of Polymer Science, 1961. **55**(162): p. 531-549.
16. Gupta, A. and R. Singhal, *Effect of copolymerization and heat treatment on the structure and x-ray diffraction of polyacrylonitrile*. Journal of polymer science: polymer physics edition, 1983. **21**(11): p. 2243-2262.