

Study on the thermal oxidative stabilization reactions and the formed structures in polyacrylonitrile during thermal treatment



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ABSTRACT

The structural evolution of polyacrylonitrile (PAN) homopolymer during thermal oxidative stabilization (TOS) was tracked quantitatively by using fourier transform infrared spectroscopy (FTIR) and curve-fitting technology. The cyclization, dehydrogenation of linear PAN macromolecule chains, oxygen uptake reactions of linear PAN macromolecule chains and cyclic structures were discussed in detail through tracking quantitatively the evolution of some specific groups. The cyclization, dehydrogenation and oxygen uptake reactions were evolved synchronously at the initial stage of TOS processes, but dehydrogenation and oxygen uptake reactions became dominant as cyclization extent above 0.7. Based on the data from FTIR and curve-fitting, a new procedure was developed to calculate the formed cyclic structures. The cyclic structures formed at 250 °C possessed length about seven successive aromatic rings; however, the cyclic structures formed at 265 °C possessed length about six successive aromatic rings. The graphite-like structures of the carbonized PAN films which were stabilized at 250 °C possessed were better than that of the carbonized PAN films which were stabilized at 265 °C.

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1. Introduction

It is well known that thermal oxidative stabilization (TOS) is an independent step for the fabrication of carbon fiber and other carbon materials from polyacrylonitrile (PAN) precursors [1–4], which has been intensively investigated by many researchers in the past decades through many methods, such as fourier transform infrared spectroscopy (FTIR) [5–11], nuclear magnetic resonance spectrum (NMR) [12–15], pyrolysis-gas chromatography (PyGC) [16,17], differential scanning calorimetry (DSC) [18–20], elemental analysis [21,22], wide-angle X-ray diffraction (WXR) [23], thermal gravimetric analyses (TGA) [24,25] and so on. During TOS of PAN polymers, cyclic oxygen-containing structures are formed through the condensation between nitrile groups, namely cyclization, oxidative uptake and dehydrogenation reactions and so on [26]. Among these reactions, cyclization reaction is of the most importance. Because cyclization reaction converts linear PAN

macromolecules into cyclic structures which are the basic intermediates for the formation of the turbostratic graphite-like structures [1,2,4]. It has been widely accepted by researchers that cyclization reaction for PAN homopolymer is initiated through a free radical mechanism [7,9,25,26].

However, a part of nitrile groups fail to convert into cyclic structures during TOS. There are three kinds of nitrile groups formed during TOS, namely unreacted nitrile, β -amino nitrile and conjugated nitrile [12,27–30]. Among these nitrile groups, β -amino nitrile stems from termination of cyclization reaction initiated by a free radical mechanism [29]. And conjugated nitrile group stems from the oxidative dehydrogenation reaction of linear PAN macromolecule chains [30]. In the past decades, intensive studies were carried out mostly to investigate the thermal behaviors and structural evolution of PAN polymers during thermal treatment or TOS. And several methods were developed to calculate the extent of cyclization reaction or the extent of TOS reaction such as FTIR, NMR, XRD and DSC and so on [7,9,14,19,23,31]. Due to the good accuracy, operability and repeatability, FTIR is the most commonly means used to characterize the structural evolution, extent of TOS or cyclization reaction of PAN polymers. G. L. Collins et al. [31] proposed a method to study the extent of cyclization reaction through

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FTIR data. And very recently, N. U. Nguyen et al. re-examined the accuracy of this method by the second-derivative and the curve-fitting operations [9]. Through the efforts of researchers, the evolution of chemical structures and reaction pathways for PAN during TOS processes become more and more clear, and some key issues, such as the role of oxygen for stabilized aromatic ladder, has been discussed [5–17]. However, to the best of authors' knowledge, there is no simple and effective method to quantitatively characterize the length of the formed cyclized or ladder structures of PAN polymers by now. This is a key issue for in-depth understanding of the TOS process and the formed resulted stabilized structures.

In the present work, FTIR technology was used to track the structural evolution of PAN in detail during TOS process. Moreover, it is the first time to make efforts to investigate synchronously the evolution of cyclization including termination reaction, dehydrogenation and oxygen uptake reactions of linear PAN chains, oxygen uptake reactions of the formed cyclic structures quantitatively by FTIR and curve-fitting technology during TOS. This procedure provides the possibility for in-depth understanding on the formed cyclized or ladder structures during TOS. Moreover, based on the data obtained from curve-fitting, a new procedure was developed to calculate the length of the formed cyclized structures.

2. Experimental

2.1. Materials

Acrylonitrile (AN) was supplied by Jilin Petrochemical Company, Jilin, China, distilled under reduced pressure and restored in a freezer at $-18\text{ }^{\circ}\text{C}$ prior to its use. Dimethyl sulfoxide (DMSO, 99%, Aldrich) and 2,2'-azobisisobutyronitrile (AIBN, 98%, Heowns) were used as received. *N,N*-dimethylformamide (DMF, >99.5%) and methanol (>99.5%) were purchased from Beijing Chemical Works, Beijing, China and used as received.

2.2. Preparation of PAN homopolymer

The sample of polyacrylonitrile homopolymer was prepared by a radical polymerization in a solution of DMSO using AIBN as initiator. The polymerization was carried out at $60\text{ }^{\circ}\text{C}$ for 10 h. Then the reaction mixture was added into excessive methanol with vigorous agitation to precipitate the polymer and then washed again with methanol for several times. At last, the polymer was dried at $60\text{ }^{\circ}\text{C}$ under vacuum to a constant weight.

2.3. Preparation of PAN film and thermal treatment procedures

Thin films of the samples were prepared for heat treatments and the following FTIR and Raman analysis. The process of PAN films was reported in our previous works [32,33]. Thermal treatment was carried out in an air oven at a constant temperature of $250\text{ }^{\circ}\text{C}$ and $265\text{ }^{\circ}\text{C}$ with a temperature accuracy of $1\text{ }^{\circ}\text{C}$ under a constant air gas flow. Carbonization of the stabilized PAN films was carried out under nitrogen condition (>99.999%) using a tube furnace. The stabilized PAN films were heated from room temperature to $1350\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$, and kept for 30 min at $1350\text{ }^{\circ}\text{C}$, subsequently cooled down to room temperature at $10\text{ }^{\circ}\text{C}/\text{min}$.

2.4. Characterization of PAN homopolymer

The Nicolet iS-50 FTIR spectrometer was used to detect the structural changes during the thermal treatment in $4000\text{--}400\text{ cm}^{-1}$ range using 64 scans at a resolution of 4 cm^{-1} . For each sample, two FTIR spectra were collected. The thickness of each film was measured by using a digital caliper (Mitutoyo 293-100).

Raman spectra of carbonized PAN films were collected using a Renishaw Via-Reflex Confocal Raman spectrometer. A linear polarized diode pumped green crystal laser with a nominal wavelength $\lambda_L = 532\text{ nm}$ was coupled to a microscope with a single-mode optical fiber. The laser power of the incident beam measured at the sample position was kept at 3 mW to prevent irreversible thermal damage to specimen surface. The Raman spectrometer was generally operated in the continuous scanning mode. For each sample, five Raman spectra were collected at different positions.

PeakFit v4.12 software (SPSS/Jandel, Scientific Software) was used to deconvolute the FTIR spectra within the range of $2300\text{--}2100\text{ cm}^{-1}$ and $1800\text{--}1000\text{ cm}^{-1}$ by fixing the peak position and varying the peak width and intensity. The Raman spectra within the range of $1000\text{--}2000\text{ cm}^{-1}$ were also curve-fitted to a Gauss+Lor area function using PeakFit v4.12 software.

The DSC of PAN powered sample was carried out in the temperature range of $50\text{--}325\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$ using a Mettler DSC-1 thermal analyzer. The PAN sample about 5 mg was scanned under nitrogen for DSC analysis. To ensure the diffusion of the gas phase, finely powdered samples of PAN (~5 mg) was used for TGA, which was carried out using a PerkinElmer TGA Pyris-1 thermal analyzer in the temperature range of $50\text{ to }325\text{ }^{\circ}\text{C}$ in nitrogen at $5\text{ }^{\circ}\text{C}/\text{min}$.

3. Results and discussion

3.1. TGA and DSC curves of PAN homopolymer

To ensure the temperature range of cyclization reaction, TGA and DSC were performed, and the corresponding results are shown in Fig. 1. The single exothermic peak in DSC curve starts from ca. $246\text{ }^{\circ}\text{C}$ and ends at ca. $266\text{ }^{\circ}\text{C}$, indicating that cyclization reaction mainly occurs in this narrow temperature range. Moreover, in this temperature range, the weight loss is very small (ca. 3.0 wt%), indicating the pyrolysis reactions can be neglected. Based on these results, the temperatures of isothermal TOS of PAN will be selected in this temperature range purposefully, such $250\text{ }^{\circ}\text{C}$ and $265\text{ }^{\circ}\text{C}$.

3.2. Structural evolution of PAN film during isothermal TOS processes

The PAN films were subjected to the isothermal TOS processes at $250\text{ }^{\circ}\text{C}$ and $265\text{ }^{\circ}\text{C}$, respectively. The samples for FTIR analysis were taken at timed intervals (for $250\text{ }^{\circ}\text{C}$: 0, 5, 10, 15, 20, 30, 40, 50 and

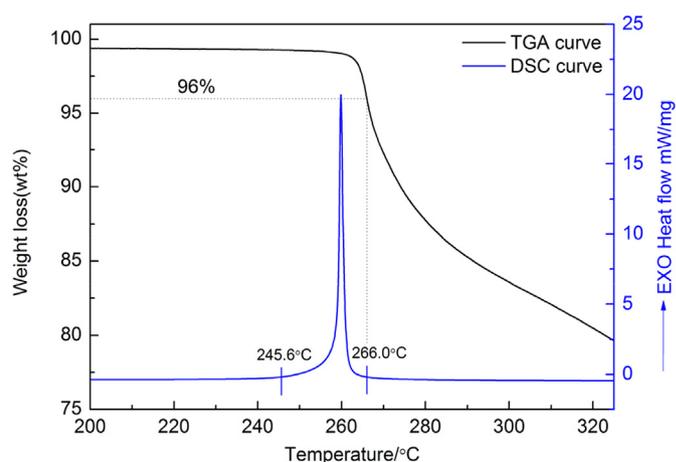


Fig. 1. TGA and DSC curves of PAN homopolymer measured at $5\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen.

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