

Effect of acrylonitrile sequence distribution on the thermal stabilization reactions and carbon yields of poly(acrylonitrile-co-methyl acrylate)



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ABSTRACT

Polyacrylonitrile (PAN) copolymers are important precursors for making high performance carbon fibers. In this study, a type of inert comonomer, methyl acrylate (MA), was copolymerized with AN, and the effects of AN sequence distribution on the cyclization, oxidation and carbon yield were systematically studied. The sequence distribution of P(AN-co-MA) could be adjusted by altering MA/AN feeding ratio during radical polymerization. The number-average sequence length of AN in the copolymers decreases quickly along with the increase of MA content in PAN. The stabilization and carbonization weight losses were determined by thermogravimetric analysis, and the corresponding chemical changes were detected by Fourier transform infrared spectrums and X-ray photoelectron spectroscopy. The thermal cyclization and oxidation reactions were separated by altering gas environment from nitrogen to air, and were monitored by differential scanning calorimetry. It is concluded that the sequence distribution of AN in P(AN-co-MA) strongly affects reaction activation energies, cyclized structures and carbon yield.

1. Introduction

Polyacrylonitrile (PAN), the most important precursor for high performance carbon fibers, makes more than 90% carbon fiber productions world-wide [1,2]. During thermal stabilization (180–300 °C), the nitrile (–C≡N) side groups in the tangled polymer chains cyclize and form a thermally stable ladder structure which allows PAN fibers to be further carbonized in an inert atmosphere at elevated temperatures in the range of 1000–2500 °C [3–6]. The stabilization process which involves complex physical and chemical changes is crucial for the structures and properties of the resultant carbon materials. Main reactions occurred in the stabilization process were illustrated in Fig. 1 [3,6,7]. Although the stabilization mechanisms of PAN-based precursors have been studied for over 60 years, there are still many uncertainties need to be clarified, such as the effect of comonomer sequence distribution and stereo-regularity of the PAN chain on the stabilization reactions [8–11]. The oxidative stabilization of PAN involves cyclization, dehydrogenation and oxidation, and release large amount of heat [12–18]. Normally, a small amount (0.5–4 wt%) of comonomer(s) is incorporated into the PAN precursor to tune solution spinnability and stimulate thermal stabilization reactions. There are

many reports regarding on the effects of comonomer types [19–22] and compositions [23–25] on the thermal stabilization of PAN. Now, it has been widely accepted that the acidic type of comonomer, such as methacrylic acid and itaconic acid, would initiate the cyclization reaction at a lower temperature than neat PAN and relieve central heat release. Whereas, the inert type of comonomer, such as methyl acrylate (MA), would improve the spinnability of PAN dope. However, the effect of AN sequence distribution on the stabilization reactions has rarely been addressed. Unlike helically arranged atactic PAN chains, ladder polymer has a planar structure. During stabilization, the cyclization of PAN normally propagates for 4–7 AN monomers and then stops due to excessive tension caused by chain configuration transformation [26–28]. As compared with PAN homopolymer, small amount of comonomer (8 wt%) in PAN copolymer could significantly reduce the average AN sequence number from infinity to ~9 [29]. The changes of AN sequence length are expected to strongly affect the propagation length of cyclization reactions, and lead to different stabilized and carbonized structures. Wiggins et al. synthesized a sequence-tunable poly(acrylonitrile-co-N-isopropylacrylamide) (P(AN-co-NIPAM)) copolymer by altering comonomer contents and injection rates during semibatch reversible addition-fragmentation chain transfer

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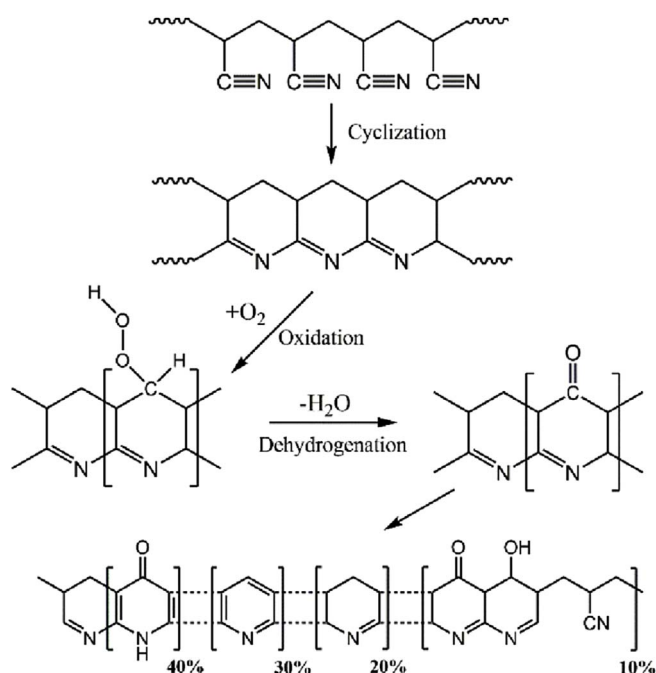


Fig. 1. Possible chemical reactions of PAN during thermal stabilization.

polymerization, and observed that the distribution of NIPAM affected the cyclization onset temperature, cyclization rate and thermal stability [30]. Since NIPAM is able to initiate PAN cyclization, beside AN sequence distribution, the stabilization reactions are also affected by NIPAM content, and it is difficult to distinct the influences of these factors on stabilization reactions and stabilized structures. By comparison, MA is a type of inert monomer that will not initiate PAN cyclization. In this study, methyl acrylate (MA) is used as comonomer to polymerize with AN. In this case, the addition of MA in PAN functions as breakpoints to divide continuous PAN chains into short AN segments, and the AN segment length distribution can be easily tuned by altering the MA monomer feed contents. Thus, we are able to clarify the effect of AN distribution on stabilization reactions and carbon yields. During previous studies, Lin et al. [31] and Wiggins et al. [30] found that the feeding rates of comonomer affected the distribution of compositions. This phenomenon can be ascribed to the different reactivity ratios of AN and the used comonomer, the uneven consumptions of monomers cause monomer concentration variations and lead to the composition changes of the resultant copolymer during polymerization. To overcome this factor, we stopped the copolymerization when the conversion degree was lower than 10%. At this stage, the monomer fraction changes are minimal and the resultant copolymer has uniform compositions and distributions. Additionally, for PAN stabilization, the formation of ladder polymer is a prerequisite to oxidation [32]. Our previous experiments found that the cyclization, oxidation and cross-linking reactions can be separated by altering gas environment from nitrogen to air during stabilization [33]. In this study, how the AN sequence length distribution affects the cyclization, oxidation, chemical compositions and carbon yield of PAN copolymers will be discussed in detail.

2. Experimental

2.1. Materials and methods

Poly(AN-co-MA) was synthesized by radical copolymerization in N,N-dimethylformamide (DMF) at 60 °C according to our previous work [34]. The comonomer feeding contents of MA were varied from none to 25 wt%. The reaction was ceased at an early polymerization stage to ensure a low conversion degree of < 10%. Powdery PAN was collected

by precipitating polymerized solution in cold DI water, then vacuum filtered and finally vacuum dried overnight. Homo-PAN (homo-polymer, ≈ 150,000 g/mol, powdery form, atactic) was purchased from Shanghai Macklin Biochemical Co., Ltd. (China) for experimental comparison.

2.2. Characterization

¹H-NMR (400.13 MHz) and ¹³C-NMR (100.61 MHz) spectra of the copolymer were acquired on a Bruker AV-III 400 MHz NMR spectrometer (9.39 T). The copolymer was dissolved in DMSO-d₆ to obtain 1 wt % and 20 wt% PAN solutions for ¹H-NMR and ¹³C-NMR measurement, respectively. The copolymer composition was calculated by ¹H-NMR and the triads fractions were analyzed by ¹³C-NMR spectrum. Typical ¹H- and ¹³C- NMR spectra are shown in Figs. S1 and S2 in supporting information, respectively. Detailed methods for deconvolution and composition calculation are included in our previous article [34]. Thermal analysis was conducted on differential scanning calorimetry (DSC, TA Q2000) and thermogravimetric analysis (TG, METTLER TOLEDO, TGA2). For DSC characterizations, PAN samples were heated at varied heating rates (2.5, 5 and 10 °C/min) under N₂ (60 ml/min) in Al₂O₃ pans from 40 to 350 °C, then quickly cool down to room temperature. Next, the samples were reheated in air under the same heating conditions. The carbon yields were calculated using TG by heating the PAN powder from 35 to 1000 °C under N₂ atmosphere at a heating rate of 10 °C/min. Fourier transform infrared spectrums (FTIR) were recorded by 16 scans at a resolution of 4 cm⁻¹ using a FT-IR spectroscopy (Bruker VERTEX 80v, US). The stabilized PAN samples were collected for X-ray photoelectron spectroscopy (XPS) study. A Thermo ESCALAB 250Xi instrument was used for XPS measurement with Al K_α X-ray source (hν = 1486.6 eV). A survey spectrum was recorded using a pass energy of 100 eV. The binding energy of the C1s from contamination of saturated hydrocarbons at 284.8 eV was used as an internal reference for calibration purpose.

3. Results and discussion

3.1. AN sequence distribution

The chemical compositions of the synthesized P(AN-co-MA) copolymers were determined by NMR. The mole fractions of the dyads and triads of PAN copolymer are calculated from NMR spectra based on our reported method [34]. The AN sequence distribution is calculated by the following equations using Alfrey-Mayo model [35–37]:

$$F_{AAA} = (p_{AA})^2 \quad (1)$$

$$F_{AAM/MAA} = 2p_{AA} \cdot (1 - p_{AA}) \quad (2)$$

$$F_{MAM} = (1 - p_{AA})^2 \quad (3)$$

$$(p_A)_x = p_{AA}^{(x-1)} (1 - p_{AA}) \quad (4)$$

$$(F_A)_x = \frac{x(p_A)_x}{\sum x(p_A)_x} = xp_{AA}^{(x-1)} (1 - p_{AA})^2 \quad (5)$$

$$\langle N_A \rangle_n = \sum_{x=1}^{\infty} x(p_A)_x = \sum_{x=1}^{\infty} xp_{AA}^{(x-1)} (1 - p_{AA}) = \frac{1}{1 - p_{AA}} \quad (6)$$

where F_{AAA} , $F_{AAM/MAA}$ and F_{MAM} are the mole fraction of the AN-centered triads. p_{AA} represents the probability of the formation of AA dyads from radical A. p_{AA} is obtained from equations (1)–(3) using the least square method. $(p_A)_x$ is the probability of a specific AN sequence with x units, and $(F_A)_x$ is the corresponding number fraction. $\langle N_A \rangle_n$ is the number-average sequence length of monomer A. The chemical compositions, triad fractions, average AN sequence number and sample abbreviations are listed in Table 1. The normalized AN fraction of AN sequences in PAN copolymers are plotted in Fig. 2.

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