



Effect of controlled tacticity of polyacrylonitrile (co)polymers on their thermal oxidative stabilization behaviors and the properties of resulting carbon films



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ABSTRACT

Due to the spatial alignment of the nitrile groups and their involvement in the cyclization reactions during thermal oxidative stabilization (TOS) procedures, stereoregularity of polyacrylonitrile (PAN) precursors is one of the most important structural parameters to afford carbon materials. To elucidate this, PAN and poly(acrylonitrile-co-itaconic acid) with higher degree of isotacticity were prepared through template-assisted free-radical polymerization in the presence of $MgCl_2$. Fourier-transform infrared spectroscopy was employed to quantitatively track the structural evolutions of the PAN (co) polymer precursors during their TOS procedures. The improved TOS efficiencies of the precursors were evidenced by high extents of cyclization, high concentrations of cyclized rings and enhanced oxygen uptakes of the isotactic PAN (co)polymers during the TOS procedures. The isotactic PAN (co)polymer precursors also exhibited relatively large heat evolutions with broad exothermic curves in differential scanning calorimetry observations, further suggesting efficient TOS procedures with safer processing conditions. The efficient TOS procedures of the isotactic PAN (co)polymer precursors resulted in carbon materials with high degrees of crystallinity and high amounts of sp^2 clusters, affording much improved electrical conductivities. This study provided knowledge on the structural characteristics of the precursors for carbon materials with pre-designed properties, which is critical for their success in high-end applications.

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1. Introduction

The demand for carbon materials is ever increasing due to their superior performances in numerous applications [1,2]. Since the 1960s, polyacrylonitrile (PAN) has been recognized as one of the most important precursors for the preparation of carbon materials [3]. Today, approximately 90% of the carbon fibers (CFs) manufactured worldwide are derived from PAN-related precursors [2,4,5]. Advanced carbon materials from PAN-related precursors, such as nanostructured carbon [6–9], porous carbon [10–12] and carbon films [13,14], have also been widely reported for energy and electronic applications. The wide acceptance of PAN as the main framework for the precursors is owed to its relatively high carbonization yield, highly tunable properties, and cost-effective production [2,15].

The characteristics of the PAN (co)polymer precursors are important for the production of carbon materials, particularly for their behaviors during thermal treatment procedures including thermal oxidative stabilization (TOS), carbonization and graphitization. To improve their behaviors during production, acrylonitrile (AN) is often copolymerized with other polar comonomers, such as methyl acrylate, acrylic acid, or itaconic acid (IA) [16,17]. Typical PAN copolymer precursors contain 93%–95% of AN units, and the remaining percentage is made up of one or more other comonomers. These comonomers disrupt the ordered nitrile-nitrile interactions and chain structure of PAN, resulting in a higher solubility of the copolymers in solvents, allowing for more-desirable macromolecular chain orientations, and ensuring high structural homogeneity of the stabilized and carbonized products. These effects ultimately produce carbon materials with improved characteristics [4,18–20]. Among the comonomers used with the PAN copolymers, the most effective comonomer is IA, likely due to the two carboxylic acid groups in its structure [17,21].

Due to the spatial alignment of the nitrile groups and their

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essential involvement in the cyclization reaction of the TOS, the stereoregularity of the PAN (co)polymer precursors is also considered a crucial factor (Fig. 1) [22]. However, the effect of the stereoregularity of the PAN on their TOS behaviors has been debated. Huang claimed that the stereoregularity of PAN was not important because of a rapid isotope-exchange reaction at elevated temperatures [23]. In contrast, Kubasova et al. reported isotacticity with a reduced induction time during the TOS of PAN [24,25]. Chand also demonstrated increased efficiency of the TOS process of isotactic PAN (i-PAN), yielding a high-performance CF [1]. Through the evaluation of kinetic parameters during the thermal treatments, the activation energy of i-PAN was also found to be lower than that of atactic PAN [26,27]. Furthermore, study on the stabilization and carbonization behavior of stereoregular copolymer has been limited, probably due to the challenging preparation procedures in the presence of the polar comonomers [1].

Although free-radical polymerization (FRP) is one of the most common methods for the preparation of PAN, the control over the stereochemistry of the polymer chains through FRP is difficult. Polymerization of the AN group in the presence of Lewis acids or salts of Lewis acids is reported to afford PAN with improved stereoregularity [28,29]. Solid-phase polymerizations for the stereoregular (co)polymerization of AN and/or IA were also reported using hexagonal crystalline metal salts [30], urea canals [31,32] or zeolites [33] as templates. The properties of i-PAN, such as solubility [34], crystallinity [31] and mechanical relaxation behaviors [35] have been studied.

In our previous reports, we have demonstrated the quantitative tracking of structure evolutions during the TOS process of the (co) polymers using Fourier-transform infrared spectroscopy (FT-IR) and peak-deconvolution/curve-fitting operations [36,37]. Controlling the IA content in the PAN copolymer was suggested to achieve better TOS efficiency [37]. PAN copolymers with blocky architectures or controlled distributions of IA were also proposed to afford better TOS and carbon properties [36].

In this study, our characterization procedures were expanded to the TOS of i-PAN and isotactic poly(acrylonitrile-co-itaconic acid) (i-PAI) for better understanding of the effects of the stereoregularity on TOS. Preparations of the PAN (co)polymers with controlled isotacticity were carefully performed through a template-assisted FRP in the presence of a Lewis acid. In addition to the carbonization behaviors of the isotactic precursors, the properties of the

resulting carbon materials were also carefully investigated. Through this study, an in-depth understanding and guideline for selecting optimized PAN-based precursors were provided for the preparation of carbon materials in high-end applications.

2. Experimental

2.1. Materials

AN (99%, Aldrich, St. Louis, MO, USA) was dried over CaH_2 , distilled under reduced pressure and stored in a freezer under nitrogen before use. IA (99%, Aldrich, St. Louis, MO, USA), 2,2-azobisisobutyronitrile (AIBN, 98%, Aldrich, St. Louis, MO, USA), dimethyl sulfoxide (DMSO, 99%, Aldrich, St. Louis, MO, USA), *N,N*-dimethylformamide (DMF, 99.8%, Aldrich, St. Louis, MO, USA) and magnesium chloride (MgCl_2 , 99.9%, 10 mesh, Alfa Aesar, Ward Hill, MA, USA) were used as received. All other chemicals and solvents were also used without further purification.

2.2. Preparation of i-PAN and i-PAI

The polymerization was conducted under a nitrogen atmosphere in a three-neck round-bottom flask, equipped with a reflux condenser and mechanical stirrer. For the preparation of the isotactic (co)polymers, hexagonal crystalline MgCl_2 was added as a Lewis acid template during the polymerization [22]. The molar ratio of the monomer to crystalline MgCl_2 was maintained to be 0.5 to yield an optimal coordination of AN to the metal salt. A representative polymerization procedure for the preparation of the isotactic (co)polymers was as follows: desired amounts of degassed AN (5.0 g, 9.4×10^{-2} mol), AIBN (0.147 g, 8.95×10^{-4} mol) and IA (0.758 g, 5.82×10^{-3} mol, in case of the preparation of i-PAI) were added to the flask containing MgCl_2 (17.94 g, 0.188 mol) at 0–5 °C. The flask was aged under nitrogen at 25 °C overnight to allow the monomers to form a coordination complex with MgCl_2 . Solid-state polymerization on the surface of MgCl_2 was then carried out by keeping the reaction mixture in a circulating oven at 70 °C for 8 h. After the polymerization, the resulting polymer was precipitated under excess amounts of water. The polymer powder was recovered by filtration and washed repeatedly with deionized water and methanol, followed by a Soxhlet extraction using boiling methanol for 8 h. The obtained polymer was then dried under vacuum at 60 °C and stored in a refrigerator in the absence of light. Separately, atactic PAN and poly(acrylonitrile-co-itaconic acid) (PAI) were prepared through a free-radical solution polymerization in DMSO at 70 °C with AIBN as the initiator, as described in our previous reports [36,37].

2.3. TOS and carbonization procedures

The film samples for TOS and carbonization studies were prepared separately in different conditions to meet the requirements of each study. To track the TOS process, the polymer films were first prepared by casting the corresponding polymer solutions (3%) in DMSO on glass plates. The solvent was evaporated by heating the samples at 80 °C for 5 min. The resulting polymer films were peeled off of the glass plates under water and washed with methanol to remove the remaining DMSO. The polymer films (2 cm × 2 cm × 20 μm) were subsequently transferred to an alumina frame and dried at 60 °C under vacuum. TOS procedures of the films were performed through isothermal heating at 220 °C in static air. The films were removed from the furnace at timed intervals for FT-IR (Thermo Nicolet 380) analyses. Each sample was analyzed by FT-IR in transmission mode at 64 scans at a resolution of 4 cm^{-1} . The detailed procedure of peak-deconvolution/curve-

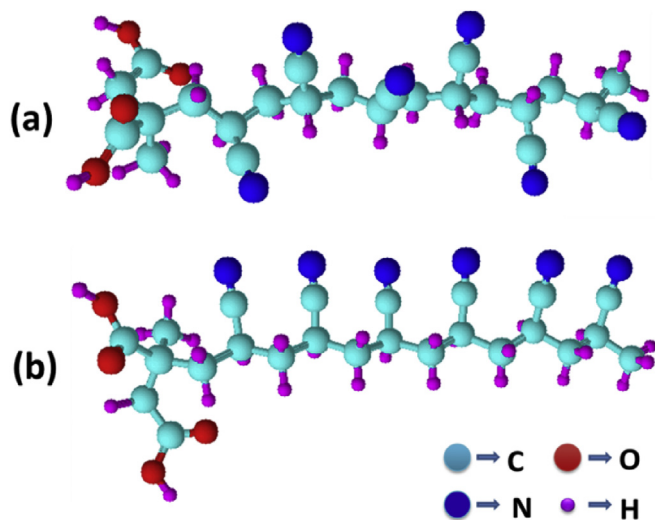


Fig. 1. Representative 3D ball and stick structures of atactic PAI (a) and i-PAI (b). (A colour version of this figure can be viewed online.)

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