



# Thermo-oxidative stabilization of polyacrylonitrile and its copolymers: Effect of molecular weight, dispersity, and polymerization pathway

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## ABSTRACT

Careful control of polyacrylonitrile (PAN) precursor properties and, in particular, the polymerization method and ensuing molecular weight and molecular weight distribution are important considerations for mitigating defects and enhancing processability of carbon fibers. Herein, a comprehensive study was performed to understand the influence of molecular weight, molecular weight distribution, and polymerization method between reversible addition-fragmentation chain transfer (RAFT) and conventional free radical (FR) solution polymerization on the cyclization behavior and structural evolution of stabilized PAN. The kinetic parameters of activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) were determined along with the cyclization index (CI) by differential scanning calorimetry (DSC) and the extent of stabilization ( $E_s$ ) was measured via fourier transform infrared spectroscopy (FTIR). Thermogravimetric analysis (TGA) was used to determine the degradation differences in the polymers. Structural characterization was performed by wide-angle X-ray scattering (WAXS). DSC and FTIR analysis indicate that cyclization initiates at lower temperature for FR polymers. Significantly, PAN-based RAFT copolymers show greater mass retention post thermo-oxidative degradation as compared to analogous FR copolymers.

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## 1. Introduction

Polyacrylonitrile (PAN) is the leading precursor material for carbon fiber production in industry and, in particular, yields the highest tensile strength in comparison to pitch and cellulose-based carbon fibers [1,2]. Traditionally, PAN is synthesized via uncontrolled free radical polymerization in an emulsion or solution leading to atactic polymers with broad dispersities and a small degree of branching. Typical carbon fiber precursors range between 70,000 and 200,000 g/mol with dispersities ( $D_M$ ) ( $M_w/M_n$ ) between 2 and 3 [2]. High molecular weight fractions can cause issues during fiber spinning and filtration such as gelation and insolubility [3]. In the carbon fiber manufacturing process, molecular weight and its distribution govern final carbon fiber properties [4–6]. Increasing molecular weight leads to increased crystallite size and smaller void sizes as well as changes in the fiber morphology [4,7].

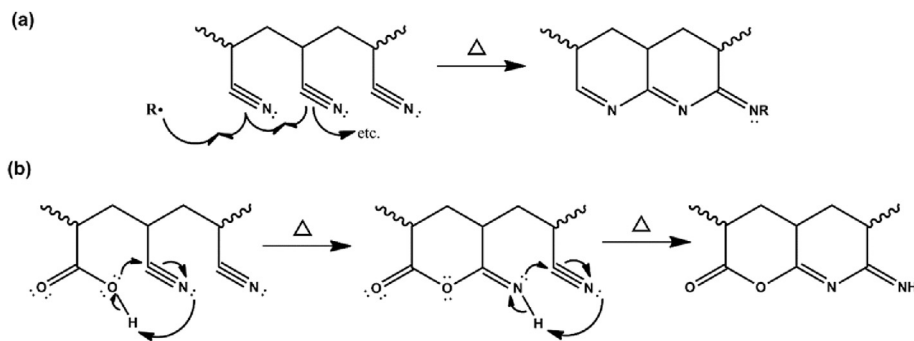
Moreover, increasing molecular weight has been shown to influence which small volatiles are released during thermo-oxidative stabilization of PAN-based precursors [8].

The cyclization of PAN into ring-closed ladder structures at temperatures above 200 °C is recognized as one of the most important prerequisites for high performing carbon fiber (Scheme 1) [1], wherein the homopolymer cyclizes according to a well-established free radical mechanism while addition of acidic comonomers introduces an ionic route for cyclization [9,10]. However, the effect of molecular weight and its distribution on the cyclization of PAN remain unresolved in the literature. Tsai et al. claim that cyclization onset temperature increases with higher molecular weight, but samples in their study had high dispersity ( $D_M$ ) (>1.8) [4]. Chernikova et al. asserted the same finding for a series of low molecular weight samples (<3000 g/mol), yet cyclization exotherms yielded several unresolved and overlapping peaks [6]. Other reports in the literature make similar claims [7], but lack hard evidence due to unreported dispersities or conflicts within the data.

Equally important to molecular weight is the polymerization mechanism. Solution polymerization is favorable due to immediate

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**Scheme 1.** Cyclization of PAN (a) homopolymer and (b) copolymer with acrylic acid.

manufacture of spinning dopes [11,12]. The two main drawbacks to solution polymerized precursors are that monomer conversion is typically only 50–70%, and that conventional solvent systems are characterized by high transfer constants leading to undesirable side reactions during polymerization [11]. It has been demonstrated that an emulsion polymerization at low temperature (22 °C) led to a smaller proportion of long chain branches than solution polymerization at higher temperature (50–60 °C), even though the solution-formed polymer had a narrower dispersity [13]. Long chain branches present in conventional free radical solution polymers hinders reputational motion of the macromolecule. Therefore, polymerization mechanism must be taken into consideration when evaluating precursor properties.

Although studies have shown that there is a molecular weight dependence on the formation PAN-based carbon fibers [6–8], it is not clear how dispersity and molecular weight affect the cyclization temperature, the extent of cyclization, and the structural changes that occur through the stabilization phase of PAN-based carbon fibers. This prompted our investigation into the thermo-oxidative stabilization of PAN of varying molecular weights and dispersities. Recently, we have demonstrated the synthesis of controlled PAN with absolute number average molecular weights exceeding 130,000 g/mol and dispersities below 1.30 via reversible addition-fragmentation chain transfer (RAFT) polymerization [14]. Herein, we compare the cyclization behavior of RAFT polymers with narrow molecular weight distributions to conventional free radical polymers with broad dispersities. Significantly, PAN-based RAFT copolymers demonstrate promising characteristics such as increased thermo-oxidative stability, which could lead to the development of carbon fibers based upon controlled polymerization techniques.

## 2. Materials and methods

### 2.1. Materials

Acrylonitrile (AN, 99%, 35–45 ppm monomethyl ether hydroquinone inhibitor, Sigma–Aldrich Chemical Co.) was passed through a neutral aluminum oxide (50–200 μm) column to remove the inhibitor. Ethylene carbonate (EC, 98%, Sigma–Aldrich Chemical Co.), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%, Sigma Aldrich Chemical Co.), N-isopropylacrylamide (NIPAM, 99%, Sigma Aldrich Chemical Co.), 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd.), 2,2'-asobis(isobutyronitrile) (AIBN, 98%, Sigma Aldrich Chemical Co.), and N,N-Dimethylformamide (DMF, 99%, Sigma Aldrich Chemical Co.) were used as received. Acrylic acid (AA, 99%, 180–200 ppm MEHQ inhibitor) was vacuum distilled to remove inhibitor.

### 2.2. Conventional free radical polymerization

A typical solution polymerization was as follows: ethylene carbonate (32.0 g), acrylonitrile (7.99 g, 151 mmol, 20 wt. %), and V-70 (9.5 mg, 0.031 mmol, stock solution in tetrahydrofuran (THF) 20 mg/mL) were charged to a 100 mL round bottom flask equipped with a magnetic stir bar. The flask was capped with a rubber stopper and placed in an ice bath and subsequently purged for 1 h under nitrogen gas before being transferred to an oil bath set to 30 °C for 8 h. When AIBN was used as the initiator the oil bath was set to 65 °C (the equivalent initiator 10 h half-life temperature). The polymer was precipitated into a 1 L bath of approximately 70:30 (v:v) deionized water and methanol followed by isolation via filtration and allowed to dry for 30 min under nitrogen. The polymer was then re-dissolved in dimethylformamide (DMF) at 20 to 25 weight percent polymer, and the solution poured over a flat surface and allowed to spread into a film. The film was coagulated by soaking in deionized water for 3–4 h followed by a 24 h Soxhlet extraction in methanol to remove residual solvent. The polymer was then dried in a vacuum oven at 60 °C overnight.

### 2.3. RAFT polymer synthesis

A typical RAFT polymerization for a molar ratio of  $[AN]_0:[CPDT]_0:[V-70]_0 = 10,000:1:0.67$  was as follows: ethylene carbonate (32.0 g), acrylonitrile (7.99 g, 151 mmol, 20 wt.%), CPDT (5.2 mg, 0.015 mmol, stock solution in dimethylformamide (DMF) 20 mg/mL), and V-70 (3.1 mg, 0.010 mmol, stock solution in tetrahydrofuran (THF) 20 mg/mL) were charged into a 100 mL round bottom flask equipped with a magnetic stir bar. The flask was capped with a rubber stopper and placed in an ice bath and subsequently purged for 1 h under nitrogen gas before being transferred to an oil bath set to 30 °C for 24 or 48 h. Polymers were precipitated in and dried in the same manner as the uncontrolled free radical polymers. Theoretical number average molecular weights,  $M_{n,theor}$ , were determined by Equation (1) [15]:

$$M_{n,theor} = \frac{M_{MW} \cdot [M]_0 \cdot conversion}{[CTA]_0} + CTA_{MW} \quad (1)$$

where  $[M]_0$  and  $[CTA]_0$  correspond to the initial monomer and chain-transfer agent concentrations, respectively.  $M_{MW}$  and  $CTA_{MW}$  correspond to the molecular weights of the monomer and chain-transfer agent, respectively.

### 2.4. Oxidation treatment

To simulate industrial processing techniques, polymer films were subjected to an oxidation treatment in a programmable oven.

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