

A photocrosslinkable melt processible acrylonitrile terpolymer as carbon fiber precursor

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Abstract

A novel photocrosslinkable and melt processible terpolymer precursor for carbon fiber has been successfully synthesized and characterized. The terpolymer was synthesized by an efficient emulsion polymerization route and has a typical composition of acrylonitrile/methyl acrylate/acryloyl benzophenone in the mole ratio, 85/14/1. It has been characterized by FTIR, NMR, intrinsic viscosity and GPC molecular weights. The composition of the monomer repeat units in the terpolymer was determined by NMR, and was almost identical to the molar feed ratios of the monomers used for polymerization. The T_g of the terpolymers, were somewhat a function of molecular weight, but were in the range 77–91 °C. The fibers were spun from the terpolymer melts unlike the conventional solution spinning method. The terpolymers when stabilized with boric acid afforded a stable melt for about 30 min at 200–220 °C, which was empirically found to be sufficiently long to spin fibers. The terpolymer with the highest molecular weight (M_n , ~48,000) was not melt processible, apparently because the melt viscosity was very high and the terpolymer degraded fast. However, terpolymers, which had an intrinsic viscosity <0.6 dL/g (NMP, 25 °C) were invariably melt processible. The initial carbon fibers produced from these terpolymer fibers upon complete carbonization exhibited good mechanical properties for proposed automotive applications; the tensile strength of the best fibers generated thus far was in the range 450–700 MPa with a strain to failure of ~0.4%. The diameter of the carbon fibers was of the order of 7 μm.

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1. Introduction

Development of lightweight and high-strength polymer matrix carbon fiber composites suitable for automotive applications is one of the thrust areas of contemporary applied polymer research. Reduction in the cost of carbon fibers is required to expand their use from the current high tech applications, e.g. aerospace and military, to more high volume markets like general-purpose automotive composites [1]. It is appropriate to briefly discuss the basic chemistry involved in the currently used technology of making carbon fibers and their melt processible precursors, and how can it be amended to obtain more cost effective carbon fibers.

The commonly used precursors for making carbon fibers are the acrylic fibers used in textile applications [2]. Chemically, these fibers are copolymers of acrylonitrile (AN) with about 3 mol% of other comonomers. The comonomers include 3–4 mol% of methyl acrylate (MA), vinyl acetate, etc. which induce solubility in the commonly used fiber spinning solvents like dimethyl formamide, and 1–2 mol% of acidic comonomers like acrylic acid or itaconic acid [2,3], which help in dyeing the fibers. A carefully controlled thermal treatment in stages brings about the metamorphosis of these textile fibers into carbon fibers [3]. The important steps of this process are termed stabilization and carbonization.

In the stabilization step, the polymer fiber is typically heated at 200–250 °C for 5–10 h in the presence of air. Consequently, the polymer containing predominantly AN units is converted from a linear structure to a ladder like structure via the intramolecular cyclization of the pendant CN groups and intermolecular crosslinking. This process is believed to occur both intra- and inter-molecularly, and competes with the polymer degradation and crosslinking reactions that take place

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simultaneously [2]. Nevertheless, an acceptable yield and quality of the stabilized fibers is achieved by operating at the right temperature and amount of oxygen [2,3]. In the next step, the stabilized fibers are carefully heated in an inert atmosphere at >1000 °C for a few hours, to remove all the non-carbon elements and to obtain a carbon fiber that has at least 97% carbon content. Hence, this step is described as carbonization. The different grades of carbon fibers are characterized by their carbon content and have different mechanical properties, notably, the tensile modulus [1,2]. The textile fibers are spun from relatively dilute solutions at mild temperatures. Presence of solvent allows (i) use of low spinning temperatures that prevent premature cyclization/crosslinking (ii) formation of very fine fibers with uniform diameter of the order of 20 μm that are critical for successful stabilization and (iii) overcomes the pseudo crystallinity [4] present in these high acrylonitrile containing fibers.

For making cost effective carbon fibers, therefore, the common approach adopted by various research groups including our laboratory [5–8] is to replace the solvent spinning process by a melt spinning process. Melt spinning requires precursors of good thermal stability but the increased thermal stability may only be obtained with a decrease in certain mechanical properties [9]. The increased thermal stability may only be obtained at the price of loss of certain mechanical properties [9]. The task of reducing the cost of carbon fiber is very challenging [10] not only because of this tradeoff, but also because the chemistry of processible precursors is poorly understood. Hence, there is a need to study the design of the melt processible carbon fiber precursors, with the objective of achieving reasonable thermal stability without missing the important mechanical characteristics. However, it has been noted in studies from our laboratory [5,11] that copolymers containing >90 mol% AN do not truly melt, and hence exhibit very high melt viscosity. Copolymers containing 85–90 mol% AN have melt viscosity in the processible range of 100–1000 Pa s at 220 °C; beyond which they start to thermally degrade [12]. The much higher content of comonomer (10–15 mol%) reduces or eliminates the melting point and hinders the cyclization of the CN groups responsible for the stabilization process. The net effect is the lowering of the mechanical properties of the copolymers containing lower amounts of AN, which may undesirably promote fiber fusion during the stabilization step rather than undergoing cyclization or cross-linking. To circumvent this problem it was thought worthwhile to marginally crosslink the fibers before stabilization. This can be achieved by electron beam irradiation or UV induced cross-linking [13]. It was, therefore, proposed to use a carefully selected UV-sensitive comonomer to afford terpolymer precursors having reasonable mechanical strength prior to stabilization.

In continuation of the AN-copolymers work [14] from our laboratory, in the present study, the design and synthesis of AN terpolymers containing MA as the major comonomer and acryloyl benzophenone, ABP (<1 mol%) as the minor comonomer intended for assisting in the UV induced cross linking is discussed. The choice of the major comonomer was

based on a study of the reactivity ratios of AN and MA, which showed that both these monomers make an excellent pair for copolymerization [14a]. The emulsion polymerization route was adopted for the synthesis of the terpolymer; the choice of the route was made following a systematic study of the possible methods of polymerization, in our laboratory [10,15,16]. Structural characterization and thermal analysis of the copolymers are reported. Both dynamic and steady shear viscosities have been studied to assess the suitability of these copolymers as melt-processible carbon fiber precursors.

2. Experimental

2.1. Materials

The monomers, AN and MA were obtained from Aldrich and used as received. ABP was synthesized using a reported procedure [17]. The chain transfer agent, 1-dodecanethiol and boric acid were also obtained from Aldrich. MgSO_4 and the initiator ammonium persulfate were obtained from EM Sciences and used as received. DOWFAX 8390 solution surfactant was obtained from The Dow Chemical Company.

2.2. Copolymer synthesis

The terpolymer synthesis was carried out in aqueous medium via an emulsion polymerization route as described below.

A 250 mL reaction flask fitted with a condenser, glass stirrer, nitrogen inlet tube and thermocouple probe was purged with nitrogen and was charged with 50 mL water containing the surfactant (2.07 g). A premix of the monomers (2.5 mL, 10% of the total) and the mercaptan (0.5 g) were added followed by the initiator (17 mg in 10 mL water). The temperature was raised to 60 °C and the remaining monomer mixture (AN, 20.5 g, MA, 5.48 g and ABP, 1.15 g) was added over a period of 2 h. At the end of addition of the monomer mixture, an extra quantity of initiator (10 mg in 10 mL water) was added through the condenser. The latex was held at 60 °C for an additional 30 min. The product was isolated by precipitation with 500 mL 1% aqueous MgSO_4 at 65 °C. The terpolymer was vacuum dried at 70 °C for 24 h (recovered yield, 85%).

2.3. Characterization

The IR spectrum was recorded using a Nicolet FTIR spectrometer. ^1H NMR spectrum was obtained with a Varian UNITY 400 MHz spectrometer using $\text{DMSO}-d_6$ as solvent. The intrinsic viscosity (IV) measurements were performed in *N*-methyl pyrrolidone (NMP) at 25 °C using a Cannon Ubbelohde viscometer. The melt viscosity was measured using a RMS 800 Dynamic Spectrometer. A steady shear frequency sweep was employed to determine the melt viscosity, and a time sweep was used to determine the stability of the polymer melt over a time of 30 min at 220 °C. Differential scanning calorimeter (DSC) was used to determine

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