Polymer Degradation and Stability 128 (2016) 149–157

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Effects of gamma ray irradiation on poly(acrylonitrile-co-methyl acrylate) fibers

Liangxiao Zhou [a], Yonggen Lu [a, *], Weizhe Zhao [a], Changling Yang [b], Junqi Jiang [a]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China
[b] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form
26 November 2015
Accepted 21 December 2015
Available online 24 December 2015

Keywords:
PAN fibers
Gamma ray
Crosslink
Scission
Heat treated

ABSTRACT

Gamma ray irradiation on PAN fibers did bring some benefits for the successive stabilization, however, it is still unclear about the structure of crosslinked bonds, effects of atmosphere and chain scission as well as initiation of cyclization. In this work, PAN fiber as well as a PAN solution was irradiated under different atmospheres. The structure of crosslinked bonds, molecular weights and thermal reactivity were analyzed. It is discovered that gamma ray irradiation on PAN brought chains crosslinking and scission as long as cyclization. The large amount of crosslinked bonds were discovered to be −C═N−N═C−, while oxygen inhibited nitriles crosslinking. The crosslinking structure rather than remained radicals initiated cyclization during thermal treatment, which was broken and reproduced polyimine radicals at higher temperature.

1. Introduction

The stabilization of polyacrylonitrile (PAN) fibers before carbonization is very important for the manufacture of carbon fibers [1]. In order to reduce the defects and ameliorate the process of stabilization, many attempts have been made ranging from chemical to physical modification. With regard to physical modification, prevalent researchers have introduced various kinds of high energy irradiation on the precursors, such as gamma ray [2–7], electronic beam [8], UV [9], laser [10], etc.

Due to its most powerful penetrability, gamma ray has been paid extensive attention on the treatment of PAN fibers in recent years. The possible changes during the irradiation could be cyclization of nitrile groups, crosslinking and chain scission, along with radicals' generation and conversion, thus transformation of radicals needs to be investigated. Irradiating PAN powder in vacuum at 77 K, Hill [7] found that gamma ray irradiation brought alkyl radicals and polyimine radicals, and during annealing at low temperature (<300 K), alkyl radicals would transform to polyimine radicals. Nevertheless, a different conversion that alkyl radicals could transform into polyene radicals was deduced by Zhao [5], who irradiated PAN film in vacuum, at room temperature. Liu [11–13] investigated the effect of irradiation under both air and vacuum atmospheres on PAN fiber at room temperature. Two kinds of radicals, alkyl and polyimine, were found, and polyimine radicals were more stable than alkyl radicals. In vacuum, more radicals were produced than in air.

Many researchers confirmed cyclization took place in PAN during irradiation. Shrinkage of PAN fiber under gamma irradiation was found by Tarakanov, who irradiated PAN fibers in air, at 293 K, which was viewed as influence of cyclization. Irradiating PAN powder in air at room temperature, Tan [3] studied chemical structure of PAN by FTIR spectra after irradiation, and found nitrile groups decreased while carbon-nitrogen double bonds (−C═N) increased. Besides this, the researcher reported that irradiated PAN fiber had less shrinkage caused by cyclization during heating process at higher temperature (>200 °C), because cyclization has partly taken place during irradiation. In our previous work [2], PAN fiber irradiated in air had less heat release during stabilization and sulfuric acid insoluble was less than dimethylsulfoxide (DMSO)'s, which verified the producing of cyclization of PAN during irradiation.

The existence of crosslinking was confirmed by Tarakanov who studied the thermomechanical performance of PAN fibers irradiated at different doses and found that irradiation restrained the elongation of PAN fiber. Verifying in the other side, Liu [11] tested

* Corresponding author.
E-mail address: yglu@dhu.edu.cn (Y. Lu).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.12.015
0141-3910/

gel fractions by measuring DMSO insoluble of PAN irradiated with different gamma ray doses and found that the gel fractions increased as irradiation doses accumulated, by which they concluded crosslinking generated by the irradiation. However, the DMSO insoluble can't distinguish crosslinking from cyclization. So by comparing deviation about insoluble of DMSO and sulfuric acid, we testified the crosslinking and cyclization taking place by irradiation under air [2].

There are two assumptions about the structure of crosslinked bonds, carbon–carbon bonds (–C–C-) and nitrogen–nitrogen bonds (–C═N–N═C-). Hill [7] deduced the crosslinked bonds to be –C–C(═NH)–C formed by alkyl radicals combining with nitrile groups. Miao [8] irradiated PAN powder in nitrogen at room temperature using electron beam, and surmised the crosslinked bonds to be conjugated carbon-nitrogen double bonds (–C═N–N═C-) characterized by FITR. However, as N–N bonds have no absorbance in FTIR spectra, the testification is insufficient. As regard of scission of PAN molecular chains, Hill [7] tested the sol-gel fraction of irradiated PAN, DMSO as solvent, and concluded PAN crosslinked with negligible scission according to Charlsby–Pinner equation. However, cyclization other than crosslinking and scission would influence the insoluble, so the conclusion is quite unsure.

The extensive attention on irradiation of PAN fibers is aroused by the expectation that it could have some benefit to the stabilization. Tan [3] studied the thermal stability of PAN fiber after irradiation and found that the initial temperature of cyclization reaction reduced, and the residue increased. Many researchers also noticed the phenomenon, and gave their conjecture about the mechanism of cyclization in irradiated PAN fibers during thermal treatment. Holding different views about the conversion of radicals in irradiated PAN fibers during annealing, Hill [7] and Zhao [5] arrived at different conclusions about the initiator of cyclization of PAN during stabilization. Hill [7] considered polyimine radicals as the initiator of cyclizaion, which were produced both directly in irradiation and conversion of alkyl radicals during annealing, while Zhao [5] deemed polyene radicals as final products of conversion of alkyl radicals during annealing and initiated cyclization. However, no matter which kinds of radicals, would extinguish before the fiber was heated to stabilization temperature (usually above 170 °C).

So far, the understanding about the effect of irradiation on the structure of PAN fibers and the successive stabilization has reached a certain depth. Existence of cyclization and crosslinking of PAN during irradiation has reached wide consensus. However, there are still some points unclear. First, what is the structure of the crosslinked bonds and how dose oxygen influence on the crosslinking? Second, whether the irradiation makes chain scission or not? Third, what kinds of structure initiate the cyclization during stabilization, original radicals produced by irradiation or other active centers?

In this work, PAN fiber was irradiated both under air and in vacuum. The gel fractions and the structure of crosslinked bonds of PAN produced by irradiation in vacuum and air were measured. In order to avoid crosslinking, a PAN solution was irradiated to testify the chain scission. The thermal reaction behaviors, the change of the radicals and the crosslinking structure during annealing and thermal treatment were investigated. Some mechanisms for crosslinking by irradiation and successive effects on cyclization are proposed.

2. Experiment

2.1. Materials

The PAN fibers were provided by one of domestic commercial carbon fiber precursor suppliers. The PAN films were prepared by coating 10 wt.% PAN/DMSO solution, and then drying at 80 °C in vacuum. The PAN films and fibers were encapsulated in vacuum glass tubes with pressure less than 0.01 MPa. The parameters about this precursor were list in Table 1.

2.2. Irradiation

These encapsulated, un-encapsulated PAN fibers, films and dilute PAN solutions were irradiated in gamma ray, derived from ^{60}Co, with dosage rate of 8.0 kGy/h. Through regulating irradiation time, five kinds of samples have been taken, with doses of 50, 100, 200, 300 and 400 kGy.

2.3. Annealing and thermal treatment

The annealing was carried out for the PAN fibers irradiated in vacuum with 400 kGy by heating the samples at temperatures of 100, 110 and 120 °C for 2 h, while the thermal treatment was carried out for the PAN fibers irradiated in vacuum and in air with 400 kGy by heating the samples at higher temperatures of 170, 190, 210, 230 and 250 °C for 2 h.

2.4. Characterization

2.4.1. Gel fractions analysis

The irradiated and annealed PAN fibers were dissolved in 75 wt.% H_2SO_4/H_2O for 24 h. The gels were washed for 10 min in 2 L water, then filtrated and dehydrated in vacuum freeze drier for 24 h. Due to partial hydrolysis of the nitrile groups (–C≡N) in PAN molecular, oxygen containing functional groups increased during dissolution, thus the derived gel mass was higher than that caused by crosslinking. We excluded the influence of hydrolysis, hydration and other causes of mass variation of the gels based on element analysis using element analyzer, Vario ELIII. Here, we consider the quantity of carbon atom as consistent. Therefore, the real gel fraction (Rg) was calculated according the (1),

$$Rg = \left(\frac{C_1}{C_0} \times \frac{W_1}{W_0}\right) \times 100\% \quad (1)$$

where C_1 and W_1 represent carbon content and weight of dry gels, and C_0 and W_0 represent carbon content and weight of fibers before dissolution.

2.4.2. UV and FTIR spectra analysis

The Fourier transform infrared spectra of PAN films have been measured by FT-IR spectrometer, Nicolet 8700. The PeakFit, a peak separation and analysis software, was utilized to study the changes of the chemical functional groups. The conjugated double bonds were characterized by UV visible spectrophotometer, Lanbda A35.

2.4.3. Molecular weight analysis of the PAN in irradiated dilute PAN solutions

The PAN in the irradiated dilute solutions was precipitated with deionized water and dried in vacuum. The molecular weight was measured by Ubbelohde viscosity and cryoscopic methods. The Ubbelohde viscosity was measured in the usual way while the cryoscopic method was carried out as follows. The dry powder was weighted for 0.088 g precisely to be dissolved into 22 ml DMSO. An ice-water bath kettle keeps circumambient temperature of solution at 0 °C. The situ temperature of solution was recorded by a high sensitive thermometer. The undercooling point on the temperature-time curve was chosen as the freezing point. After comparing with freezing point of pure DMSO, freezing point decrease of every sample was calculated. Since the molar concentration of the solute is proportion to the freezing point decrease of