Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Synthetic Metals 153 (2005) 165–168
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Zone-reacted poly(*p*-phenylene vinylene) films. Changes in mechanical properties and microstructure by acid doping

H. Okuzaki*, N. Ikeda, I. Kubota, T. Takahashi

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-4-37 Takeda, Kofu 400-8511, Japan

Abstract

The doping of highly oriented poly(*p*-phenylene vinylene) films prepared by the zone-reaction method was performed with various acids, HCl, H_2SO_4, and H_3PO_4. The changes in the microstructure, electrical, tensile, and viscoelastic properties of the resulting films were studied. It was found that the doping of HCl and H_2SO_4 increased the electrical conductivity to 186 and 61 S cm^{-1} at the doping time of 6 and 1.5 h, respectively. A further doping, however, lowered the conductivity, which was associated with the relaxation of molecular orientation. The zone-reacted film doped with HCl preserved Young's modulus and tensile strength as high as 44.7 and 0.73 GPa, where dynamic storage modulus was 49 GPa at 25°C and held 21 GPa at 400°C.

Keywords: Tensile drawing; Semiconducting films; Poly(phenylene vinylene) and derivatives

1. Introduction

Poly(*p*-phenylene vinylene) (PPV) and its derivatives have attracted considerable attention because of their potential applications in electrical and optical devices, such as light-emitting diodes [1] or solar cells [2]. It is of great importance to produce high-performance PPV not only for the practical use but also for approaching the intrinsic mechanical and electrical properties. Karasz et al. prepared high-performance PPV films by uniaxial stretching/annealing method, in which Young's modulus and tensile strength reached 40 and 0.5 GPa, respectively [3]. We have previously developed the zone-reaction method capable of orienting the molecular chains simultaneously with thermal reactions, and applied it to the PPV precursor films [4]. It was found that the zone-reacted PPV film had extremely high orientation of molecular chains in the drawing direction with Young's modulus and tensile strength as high as 69 and 1.3 GPa, respectively. To the knowledge of the authors, however, there are few reports on mechanical properties of PPV in the doped state though the doping gives rise to the structural change of polymer chains as well as the dimensional change of the specimen. The present paper deals with the study on doping of the high-modulus and high-strength zone-reacted PPV films with various acids, HCl, H_2SO_4, and H_3PO_4, and changes in the microstructure, electrical, tensile, and viscoelastic properties of the resulting films are investigated.

2. Experimental

2.1. Preparation and doping of zone-reacted PPV film

PPV precursor was synthesized by polymerization of *p*-xylenebis(dietylsulfonium chloride) using the method of Karasz et al. [5]. The precursor film was prepared by casting the solution on a glass plate and allowing it to solidify by evaporation of solvent at 50°C for 12 h. Zone drawing and zone reaction were performed with a tensile tester where a narrow band heater (2 mm thick) was placed on its crosshead [6]. The film (40 mm long and 1mm wide) was suspended from the strain gauge of the tensile tester, and then the desired tension was applied to the lower end by mounting a dead weight. The zone heater was moved in the direction from lower to upper end at a constant speed of 20 mm min^{-1} in air. The doping was carried out by dipping the zone-reacted PPV film in concentrated HCl, H_2SO_4, or H_3PO_4 solutions at room temperature under a free loading condition. After doping, the film was soaked in a large amount of acetonitrile and dried under vacuum.

* Corresponding author. Tel: +81-55-220-8554; fax: +81-55-220-8554;
E-mail: okuzaki@yamanashi.ac.jp

0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.199

2.2. Measurement

The draw ratio was determined by measuring the distance between marks put on the surface of the film prior to drawing. The PPV content (α, defined as the ratio of PPV repeating unit, was evaluated by elemental analysis. The degree of crystallinity (X_c) was measured from wide-angle X-ray diffraction patterns, and orientation factor of crystallites (f_c) was evaluated by using the Wilchinsky method [7]. The apparent crystallite size normal to the (hkl) plane (D_{hkl}) was estimated from Scherrer's equation

$$D_{hkl} = \lambda / \beta \cos\theta_{hkl} \quad (1)$$

where λ, β, and θ_{hkl} were the wavelength of the CuKα beam (1.542 Å), the half-width of the diffraction peak in units of radians, and one half of the diffraction angle, respectively. The electrical conductivity was measured at 25°C by a normal four-probe method with a digital multimeter. The tensile properties were measured with a tensile tester, Tensilon II (Orientec Co. Ltd.), at a constant strain rate of 10% min^{-1} (chuck distance 20 mm, head speed 2 mm min^{-1}) under thermostatic conditions (25°C, 50% RH). Young's modulus, tensile strength, and elongation at break were calculated from the stress-strain curves and represented average values of at least ten tests. The dynamic viscoelastic properties, storage modulus and loss tangent, were measured with a dynamic viscoelastometer, VIBRON DDV-II (Orientec Co. Ltd.), under a frequency of 110 Hz over a temperature range from room temperature to 400°C at a heating rate of 2.5°C min^{-1} in a nitrogen atmosphere.

3. Results and Discussion

3.1. Zone-reaction

The zone-reaction method consists of two processes: zone drawing (ZD) and zone reaction (ZR). The ZD is carried out on the original precursor film at low heater temperatures (100-220°C) for the purpose of orienting the precursor chains. The ZR is subsequently performed on the ZD film at higher heater temperatures (220-280°C) and higher applied tensions aimed at converting the diethylsulfonium unit to PPV by elimination of diethylsulfide and hydrochloric acid simultaneously with further drawing. The optimization of heater temperature and applied tension for the ZD and ZR is described elsewhere [4]. The draw ratio, degree of crystallinity (X_c), crystallite size normal to the (110) plane of the monoclinic unit cell of the PPV crystal (D_{110}) [8], and orientation factor of crystallites (f_c) are significantly increased by the zone drawing, which demonstrates that the crystallites are highly aligned in the drawing direction and/or amorphous chains are changed into oriented crystallites. On the other hand, the PPV content (α) rises stepwise with the processes and reaches near 1 for the ZR film, indicating that the precursor unit is almost converted into PPV.

3.2. Changes in conductivity and structure by acid doping

The doping is performed by dipping the ZR film in various acid solutions at room temperature under a free loading condition, and time dependence of the electrical conductivity in the drawing direction is shown in Fig. 1. A rapid and significant uptake of HCl and H_2SO_4 occurs where the weight gain attains 38% and 164%, corresponding to the doping ratio of 1.1 and 1.7, respectively. On the other hand, H_3PO_4 is ineffective in doping. The doping with HCl and H_2SO_4 increases the electrical conductivity to 186 and 61 S cm^{-1} at the doping time of 6 and 1.5 h, respectively, which is considered as the oxidation of PPV to produce charge carriers where anions are intercalated between polymer chains as counter ions [9]. However, the doping of PPV with protonic acids has not been fully understood yet [10]. In fact, HCl is a strong protonic acid but non-oxidative. Han et al. have found that non-oxidizing protonic acids can be effective dopants for a wide range of conjugated polymers [11]. The mechanism of protonic acid doping appears to involve direct protonation of the polymer backbone followed by an internal redox process that gives polarons as the predominant charge defects, similar to polyaniline [12].

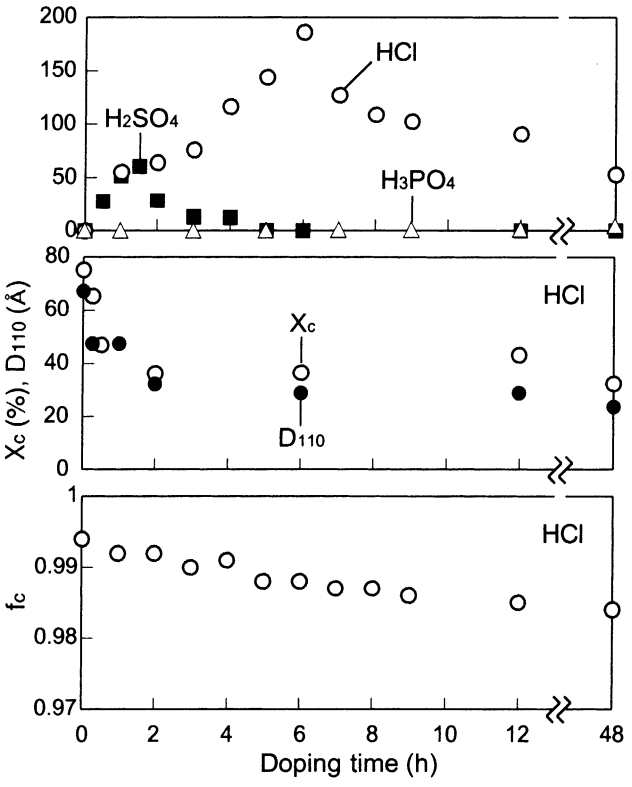

Fig. 1. Changes in electrical conductivity, crystallinity (X_c), apparent crystallite size normal to the (110) plane (D_{110}), and orientation factor of crystallites (f_c) for the ZR films doped with HCl, H_2SO_4, and H_3PO_4.