Polymer 40 (1999) 2625–2629

polymer

Mechanical properties and structure of zone-drawn poly(*p*-phenylene vinylene) films

Hidenori Okuzaki*, Yoko Hirata, Toshio Kunugi

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Yamanashi University, 4-3-11 Takeda, Kofu 400, Japan

Received 6 April 1998; revised 4 June 1998; accepted 25 June 1998

Abstract

The zone-drawing (ZD) method was applied to poly(*p*-phenylene vinylene) (PPV) precursor films under various applied tensions and heater temperatures. The ZD precursor films were successively converted to PPV by heat treatment, and the structure and mechanical properties of the resulting ZD-PPV films were investigated. It was found that the draw ratio, orientation function, crystallinity and apparent crystallite size of the ZD-PPV films were 8.0, 0.74, 65.2% and 47.5 Å, respectively. The mechanical properties were improved by the ZD, and the dynamic storage modulus of the ZD-PPV film reached 33.7 GPa at room temperature and held at 11.5 GPa even at 300°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*p*-phenylene vinylene); Zone-drawing method; High modulus

1. Introduction

Poly(*p*-phenylene vinylene) (PPV) has been paid considerable attention due to its properties, such as electrical conductivity [1,2], electro- or photoluminescence [3], and non-linear optical response [4], which have potential applications in electrical and optical devices. Moreover, PPV is expected to be a high-performance polymer with high modulus and high thermal stability [5], because of its rigid structure consisting of alternating phenylene and vinylene groups. However, little is known about the dynamic viscoelastic properties of PPV. The temperature dependence of the viscoelastic properties can provide us with information on dynamic and loss moduli, mechanical dispersion and thermal stability.

We have succeeded in preparing high-modulus and high-strength films and fibers from widely-used polymers, such as polyolefines [6], polyesters [7] and nylons [8], by the use of the zone-drawing (ZD) technique, developed in our laboratory. We have reported previously that the mechanical and electrical properties of electrochemically synthesized polypyrrole films are improved by zone-drawing [9].

The present article deals with the application of the ZD method to PPV precursor films for the purpose of improving the mechanical properties. The changes in the structure and mechanical properties of the resulting films are investigated.

2. Experimental

2.1. Preparation of PPV precursor films

The PPV precursor films were prepared using the method of Karasz and co-workers [10]. *p*-Xylene-bis(diethylsulfonium chloride) monomer was synthesized by reacting α,α'-dichloro-*p*-xylene ($0.6\ \mathrm{mol\ l^{-1}}$) with diethyl sulfide ($1.8\ \mathrm{mol\ l^{-1}}$) in methanol solution at 50°C for 24 h. The methanol was evaporated and the monomer was precipitated from cold acetone, filtered and then dried overnight in a vacuum. Polymerization was carried out by mixing the monomer ($0.2\ \mathrm{mol\ l^{-1}}$) and sodium hydroxide ($0.2\ \mathrm{mol\ l^{-1}}$) at 0°C for 1 h under a nitrogen atmosphere. After polymerization, the solution was neutralized by addition of an aqueous solution of 0.1 N HCl and then purified by dialysis in deionized pure water for 3 days. The precursor film was prepared by casting the dialyzed solution on a glass plate at 50°C for 12 h. The resulting film was flexible and found to be almost amorphous from an X-ray diffraction photograph. The precursor film had a fluorescent green color, which was attributed to the formation of short conjugated PPV units [11]. Indeed, the elemental analysis indicated that the ratio between the diethylsulfonium chloride unit and the PPV unit was about 1:1. Gagnon et al. [12] demonstrated that a freshly cast film had a ratio of 4:1, which stabilized to a ratio of about 1:2 after 3 weeks at room temperature. To obtain a high reproducibility for the

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* Corresponding author. E-mail: okuzaki@ab11.yamanashi.ac.jp

PII: S0032-3861(98)00511-4

zone-drawing, the PPV content of the newly prepared film was checked prior to drawing.

2.2. Zone-drawing and thermal conversion

The zone-drawing was carried out using a tensile tester equipped with a narrow band heater (2 mm thick) to the cross-head. The heater temperature was held constant over the experimental period by a thermoregulator. The upper end of the precursor film (40 mm long, 2 mm wide, 17 μm thick) was fixed to a strain gauge and the desired tension was applied to the lower end by weighting. The band heater was moved in the direction from the lower to the upper end at a constant speed of 20 mm min^{-1}. As well as the apparatus being simple and the procedure quite easy, this method has the following advantages: (1) the applied tension acts concentrically and effectively on the quite narrow area of the specimen; (2) the thermal decomposition or oxidation of the specimen can be minimized because the heating time is very short (a few seconds); and (3) the dimensional stability of the zone-drawn films or fibers at elevated temperature is fairly improved. The thermal conversion of the zone-drawn precursor films was performed with an electric furnace (20 cm long and 10 cm in diameter) in a nitrogen stream under isometric conditions.

2.3. Measurements

The draw ratio was determined by measuring the distance between marks put on the surface of the film prior to drawing. The degree of crystallinity, defined as the ratio of the peak area of the diffraction from the crystallites to total diffraction, was measured from wide angle X-ray diffraction patterns. The apparent crystallite size normal to the *hkl* plane (D_{hkl}) was estimated from Scherrer's equation:

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta_{hkl}}, \tag{1}$$

where λ is the wavelength of the Cu K$_\alpha$ beam (1.542 Å), β is the half-width of the diffraction peak, θ_{hkl} is half of the diffraction angle and K is the Scherrer constant (=0.9). The wide angle X-ray diffraction photographs were taken with Ni-filtered Cu K$_\alpha$ radiation (40 kV, 20 mA) by an X-ray generator (Rigaku). The distance between sample and X-ray film was 40 mm, and exposure time was 4 h.

The orientation function (f) was evaluated with an FTIR spectrometer (Pargamon 1000, Perkin Elmer). The dichroic ratio (D), defined as the ratio between absorption parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the drawing direction, was estimated as follows [12]:

$$f = \left[\left(\frac{D-1}{D+2}\right)\left(\frac{D_0+2}{D_0-1}\right)\right], \tag{2}$$

where $D_0 = 2\cot^2\alpha$, and α is the angle of the absorption transition moment to the molecular chain axis. The estimation of f was carried out using the absorption of *trans*-vinylene C–H out-of-plane bending [12] at 965 cm^{-1}, where the absorption transition moment, α, was 84° [13].

The thermogravimetric (TG) thermogram was measured with a TG-DTA 2000S (MAC Science). About 20 mg of dry film was weighed in an aluminum pan and the measurement was carried out at a heating rate of 2°C min^{-1} under a nitrogen atmosphere.

The dynamic viscoelastic properties, storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) were measured with a dynamic viscoelastometer (Vibron DDV-II; Orientec) at 110 Hz from room temperature to 340°C at a heating rate of 2°C min^{-1} under a nitrogen atmosphere.

3. Results and discussion

3.1. Optimum conditions for the zone-drawing and thermal conversion

The objective of the zone-drawing is to achieve the high molecular orientation of the precursor film without simultaneous conversion to PPV, so that the zone-drawing is performed under moderate heater temperatures. Fig. 1 shows the dependence of orientation function (f) on draw ratio. It is found that f increases with the draw ratio, regardless of the heater temperature and the tension applied, and attains a value of 0.83 at a draw ratio near 8. Murase et al. [1] found that the PPV precursor film could be stretched up to 10-fold with a uniaxial stretching machine at a temperature between 100 and 300°C. The relatively small draw ratio in the present system may be due to the high PPV content of the original film, which lowers the

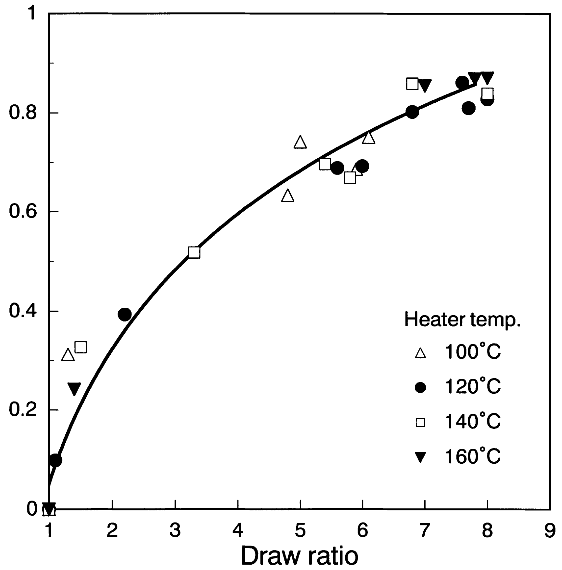

Fig. 1. Relation between draw ratio and orientation function (f) for the zone-drawn precursor films at various heater temperatures. f was determined from IR dichroism using the absorption of *trans*-vinylene C–H out-of-plane bending at 965 cm^{-1}.

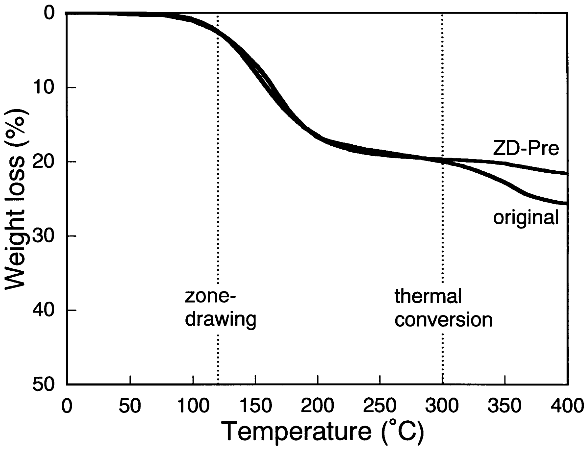

Fig. 2. TG thermograms of the original and ZD-Pre films. The measurements were carried out at a heating rate of 2°C min^{-1} under a nitrogen atmosphere.

drawability. In consideration of the drawability and reproducibility, the optimum heater temperature and applied tension are determined to be 120°C and 10 MPa, respectively.

In order to determine the optimum conditions for the thermal conversion, the TG thermogram is measured for the original and zone-drawn precursor (ZD-Pre) films, and the results are shown in Fig. 2. The TG thermograms show two major steps of weight loss, at 100–200°C and 350–400°C. The first step corresponds to the elimination of diethyl sulfide and hydrochloric acid [14,15], and the second step may be attributed to the thermal decomposition of the polymer. One can see that the TG thermogram of the ZD-Pre film is well overlapped with that of the original film up to 300°C. This indicates that the elimination reaction does not occur during the zone-drawing under optimum conditions. On the other hand, the weight loss of the ZD-Pre film is relatively small compared with the original film above 300°C. This fact demonstrates that the thermal stability of the film is improved by the zone-drawing. Thus, the thermal conversion of the ZD-Pre to ZD-PPV was carried out at 300°C for 1 h under a nitrogen atmosphere.

Table 1
Thickness, draw ratio, orientation function (f), crystallinity (X_c) and crystallite size (D_{110}) for various films

Film	Thickness (μm)	Draw ratio	f	X_c (%)	D_{110} (Å)
Original	17	–	–	–	–
ZD-Pre	14	8.0	0.83	62.4	52.7
ZD-PPV	6	8.0	0.74	65.2	47.5

3.2. Superstructure of the ZD-Pre and ZD-PPV films

Fig. 3 shows the IR spectra of the original, ZD-Pre and ZD-PPV films without polarizers. It is seen that the spectra of the original and ZD-Pre films are similar, having absorptions at 965 and 3024 cm^{-1} corresponding to the *trans*-vinylene C–H out-of-plane bending and *trans*-vinylene C–H stretching bands, respectively. This indicates that the original and ZD-Pre films already contain the PPV units formed during the film casting [14,15], which is consistent with the elemental analysis data. After the heat treatment, the absorption of the C–S stretching band at 632 cm^{-1} disappears, while the absorptions at 965 and 3024 cm^{-1} increase, indicating that the thermal conversion is completely achieved.

The thickness, draw ratio, orientation function, crystallinity and apparent crystallite size normal to the (110) plane for the ZD-Pre and ZD-PPV films are summarized in Table 1. The large decrease of the thickness of the ZD-PPV film is attributed to the elimination of diethyl sulfide and hydrochloric acid under the isometric conditions where the length of the film remains constant. The decrease in f for the ZD-PPV film may be due to the relaxation of molecular orientation during the thermal conversion. The apparent crystallite size decreases by thermal conversion in spite of the fact that the crystallinity increases slightly. It can be considered that the crystal lattice changes by the elimination reaction. In fact, the X-ray diffraction peak for the ZD-Pre film at $2\theta = 18.7°$ corresponding to a d-spacing of 4.72 Å continuously shifts to higher diffraction angle, indicative of

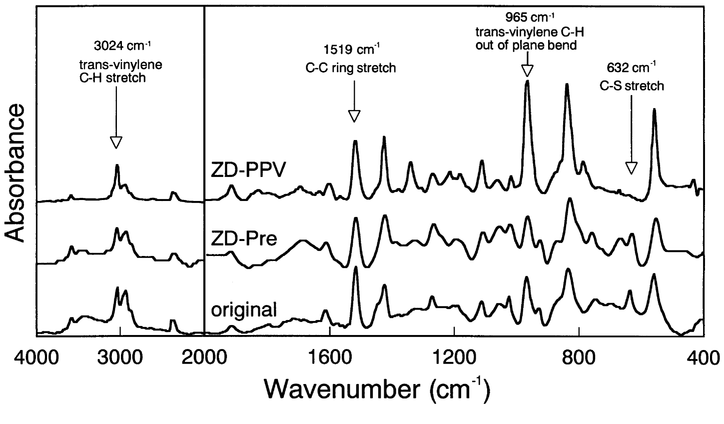

Fig. 3. FTIR spectra of the original, ZD-Pre and ZD-PPV films.

Fig. 4. Wide angle X-ray diffraction photographs of the original, ZD-Pre and ZD-PPV films.

a decrease in the *d*-spacing. The resulting ZD-PPV film has a diffraction peak at $2\theta = 20.1°$, corresponding to a *d*-spacing of 4.4 Å. This tendency can also be seen in the wide angle X-ray diffraction photographs shown in Fig. 4.

3.3. Mechanical properties of the ZD-Pre and ZD-PPV films

The temperature dependence of the storage modulus (E') for various films is shown in Fig. 5. E' increases stepwise with the processing over the whole experimental temperature range, and the value for the ZD-PPV film at room temperature reaches 33.7 GPa and remains at 11.5 GPa even at 300°C. The temperature dependence of the loss tangent (tan δ) for various films is shown in Fig. 6. One can see that two clear mechanical dispersion peaks appear at 140 and 310°C for the original film. These mechanical dispersion peaks decrease in height and shift to higher temperatures for the ZD-Pre film, although the chemical structure is the same for the original and ZD-Pre films. This demonstrates that the orientation and/or crystallization of molecular chains suppresses the micro-Brownian motion of large amorphous segments. Furthermore, the dispersion peak at lower temperature disappears for the ZD-PPV film. To explain these mechanical dispersions, the original undrawn film was heat treated with an electric furnace at various temperatures for 1 h and dynamic mechanical measurements of the films obtained were made. It was found that the dispersion at 140°C gradually decreased in height and shifted to higher temperatures with increasing treatment temperature, and finally disappeared at treatment temperatures above 300°C. On the other hand, the mechanical dispersion at 310°C remained even after heat treatment at 300°C. Thus, the mechanical dispersions at 140 and 310°C can be ascribed to the glass transitions of the precursor and PPV, respectively.

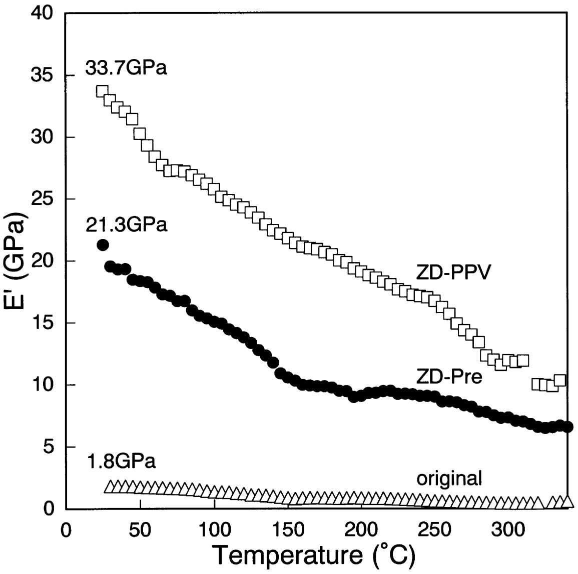

Fig. 5. Temperature dependence of dynamic storage modulus (E') for the original, ZD-Pre and ZD-PPV films (frequency: 110 Hz; heating rate: 2°C min^{-1}).

4. Conclusions

The ZD method was applied to poly(*p*-phenylene vinylene) precursor films to improve the mechanical properties and the following results were obtained.

1. The orientation function of the ZD-Pre film increased with the draw ratio, regardless of the heater temperature and the tension applied.

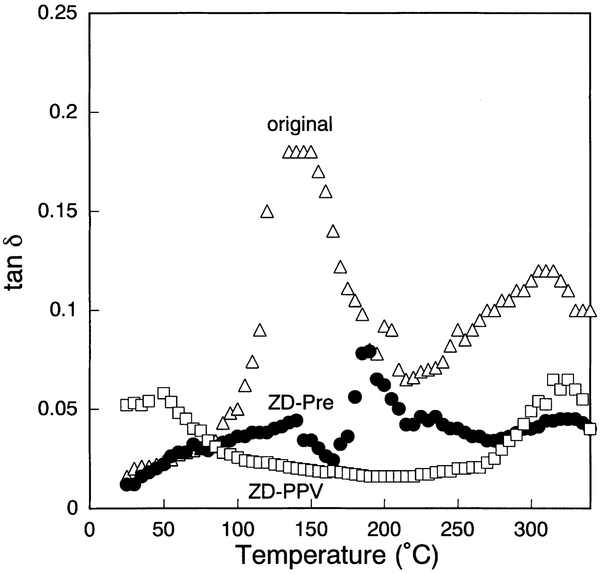

Fig. 6. Temperature dependence of the loss tangent (tan δ) for the original, ZD-Pre and ZD-PPV films (frequency: 110 Hz; heating rate: 2°C min^{-1}).

2. The draw ratio, orientation function, crystallinity and apparent crystallite size for the resulting ZD-PPV film were 8.0, 0.74, 65.2% and 47.5 Å, respectively.
3. The dynamic storage modulus of the ZD-PPV film attained a value of 33.7 GPa at room temperature and held at 11.5 GPa at 300°C.

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