Cold Stretching of PPV with Water as a Plasticizer

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ABSTRACT: PPV precursors were prepared via the precursor route. The free-standing films were stretched at room temperature under an atmosphere of water vapor. Stretch ratios of up to nine could be attained easily. This procedure is less dependent on factors such as film thickness and freshness than hot stretching. Molecular alignment is at least as good as in hot-stretched films, as proved by FTIR dichroism measurements. Detailed IR results are presented. In addition to providing an experimentally easier way to obtain oriented PPV films, this procedure also allows to produce oriented, noneliminated PPV precursor films. This new way of stretching might also be applicable to the precursors of other conjugated polymers.

Introduction

Oriented poly(phenylenevinylene) (PPV) films are of considerable interest, both from an experimental, practical, and theoretical point of view. Up until now, oriented PPV was almost exclusively prepared *during* the thermal conversion of the precursor.[1−9] This way, the evaporating solvent and the elimination products (i.e., tetrahydrothiophene and HCl) are thought to behave as plasticizers, thus making it possible to stretch the film without tearing. Great care is to be taken, however, since film thickness, film freshness, temperature, and stretching rate are important factors influencing the stretching process.

The only report of cold stretching of PPV with the help of a plasticizer found in the literature is that by Massardier et al.[10] reporting on the stretching of PPV in methyl alcohol. In this paper, we choose to use water vapor as a plasticizer, in analogy to the stretching of PVA films.[11]

Experimental Section

PPV was synthesized following a slight modification of the precursor route, first proposed by Wessling[1] and later modified by Lenz et al.[12]

A 17 g sample of α,α′-dichloro-*p*-xylene and 26 mL of terahydrothiophene (THT) were heated in 100 mL of methanol at 50 °C. After 24 h, the mixture was cooled to room temperature and was then concentrated by evaporation to a highly viscous solution, making sure that no precipitation occurred. Cold acetone (0 °C) was slowly added, until a white powder precipitated. This *p*-phenylenedimethylene bis(tetrahydrothiophenium chloride) was then filtered and dried in vacuo.

A 15 g sample of the bis-sulfonium salt was dissolved in 400 mL of deionized water, cooled in an ice bath, and purged with nitrogen. A 90 mL aliquot of 0.5 M NaOH solution was slowly added, and the mixture was allowed to polymerize at 0 °C, without stirring. After 1 h, the reaction was quenched by adding 1 M HCl until the pH was slightly acidic.

The resulting highly viscous solution was dialyzed against deionized water for a period of approximately 1 week (Spectra/Por membrane with a molecular weight cutoff of 6000−8000 was used). The precursor films were cast onto silanized glass plates. After evaporation of the solvent, the colorless to light-green films could easily be peeled off and had a typical thickness of approximately 6 μm. The film was then cut into strips of approximately 6 by 2.5 cm. These strips were stretched on an Instron tensile tester, equipped with a controllable atmosphere chamber. The films were mounted into the tester, with an initial distance between the grips of 2 cm. A beaker with approximately 200 mL of boiling water was then placed in the chamber. The chamber was closed, and the atmosphere was allowed to equilibrate for 1 min. Then, the stretching started with a constant speed of 2 cm/min. During stretching, the temperature raised somewhat due to the hot vapor, but the overall temperature in the chamber never exceeded 40 °C. The stretched precursor films were then mounted into a holder and placed into an oven under nitrogen atmosphere. The temperature in the oven was raised to 300 °C and held at that temperature for 3 h, to achieve complete elimination. The absence, in the infrared spectra, of the C−S stretching mode and C−Cl stretching mode at 610 and 630 cm^{-1}, respectively, proved that the elimination was complete. Also, no carbonyl bands were detected, which shows that the samples did not undergo oxidative degradation.

SEM measurements were taken on a JEOL 1200 EX microscope, at 40 kV and a magnification of 800×. Gold sputtered films of a draw ratio 5 were investigated.

Mid-IR spectra were recorded on a Bruker IFS 66v spectrometer using a Ge/KBr beam splitter and a Globar source. The standard DTGS was preferred over the more sensitive MCT detector in view of the higher linearity of the former. The interferograms were recorded with a resolution of 1 cm^{-1}, averaged over 200−400 scans, Happ-Genzel apodized, and Fourier transformed with a zero-filling factor of 4. A Graseby Specac grid polarizer was mounted in front of the sample films, which had a thickness of approximately 6 μm. In the infrared spectra (Figure 2) the films showed a significant interference fringe, which was exploited to measure the film thickness. The refractive indices for light polarized parallel and perpendicular to the stretching direction required for the calculation of the thickness were taken to be 2.1 and 1.5, respectively.[2]

Results and Discussion

Stretching. Cold stretching of PPV precursor films proves to be very easy. Whereas in hot stretching, the

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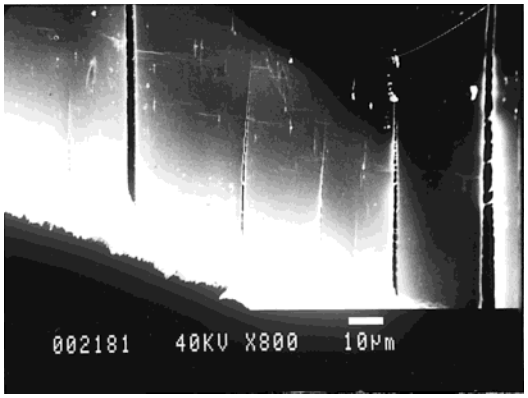

Figure 1. SEM picture of a stretched film (draw ratio = 5), showing texture in the stretch direction only (top to bottom) and not perpendicular to it. The surface appears to be dense and flat.

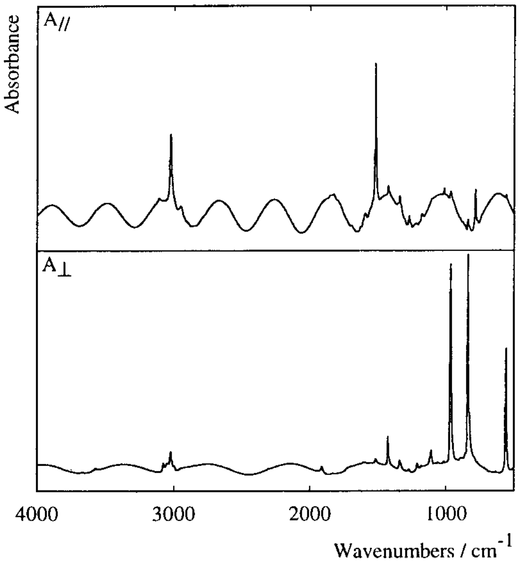

Figure 2. FTIR spectra of a fully eliminated PPV film: top, polarization parallel to the stretch direction; bottom, polarization perpendicular to the stretch direction.

stretching temperature, temperature program, stretching speed, film thickness, and film quality play major roles, they seem to be less important in cold stretching with water vapor. The operation temperature is at or slightly above room temperature. The temperature during stretching never exceeded 40 °C. This precludes any elimination of the precursor, and the films remain light-green in appearance. This is most likely due to the short time (less than 10 min) the film is exposed to 40 °C and to the previously proposed stabilizing effect of water on the precursor.[13]

Film thickness does not affect the process: films of approximately 6 and 50 μm could be stretched without altering the conditions to any great extent. Thicker films only need a somewhat longer equilibration time (e.g., 2 min) in order to allow the water vapor to diffuse into the film more completely.

The influence of film freshness was shortly tested. Some films were exposed to air and sunlight for some time and became partly eliminated with a light yellow appearance. Those films were stretched as easily as fresh ones.

The reproducibility of the process is excellent. Film tearing seldomly occurred, and stretch ratios of 7−9 can be obtained routinely.

SEM. The stretched and fully eliminated films were studied with scanning electron microscopy. The micrograph of a film of stretch ratio 5 is shown in Figure 1. No microvoids are detected, and only some features are noted in the stretch direction. This proves the absence of crazing as this would cause features perpendicular to the stretch direction.[4] This was expected because high stretch ratios could be attained without tearing. It also shows a relatively flat and even surface, which is in agreement with the observation of clear interference patterns in the FTIR spectra (Figure 2), indicating a macroscopic uniformity of the films.[13]

FTIR Analysis. Following the analysis of Zbinden[14] for the case of partial axial orientation, we determined the degree of orientation from IR dichroic measurements. The model describes the molecules in a stretched polymer film as rigid chains, becoming oriented preferentially along the stretch direction, but retaining a random distribution with respect to rotation about their axis. The fraction of the chains pointing in a specified direction, at an angle θ to the stretch direction, is given by the rotationally symmetric distribution function $u(\theta)$, which is normalized:

$$\int_0^{2\pi} u(\theta)\, \mathrm{d}\theta = 1 \tag{1}$$

In this model, the dichroic ratio R can be expressed as

$$R = \frac{A_{\parallel}}{A_{\perp}} = \frac{2\cos^2\alpha + s}{\sin^2\alpha + s} \tag{2}$$

where $A_{\parallel}$ and $A_{\perp}$ are equal to the integrated absorbances of a selected vibrational mode, for IR radiation polarized parallel and perpendicular to z (= stretch direction), respectively, and α is the angle between the transition dipole for the mode and the chain axis; s is the orientation parameter defined as

$$s = \frac{F}{1 - \frac{3}{2}F} \tag{3}$$

where

$$F = \int_0^{\pi/2} \sin^2\theta\, u(\theta)\, \mathrm{d}\theta \tag{4}$$

The orientation parameter is related to the Hermans orientation function[15] f, according to

$$f = \frac{2}{3s + 2} \tag{5}$$

In general, the form of $u(\theta)$, which determines the orientation parameter s, is unknown. To obtain a value for s, it is assumed that the angle α for the selected IR-active vibration is known, and then s can be calculated from the measured dichroic ratio, R, using relation 2. This value of s can subsequently be used to find the values of the angle α of the other vibrational modes.

Figure 2 shows the polarized IR spectra of a freshly prepared PPV film with a draw ratio of 5 and a thickness, determined from the interference fringes, of approximately 6 μm.

Table 1 shows the IR dichroic ratios for the selected modes at various stretch ratios. It shows clearly that the modes at 557, 838, 966, and 1424 cm^{-1} are perpendicular (π) modes, while the ones at 1013, 1271, and

Table 1. Measured Dichroic Ratios for Some Selected Modes as a Function of Stretch Ratio

stretch ratio	selected modes (cm^{-1}) 557	838	966	1013	1271	1424	1518
1	0.59	0.56	0.66	1.5	1.3	0.82	1.7
1.5	0.19	0.25	0.23	2.9	2.6	0.57	5.8
2	0.060	0.092	0.12	3.9	3.4	0.47	13
2.5	0.048	0.084	0.091	4.2	3.4	0.41	17
3	0.048	0.074	0.088	4.0	4.1	0.44	20
4	0.036	0.065	0.071	4.2	3.9	0.44	20
5	0.031	0.044	0.051	5.5	3.4	0.42	27
6	0.027	0.042	0.040	4.8	4.0	0.44	29

Table 2. Orientation Function *f* as a Function Stretch Ratio[a]

stretch ratio	orientation function *f* this work	orientation function *f* hot stretch
1	0.32	0.19
1.5	0.74	
2	0.91	0.83
2.5	0.93	
3	0.93	0.91
4	0.95	0.94
5	0.95	0.96
6	0.96	0.95

[a] The orientation function for hot stretching[8] is included for comparison.

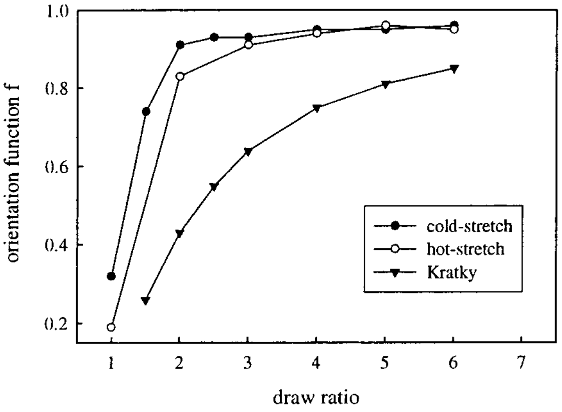

Figure 3. Comparison of the degree of orientation in cold-stretched (this work) and hot-stretched[8] PPV films as a function of the stretch ratio. The value predicted by the Kratky model[14] is also included for comparison.

Table 3. Calculated Angles α (the Angle (deg) between the Dipole Transition Moment for a Given Mode (cm^{-1}) and the Chain Axis) and Their Assignment (from Ref 2) for Selected Modes at Different Stretch Ratios[a]

selected modes	α	α (ref 2)	assignment from ref 2
838	83	83	phenylene ring C−H out-of-plane bend
966	82	84	trans vinylene C−H out-of-plane bend
1013	33		C−H in-plane bend
1271	36		C−H in-plane bend
1424	66	64	C−C ring stretch
1518	13	9	C−C ring stretch

[a] The angles α found in ref 2 are included for comparison.

1518 cm^{-1} are parallel (σ) modes. It is apparent from Figure 2 that these modes show great anisotropy. The strength of the dichroism for the mode at 784 cm^{-1} is such that when IR radiation is polarized perpendicular to the stretch direction, the intensity of the 784 cm^{-1} band was reduced to virtually zero, preventing meaningful dichroic ratios from being measured. This is a clear indication that the films are highly oriented. The mode at 557 cm^{-1} is known to be due to the phenylene out-of-plane ring bend,[2] which should have an angle α of 90°. Using this value of α, we calculated the *s* and *f* values for each stretch ratio. The *f* values are shown in Table 2. If α were smaller than 90°, the calculated *s* value would be lower. Thus, the obtained *s* values are minimum values (minimum orientation) consistent with the observed dichroic ratios. As can be seen from Figure 3, the observed orientation of the PPV films is, at least at the lower stretch ratios, far higher than predicted by the Kratky model. This model assumes that the molecular orientation of a chain segment corresponds to the macroscopic deformation of the sample.[14,16,17] It is generally accepted that the Kratky model predicts an upper limit for the molecular orientation in semicrystalline polymers. Apparently, a better orientation is obtained during stretching and the subsequent thermal elimination than could be theoretically expected. Previous workers have attributed this to the chemical modification during the elimination process,[13] although a precise explanation remains to be found.

Figure 3 also shows that the orientation obtained in cold stretching with water vapor is higher than in hot stretching, at least for the lower stretch ratios. A possible explanation is the following. In hot stretching, the elimination process starts already in the early phase of the stretching. Therefore, partially eliminated, and thus more rigid, domains are formed at an early stage. When these domains are not oriented perfectly in the stretch direction, it will be (relatively) more difficult to orient them later on during the stretching process. In cold stretching, on the other hand, the precursor chains are first oriented in the stretch direction, and only after this orientation is completed, the conversion to the rigid, fully eliminated PPV is accomplished. Since very high degrees of orientation are obtained at relatively low stretch ratios, this difference will only be noticed at the lower stretch ratios.

One also notices (Table 2 and Figure 3) that the orientation (*f*) in the nonstretched films is higher than the corresponding value found in ref 8. This difference can only be caused by (small) differences in preparation and elimination procedures of the films used. To investigate whether a higher starting value of *f* at the $l/l_0 = 1$ already explains the higher *f* values in our cold-stretched films, at the lower stretch values ($l/l_0 < 3$), we also performed measurements on hot-stretched films that were otherwise treated in exactly the same way as the cold-stretched films. We observed $f = 0.87$ for such a hot-stretched film at a stretch ratio of 2. This is about the same as $f = 0.83$ found in ref 8 and indicates that the higher degree of orientation in cold-stretched films is not only due to a higher starting orientation in the nonstretched films.

From the observed dichroic ratios and the orientation parameters *s* the angles α were calculated. Table 3 gives values for the angles α, averaged over all the stretch ratios except 1 and 1.5. The latter are not included because their α values deviate significantly from those at higher stretch ratios. A possible explanation is that the dichroic ratios are close to unity for the lower stretch ratios. Thus, a small error on the measured intensities results in a large error on the calculated angle α. For comparison, we also show the values for α obtained from measurements on hot-stretched films.[2]

Conclusions

Cold stretching using water vapor as a plasticizer provides a new way to prepare aligned PPV films and thus an alternative for hot stretching. It avoids the problems of film tearing. The molecular orientation is at least as good as in hot-stretched films, and for the lower stretch ratios it is even better. Measurements of various IR modes at different stretch ratios are consistent with each other. They confirm previously measured values of α^2 and extend the number of modes for which the angle α is known. This method also makes it possible to produce high-quality films of oriented, non-eliminated precursor films. This possibility can be helpful in the future to get to a better understanding of the elimination process in oriented films. Finally, this new method of stretching PPV might be applicable to the precursors of other conducting polymers as well.

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