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Raman and FTIR Studies of the Effects of Draw Ratio and Side Chain Length on the Molecular Orientation of Polyester Films

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Introduction

The measurement of molecular orientation in liquid crystalline polymers is of great importance due to the potential in obtaining ultra-high modulus materials[1]. It is thus necessary to accurately characterize the degree of molecular orientation in both the bulk and films, under various processing conditions. In this work we combine laser Raman and FTIR spectroscopy measurements in order to determine the degree of molecular orientation in uniaxially oriented polyester films, as a function of the draw ratio, and further quantify the effects of side chain length.

Experimental

A model polyester with hexyl (PES 3:3/C6 and PES 3:1/C6) and dodecyl (PES 3:1/C12) side chains was employed, details of the synthesis and characterization are provided elsewhere[2]. The molecular weight, determined from intrinsic viscosity, was about 35,000. Typically, the chemical structure of PES 3:3/C6 is shown schematically in scheme 1. Films of nearly uniform thickness (30±2 μm) were obtained after casting from a 6% solution in chloroform. They were uniaxially oriented by drawing in an oven at about 270^0 C. Draw ratios, λ, were between 1.5 and 3.5.

The Raman spectra were excited with an Ar^+ laser (100 mW at 514.5 nm), and the scattered light at 90^0 was collected at the slit of a double monochromator, coupled with a PMT, through an analyzer and a quarter wave plate. Measurements were carried out at three different geometries of the drawing direction with respect to the incident laser beam: perpendicular (90^0), parallel (0^0) and at 45^0. Infrared spectra were measured in the transmission mode on a Bruker vacuum spectrometer (IFS 113v). Further details can be found in reference 3.

Results and Discusssion

Typical Raman spectra from PES 3:3/C6 at various λ and for perpendicular sample position, are depicted in Fig. 1. The peaks are much more pronounced in the VV mode rather than in the HV mode, suggesting that vibrations along the direction of stretching are much stronger than in the combinations of polarizations, thus a significant degree of molecular orientation along the stretching direction. In order to determine the degree of molecular orientation, the 1616 cm^{-1} Raman band was chosen because it is a strong, well-resolved, and well-known band, attributed to the C=C stretching mode in the C_1-C_4 direction of the benzene ring[4]. In order to quantify the molecular orientation, we have adopted the analysis of Pigeon et al[5]. Under the assumption of uniaxial symmetry of the samples, the problem of determining the second and fourth orientation moments (P_2 and P_4) leads to a system of five nonlinear algebraic equations for the Raman scattering intensity at various geometries. This introduces a high degree of ambiguity, and to overcome this problem the Raman tensor of the 1616 cm^{-1} line was assumed cylindrical, i.e. the two components of the polarizability tensor perpendicular to the plane of the ring, and perpendicular to the C_1-C_4 direction are of the same sign and magnitude, a reasonable assumption due to symmetry considerations[4]. Thus, we end-up with:

$$P_2 = \frac{(-x^2 - 2x)M - 1 + 4x}{(-x^2 + x)M + 4x - 4} \qquad (1)$$

$$P_4 = \frac{(8x^2 - 16x + 8)Q - 64x^2 - 32x - 24}{(8x^2 + 8 - 16x)(2 + Q)} \qquad (2)$$

where M and Q are functions of the experimental Raman scattering intensities (at various measuring angles and polarizations), and x is determined from the depolarization ratio, ρ, of the isotropic sample[3,6].

The average of P_2 from FTIR wass calculated from[7]:

$$P_2 = \frac{(D - 1)}{(D + 2)}\frac{(D_o + 2)}{(D_o - 1)} \qquad (3)$$

where D is the dichroic ratio, which is a measure of adsorption anisotropy, and $D_o = 2\cot^2\psi$ is the dichroic ratio for perfect orientation, with ψ the angle between the direction of the vibrational transition moment and the polymer chain axis. Typical FTIR measurements are depicted in Fig. 2. Several IR bands exhibit saturation effects when the radiation is polarized parallel to the stretching direction of the film; this is attributed to a combined effect of the large film thickness and the strong absorption by the film under parallel polarization of radiation. In the spectral region typical of CC stretching vibrations of the aromatic rings, we focus on the band centered at 1605 cm^{-1} because this band is well resolved from the other CC components, and is the IR counterpart of the 1616 cm^{-1} Raman. Indeed, the para-disubstituted benzene ring of PES 3:3/C6 has no center of symmetry and, therefore, the mode giving rise to the Raman band at 1616 cm^{-1} becomes infrared active as well[8]. Comparisons of the determined P_2 values obtained from the Raman and FTIR are shown in Fig. 3. Results exhibit the same trend with λ. This confirms the fact that the two techniques are probing the same orientation. P_4 values follow the right trend and fall within the acceptance range[9]. The corresponding X-ray diffraction P_2 data were found to be clearly higher. We suggest that this discrepancy is justified by the fact that Raman and FTIR, which are sensitive to the vibration of a particular group, measure the average molecular orientation, whereas orientation information from X-ray diffraction originates mainly from layer reflection of the larger liquid crystalline domains.

Finally, the above analysis was employed for determining the effects of side chains on the molecular orientation (PES 3:1/C6 and PES 3:1/C12). It was found, surprisingly, that polyester films with dodecyl side chains possess higher P_2 than those with hexyl side groups, at all draw ratios investigated (Fig. 3). This is also reflected in the relevant Raman measurements (Fig. 4), where the difference in depolarization ratio between the two cases C6 and C12, is apparent. It is proposed that this result reflects the higher flexibility of the longer side chains. This is in agreement with depolarized Rayleigh studies on macromolecular conformation in dilute solution of these molecules[10], which reveal a stronger optimal anisotropy of the chains with C12 side groups compared to the ones with C6.

Acknowledgements

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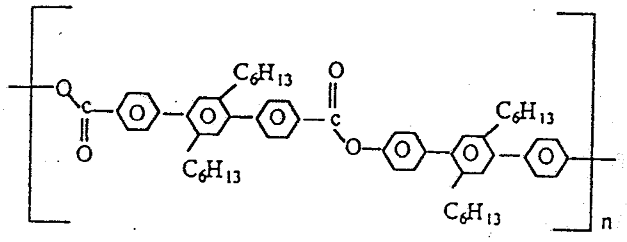

Scheme 1: Molecular structure of PES 3:3/C6

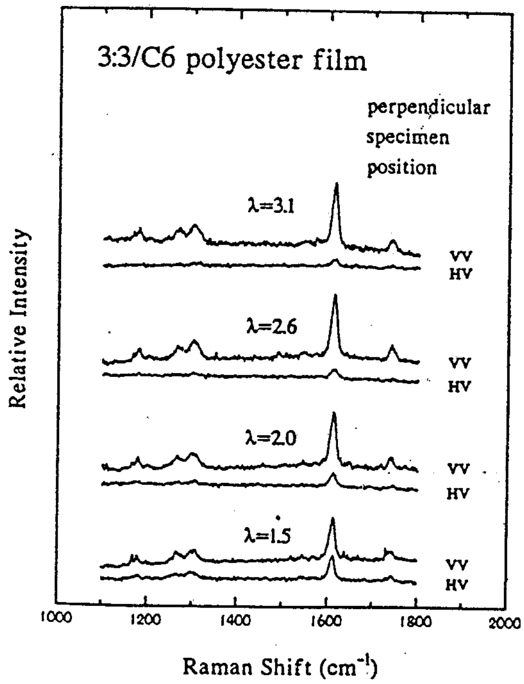

Fig. 1: Raman spectra for PES 3:3/C6 at different draw ratios

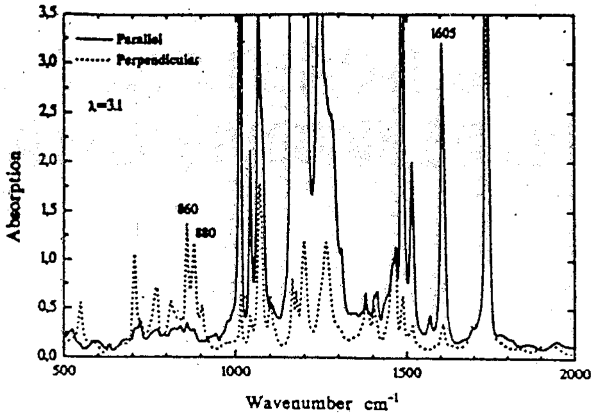

Fig. 2: IR spectra for PES/C6 at λ=3.1

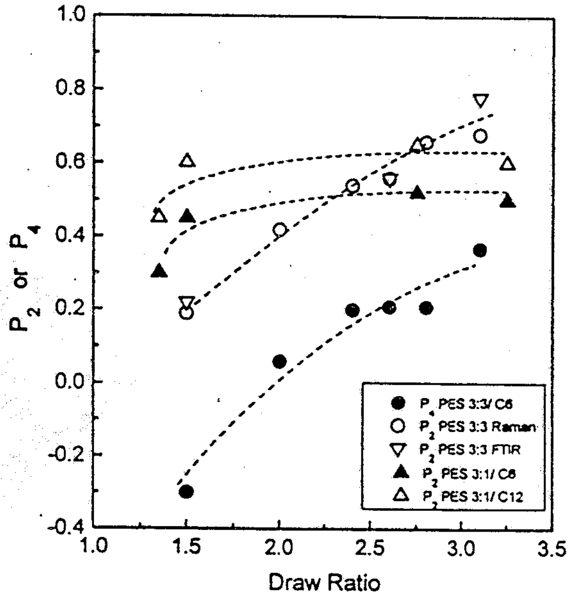

Fig. 3: P_2 and P_4 of PES 3:3/C6, PES 3:1/C6 and PES 3:1/C12 vs draw ratio. Lines are drawn to guide the eye

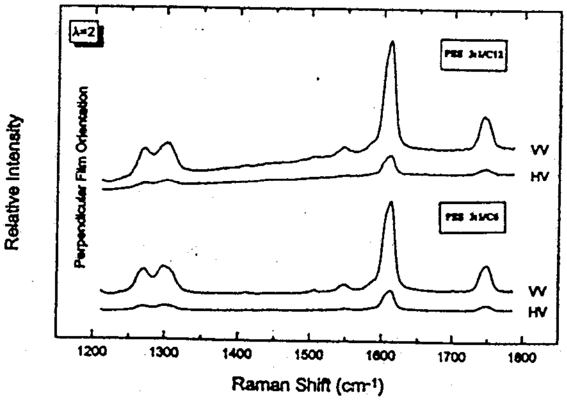

Fig. 4: Raman spectra of PES 3:1/C6 and PES 3:1/C12 at λ=2