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Infrared and fluorescence spectroscopy investigation of the orientation of two fluorophores in stretched polymer films

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ABSTRACT

The simultaneous orientation of poly(1,4-butylene)succinate (PBS) and 4,4′-bis(2-benzoxazolyl)stilbene (BBS) or 2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (BBT) in PBS–BBS and PBS–BBT films was investigated during stretching at 80 °C, about 33 °C below the PBS melting temperature. The PBS orientation was first investigated using the 3430 cm^{-1} infrared band and its order parameter $<P_2>$ goes from 0.36 at a local strain of 359% for pure PBS to 0.66 in blends containing 6 wt % of BBT at a local draw ratio of ≈350% (or 0.56 with 5 wt % of BBS). At the same time, BBT shows in the same films an orientation parameter $<P_2>$ reaching a maximum of 0.31 at a local strain of ≈350%, using the 1580 cm^{-1} band. Since polarized FT-IR was unable to provide the orientation of BBS due to overlapping bands with PBS, polarized fluorescence spectroscopy was then used and reveals an apparent order parameter of 0.32 for BBS monomers (or 0.34 for BBT monomers), but to no orientation of BBT aggregates and BBS excimers. In other words, the two small molecules behave similarly in terms of orientation independently of their molecular shape and packing. BBS and PBS both exhibit a sharp increase of S and $<P_2>$ when reaching a BBS concentration of ≈0.08 wt %, whereas BBT and PBS show a smooth increase of S and $<P_2>$, respectively, in films containing BBT. The sharp increase, or transition in orientation, is accompanied by a conversion of BBS from monomers to excimers, whereas BBT-containing films show a regular increase of the number/size of BBT aggregates. These results indicate that the dye (BBS or BBT) has a profound influence on the orientation of the semi-crystalline polymer (PBS) since its $<P_2>$ almost doubles at dye concentrations above 0.08 wt %. The results also suggest that the use of a fluorescent probe to follow the polymer chain orientation is not applicable for such systems.

1. Introduction

It has been demonstrated by several groups that luminogenic materials, i.e., polymers in which a small quantity of a fluorescent dye is dispersed, can be used as chemical sensors [1–4]. At very low dye concentrations, the system exhibits monomer emission, indicating a molecular dispersion of the dye inside the polymer. Above a certain critical concentration, which depends upon the solubility of the dye into the polymer matrix, the system exhibits excimer emission indicating dye aggregation [4–8].

Among many other parameters, it has been shown that the mechanical deformation of the system induces a transition from excimer emission to monomer emission due to the breakup of the aggregates during the deformation [3,9,10]. For example, Crenshaw et al. have dispersed cyano-substituted oligo(phenylenevinylene) derivatives into polyethylene and observed a color change upon deformation, greatly influenced by the degree of crystallinity of the polymer [9]. A second example is that of Pucci et al. who have studied a different system: a stilbene derivative in poly(1,4-butylene succinate) (PBS), a semi-crystalline polymer [10]. Both studies emphasize the presence of aggregates of the order of microns before stretching and the importance of the crystallinity of the polymer.

However, even if the color change upon deformation is well documented in these studies as well as the corresponding fluorescence emission spectra, the analysis remains qualitative. In this work, our goal is to determine quantitatively the orientation of both the dye and the polymer as a function of deformation and dye concentration. For that purpose, we have selected a system that we [11,12] and others [10] have already studied. We used polarized Fourier transform infrared (FT-IR) spectroscopy [13–17], which is

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a powerful technique for studying the orientation of multi-component systems since the different components may be differentiated via specific infrared bands, e.g., in semi-crystalline polymers [13,15,18], polymer blends [19–23] or block copolymers [24]. However, it requires a relatively high concentration of small molecule. On the other hand, polarized fluorescence spectroscopy can detect much smaller concentrations, making both techniques complementary. The results show that the orientation of the polymer is much larger than the orientation of the dye and that both are significantly affected by the dye concentration.

2. Experimental

2.1. Materials

4,4′-bis(2-benzoxazolyl)stilbene (97%, melting point > 300 °C) and 2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (99%, melting point ~ 200 °C) (Scheme 1) were purchased from Aldrich Chemicals and used without further purification.

Poly(1,4-butylene succinate) (PBS) ("Bionolle 1001") (Scheme 1) was graciously supplied by the Showa Highpolymer Company (Japan). PBS is a semi-crystalline polymer, characterized by a glass transition temperature of −34 °C and a melting temperature of 113 °C.

2.2. Sample preparation

The dye–polymer films, PBS–BBS and PBS–BBT, were prepared by melt-processing in a DDRV501/DIGI-SYS Plasti-Corder Brabender mixer by mixing about 20 g of PBS and 0.01 to 5 wt % of BBS, or 0.01 to 6 wt % of BBT, at 200 °C for BBS and 180 °C for BBT, and at 50 rpm for 10 min. The resulting material was compressed and molded between two aluminum foils in a Carver Laboratory Press, under a pressure of 9 tons/m^2 below the fluorophores melting temperatures. The samples were then put in a cold press and were left to cool at ~10 °C/min to room temperature before removal from the press, under a pressure of 2 tons/m^2, resulting in films with thicknesses of 40–100 μm.

Films used for mechanical deformation were prepared in a dogbone shape having a width of 4 mm and a length of 12 mm between the slits. Films were stretched at 80 °C, far above the PBS glass transition temperature of −34 °C and below its melting temperature of 113 °C, using an Instron model 5565 tensiometer, equipped with an environmental chamber and a 1 kN load cell. Stretching was performed at an elongation rate of 0.1 mm/s with an initial distance between the clamps of 2.5 cm, resulting in a non-homogeneous deformation. To prevent slippage during stretching, Pyrotape was fixed to the extremities of each strip. The actual local draw ratios (λ) were measured from the displacement of ink-marks drawn 1 mm apart onto the films before stretching as follow: $\lambda = (L_f - L_i)/L_i$ with L_f and L_i the final and initial length between marks, respectively. Following drawing, the chamber door was immediately opened and the temperature allowed dropping quickly to room temperature in order to freeze the orientation.

2.3. Polarized Fourier transform infrared (FT-IR) and polarization modulation infrared structural absorbance spectroscopy (PM-IRSAS) measurements

Static polarized FT-IR spectra were recorded with a minimum of 128 scans per sample at a 4 cm^{-1} spectral resolution using a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride detector and a KRS-5 wire-grid polarizer (Optometrics).

Polarization modulation infrared linear dichroism was first used by Buffeteau et al. [25–27] for measuring quantitative dichroic difference spectra and enabled the dynamic study of fast deformation and relaxation processes [20–22,28–33]. PM-IRSAS, a technique based on the same concepts and described in detail by Liang et al. [34], allows recording the individual p- and s-polarized spectra by switching the polarization plane of the infrared radiation at high frequency, permitting a direct measurement of the dichroic difference ($\Delta A = A_p - A_s$) spectrum with high sensitivity and 200 ms time resolution [22]. The orientation function, $<P_2>$, is calculated according to [35]:

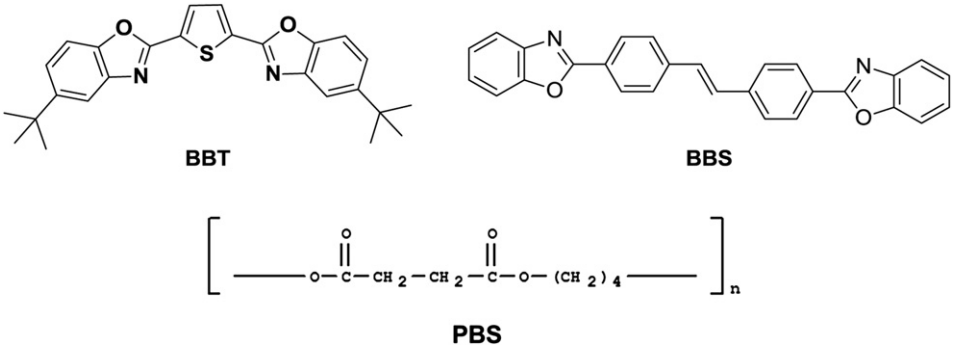
$$\langle P_2 \rangle = \left(\frac{2}{3\cos^2\alpha - 1}\right)\left(\frac{\Delta A}{A_p + 2A_s}\right) = \left(\frac{2}{3\cos^2\alpha - 1}\right)T_2 \qquad (1)$$

where α is the angle between the transition dipole moment of the selected vibration and the main chain axis of the polymer. The limiting values of $<P_2>$ are 0 and 1 for random and perfect orientation along the stretching direction, respectively.

PM-IRSAS spectra with a resolution of 8 cm^{-1} were acquired with the same spectrometer using a side-port optical setup and two-channel electronic processing similar to that described elsewhere [25–27,33,34]. Briefly, a linear polarizer, a photoelastic modulator (PEM-90, type II/ZS50, Hinds Instruments) operating at 100 kHz ($2f_m$), a lock-in amplifier (Stanford Research Systems, SR830) with a 30 μs time constant, and two dual-channel electronic filters (Frequency Devices, 90TP/90IPB) were used to generate the double modulation and to isolate the experimental signals. A liquid nitrogen-cooled photovoltaic InSb detector (EG&G Judson) was used.

2.4. Fluorescence measurements

Fluorescence emission spectra were recorded at ambient temperature in 10 mm cuvettes by excitation of the solution at its corresponding absorption maximum, by using front-face geometry in an



Scheme 1. Structures of 2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (*BBT*), 4,4′-Bis(2-benzoxazolyl)stilbene (*BBS*) and poly(1,4-butylene succinate) (*PBS*).