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A Clear-Cut Experimental Method to Discriminate between In-Plane and Out-of-Plane Molecular Transition Moments

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Energy (light frequency) and intensity of electronic and vibrational transitions are widely used in structural chemistry. On the other hand, polarization, i.e., the direction in the molecular framework of the transition moment vectors, is much less studied. This is mainly due to the intrinsic difficulties in making polarization measurements, which need a molecular orientation control.

The most simple techniques to get molecular alignment are based on the use of anisotropic solvents, mainly of stretched polymers.[1] According to that method the organic molecule is absorbed in the amorphous phases of semicrystalline films of polyethylene or of polyvinylalchool, uniaxially stretched at high draw ratios. This method has been greatly successful and has been applied in several dozens of papers[2] to hundreds of organic molecules.

However, the orientation control of the solute molecules is generally poor, since they are absorbed in poorly oriented polymer amorphous phases (orientation factors generally lower than 0.5).[3] Moreover, the molecules are assumed to be oriented with their smallest cross section nearly perpendicular to the stretching direction (as schematically shown for indole in Figure 1A). As a consequence, linear dichroism (LD) measurements do not allow an easy discrimination between in-plane and out-of-plane transition moment vectors, mainly for low-symmetry molecules.

In this communication, we show that organic molecules can be more efficiently oriented by absorbing them as guest of the crystalline nanoporous δ phase[4−7] of uniaxially stretched syndiotactic polystyrene (s-PS) films. As usual for semicrystalline polymeric films, high degrees of crystalline phase orientation can be easily reached (e.g, orientation factors higher than 0.9 for draw ratios, λ = final length/initial length, larger than 3).[7] This nanoporous s-PS δ phase presents per unit cell eight styrene monomeric units and two identical cavities,[4] where volatile organic molecules with a volume smaller than 200 Å^3 can be hosted,[5] generally producing a single occupancy of each cavity.[6] Moreover, it has been clearly demonstrated that after guest sorption at low activities, or partial desorption procedures, the guest molecules are mainly located in the crystalline host phase, while their concentration in the prevailing (generally $\geq$60 wt %) amorphous phase can be negligible.[5]

This new molecular alignment method not only ensures higher degrees of guest orientation but also a new kind of guest orientation. In fact, planar molecules are oriented with their smallest cross section nearly parallel to the stretching direction,[6,7]as schematically shown for indole in Figure 1B. As a consequence, in-plane and out-of-plane transition moment vectors maximize their absorption intensities for light polarization nearly perpendicular and parallel to the stretching direction, respectively. Hence, simple LD = ($A_{\parallel} - A_{\perp}$) measurements by polarized spectra of uniaxially stretched s-PS films, including planar guest molecules into the nanoporous crystalline δ phase, can allow an easy discrimination between in-plane and out-of-plane transition moment vectors of the guest.

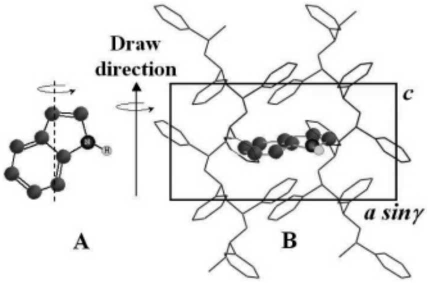

Figure 1. Schematic representation of the preferential orientation of a planar molecule (indole): (A) in the amorphous phase of uniaxially stretched polymeric films (B) in the cavity of the s-PS host δ crystalline phase (along *b* projection; for clarity of presentation, only the guest molecule is represented as sticks and balls). The arrows close to the draw direction emphasize that the stretched samples present a cylindrical symmetry.

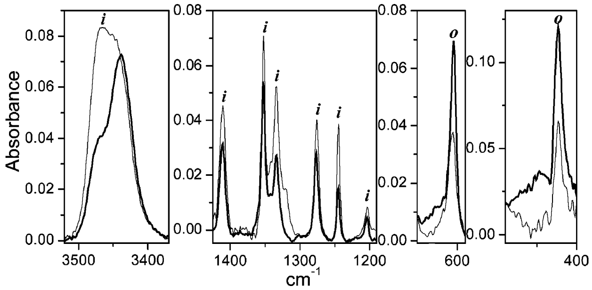

Figure 2. FTIR spectra of indole being guest of the nanoporous δ phase of uniaxially stretched s-PS films, taken with polarization plane perpendicular (thin lines) and parallel (thick line) to the draw direction. The spectra have been obtained by subtracting the polarized spectra of the polymer host. Due to the guest plane orientation nearly perpendicular to the draw direction (Figure 1B), in-plane (i) and out-of-plane (o) vibrational modes can be immediately identified.

Just as an example, the FTIR spectrum of indole molecules being guest (4.1 wt %) of the nanoporous δ phase of a uniaxially stretched s-PS films ($\lambda \approx 3$, $f_c \approx 0.9$), taken with polarization plane parallel (thick lines) and perpendicular (thin lines) to the draw direction are shown in Figure 2. The spectra have been obtained by subtracting out the polarized spectra of the polymer host. The reported spectral ranges are those with most relevant indole peaks and with negligible disturbance from the s-PS peak subtraction. Due to the guest plane orientation nearly perpendicular to the draw direction (Figure 1B), in-plane (i) and out-of-plane (o) vibrational modes can be immediately identified, since they maximize the absorption intensities for light polarization nearly perpendicular ($A_{\perp}$) and parallel ($A_{\parallel}$) to the stretching direction, respectively (see labeled peaks in Figure 2).

A detailed comparison between the FTIR peak positions (ν, cm^{-1}) and their relative dichroism (LD^r = LD/$A^{\text{isotropic}}$ = $3(A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$) for indole molecules being absorbed in the amorphous phase of stretched polyethylene[8] or in the crystalline δ phase of s-PS, is reported in Table 1. With the exception of the

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Table 1. FTIR Peak Positions (ν) and Their Relative Dichroism (LD^r) for Indole Molecules Being Absorbed in the Amorphous Phase of Polyethylene or in the Crystalline δ Phase of s-PS

ν, cm^{-1} PE[2e]	ν, cm^{-1} δ sPS	LD^r_{AM} PE[8]	LD^r_{CRYS} δ sPS	ν, cm^{-1} PE[8]	ν, cm^{-1} δ sPS	LD^r_{AM} PE[8]	LD^r_{CRYS} δ sPS
3490	3473	0.04	−0.71	1085	1090	0.10	−0.76
	3439		0.06	1064	1064	0.52	−0.35
1620	1620	0.44	−0.47	1010	1010	0.59	−0.41
1576	1578	0.10	−0.41	898	895	0.53	−0.36
1513	1511	0.07	−0.59	765	765	−0.47	1.35
1408	1410	0.60	−0.45		722		1.26
1352	1352	0.00	−0.45	607	607	0.07	−0.43
1332	1334	0.49	−0.53	602	604	−0.66	1.47
1275	1275	0.64	−0.49	572	572	−0.63	1.36
1243	1245	0.06	−0.61		424		1.23
1203	1203	0.02	−0.38				

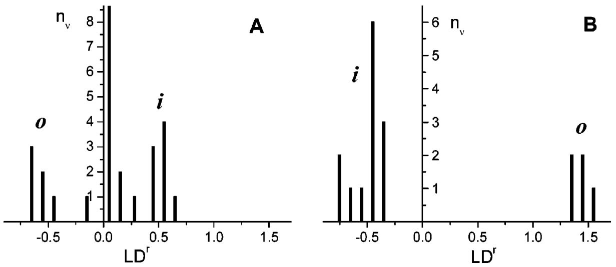

Figure 3. Histograms of the number of IR peaks (n_ν) versus linear dichroism (LD^r) for indole molecules absorbed in the polyethylene amorphous phase[8] (A) or in the s-PS δ crystalline phase (B).

highly sensitive N−H stretching region (3500−3430 cm^{-1}), the different guest environment does not change significantly the peak position. On the other hand, the observed dichroic ratios are strongly dependent on the guest orientation with respect to the draw direction.

This is clearly apparent by histograms of the number of IR peaks (n_ν) versus LD^r showing a poor (Figure 3A) or a clear-cut separation (Figure 3B) between in-plane and out-of-plane vibrations, for indole molecules absorbed in the polyethylene amorphous phase[8] or in the s-PS δ crystalline phase, respectively.

Of course, more accurate information can be achieved by collecting FTIR polarized spectra of a same guest for a set of s-PS films presenting different degrees of orientation of the host crystalline phase. In particular, for each guest peak, the order parameter $S = (A_\parallel/A_\perp - 1)/(A_\parallel/A_\perp + 2)$ can be plotted versus the orientation factor of the host crystalline phase (f_{host}, e.g., evaluated on the basis of the dichroic ratio of the 571 cm^{-1} peak).[7] This is shown, for instance, by the S vs f_{host} plots of Figure 4, for few representative FTIR peaks of four different planar guest molecules: benzene, mesitylene, naphthalene, and indole, presenting D_{6h}, D_{3h}, D_{2h} and C_s symmetries, respectively.

In the plots of Figure 4 positive and negative slopes correspond respectively to out-of-plane and in-plane vibrational modes, and the related symmetry species (explicitely indicated in the plots of Figure 4) can be immediately established.

It is worth adding that, from line slopes such as those of Figure 4, it is possible to evaluate the α angles between the transition moment vectors of the guests and the host chain axis (crystallographic c axis).[7] Moreover, on the basis of independent evaluation of the transition moment directions with respect to the molecular structure, more accurate information relative to the location of the guest molecule into the cavity of the s-PS δ phase can be achieved. Alternatively, if accurate information of the guest location is available, e.g. by X-ray diffraction structure characterization,[6] the transition moment vector directions with respect to the guest molecular structure can be determined.

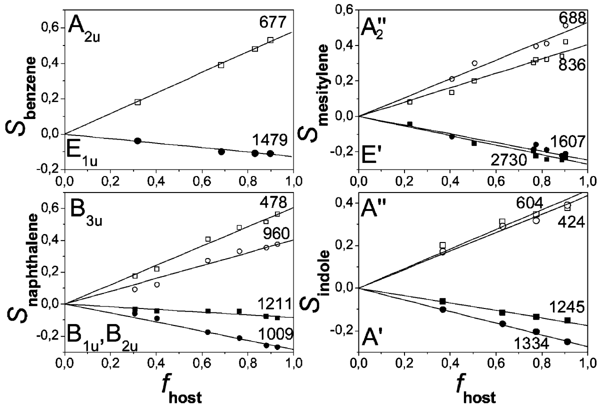

Figure 4. Infrared order parameter S vs the orientation factors of the host polymeric phase (f_{host}), for some vibrational peaks (cm^{-1}) of benzene, mesitylene, naphthalene and indole guest molecules.

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