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Solvent Evaporation Induced Liquid Crystalline Phase in Poly(3-hexylthiophene)

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S *Supporting Information*

ABSTRACT: We report on the evolution of the chain orientation of a representative π-conjugated polymer, poly(3-hexylthiophene) (P3HT), during the solution-casting process, as monitored using polarized Raman spectroscopy. These measurements point to the formation of a liquid-crystalline phase of P3HT solutions within a specific time period during solvent evaporation, which leads to a conducting channel. These conclusions are based on the angular dependence of polarized Raman scattering peaks, the anisotropy in the fluorescence background signal, analysis of the scattering-peak shape, and direct observations of the three-phase contact line in an optical microscope under crossed polarizers. These results shed new light on the evolution of chain alignment and thus materials nanostructure, specifically in solution-processed P3HT and more generally in π-conjugated systems. They may further enable the design of improved materials and processes for this important class of polymers.

Polymeric semiconductors are particularly attractive in that when appropriately functionalized, they offer process advantages via solution deposition for application to field-effect transistors (FETs).[1,2] Their use, however, is restricted to optoelectronic devices because of their relatively low charge mobility.[3−5] The limitation of charge mobility in polymer electronics is mostly due to both imperfect local order in microcrystalline domains and macroscopic barriers such as grain boundaries, which behave as defect sites for charge hopping.[6] As charge mobility strongly depends on the packing of chains, extensive research has been carried out to understand the structure−property relationships. This work has focused on parameters dealing with molecular weight,[7] regioregularity,[8,9] and processing using various solvents,[10] all of which affect the final morphology of the conjugated film, resulting in increased charge mobility. It has been reported that in the solution-casting process, these structural changes result from the behavior of polymer chains in the solvent during film formation,[11,12] and the resulting conformations of conjugated polymers in solvents play a crucial role in determining the electrical properties. Nevertheless, a coherent picture of the formation of the conducting channel in organic FETs and the role of polymer relaxation in the solution process is incomplete.[13]

In a separate study,[14] we elucidated the process of conducting channel formation via drop-casting by measuring the drain current of a two-point-contact field-effect transistor (FET) as a function of solvent evaporation time. The evolution of the drain current with the deposition of solutions of poly(3-hexylthiophene) (P3HT) in various solvents having different boiling points presented an interesting result: it was found that the drain current increases abruptly to its maximum value and gradually decreases before leveling off. (Drain current data can be found in the Supporting Information.) This result suggests that the chain orientation of P3HT evolves with solvent evaporation and time.

In the present work, in an effort to understand the evolution of electrical properties in terms of the molecular characteristics of the P3HT film, we used polarized Raman spectroscopy to monitor the change in the orientation of the polymer chains as the solvent evaporated. In our study, regioregular head-to-tail P3HT was used in a high-boiling-point solvent, 1,2,4-trichlorobenzene (TCB), for accurate monitoring of the orientation of polymer chains with time. We utilized in situ polarized Raman spectroscopy to provide insight into the characteristic phase behavior by analyzing the peak positions and peak shapes of the normal-mode vibrations that are invariably affected by an underlying phase transition. The development of orientation of P3HT chains during film formation was monitored by recording the polarized Raman spectra as a function of the angle θ between the arbitrary direction of the long-chain backbone and the polarization direction of the incident light by rotating the sample stage. (Details of the experiments are described in the Supporting Information.)

Figure 1 shows the Raman spectra of P3HT as a function of θ, an angle between the incoming polarization direction and the arbitrary direction of the long-chain backbone, obtained 660 min after deposition of the solution on a substrate. The peaks at 1443 and 1378 cm^{-1} are attributed to the C═C and C−C stretching vibrations in the thiophene ring, respectively.[15−18] It is clear from the angular dependence of the intensities of these Raman peaks that P3HT chains have anisotropic ordering. Other evidence of the anisotropic nature of the P3HT chains comes from the observation that the fluorescence background of the Raman spectra also displays a strong angular dependence.

It was only for the period of approximately 630 to 720 min after solution deposition that we were able to detect the angular dependence in the polarized Raman spectra relative to the entire elapsed time during which measurements were obtained (0−1200 min). It is noteworthy that in all of the spectra showing angular dependence, we could detect characteristic peaks of pure solvent that were distinct from those of pure P3HT. In particular, the peak at 667 cm^{-1} attributed to the C−Cl stretching mode of 1,2,4-TCB[19] can be clearly seen in those spectra (see the peaks marked by

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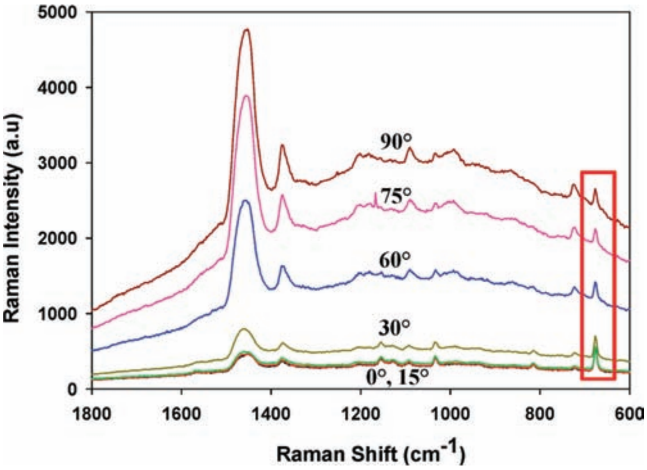

Figure 1. Polarized Raman spectra measured 660 min after deposition of the solution at room temperature. Spectra were consecutively recorded as a function of the angle θ between the incoming polarization direction and the arbitrary direction of the long-chain backbone at 15° intervals. Peaks within the red square at 677 cm^{-1} are attributed to the C−Cl stretching mode of 1,2,4-TCB.

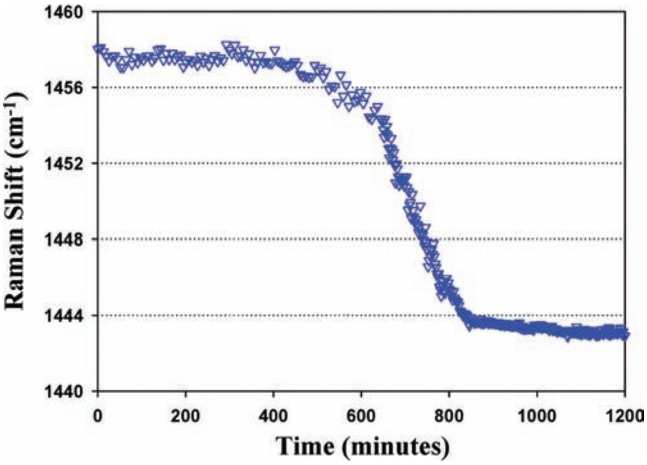

Figure 2. Variation of the frequency assigned to C═C stretching in the thiophene ring as a function of evaporation time.

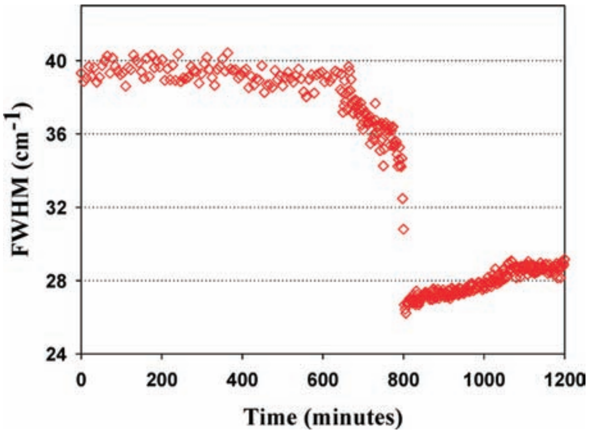

Figure 3. Time evolution of the FWHM of the Raman peak assigned to C═C stretching in the thiophene ring.

the red square in Figure 1), which implies that a non-negligible amount of solvent remained. No angular dependence was discernible before the time period noted above, which is evidence of considerable mobility of the polymer chains in the solution up until this time. At longer times, it is thought that continued solvent evaporation produces polycrystalline states consisting of nanoscale domains among which a large distribution of crystal orientations arises.[20] Accordingly, the anisotropic nature of the nanoscale domains was statistically averaged out because the polarized intensities were recorded from a micrometer-sized area (the diameter of the focused laser spot was 15 μm). (Representative spectra from outside the 630 to 720 min period are shown in the Supporting Information.) On the basis of the evolution of the anisotropic nature of the polarized Raman spectra (connoting long-range orientation of the P3HT chains) and the considerable quantity of residual solvent as judged by the characteristic peaks of 1,2,4-TCB, we propose the possibility of a phase transition from an isotropic solution state to a liquid-crystalline phase followed by evolution of the solid state consisting of nanoscale crystalline domains as the solvent further evaporates.

The existence of a liquid-crystalline phase during solvent evaporation is supported by P3HT backbone peak analysis: the vibrational features observed for structural units in molecules are significantly affected by the presence of intermolecular interactions, and interchain interactions in π-conjugated systems such as P3HT induce a change in the extent of $\pi-\pi$ overlap.[21,22] It has been elucidated that the vibrational frequency of the C═C stretching mode of the thiophene ring is the principal feature supporting extended conjugation in thiophene-based conducting materials.[16,17,23] In this respect, the variation in peak frequency of the C═C stretching mode is an effective indicator of the presence of P3HT backbone interactions. Figure 2 presents the time evolution of this vibrational frequency, showing that the peak frequency of this band gradually decreased by 15 cm^{-1} during the transition from the isotropic solution state (1458 cm^{-1}) to the fully dried film state (1443 cm^{-1}). Such a frequency shift can be interpreted as the extension of conjugation upon solvent evaporation, on the basis of reported results indicating that the position of the Raman band associated with C═C stretching is very sensitive to the extent of conjugation and that its wavenumber decreases as the conjugation is extended.[16,23] The variation in the extent of conjugation arises from strong interactions between neighboring chains as they begin to order into a closely packed structure. The damping effect that tends to reduce the oscillations as a result of strong interactions between neighboring chains is likely responsible for the shift to lower frequency.[24] A distinctive characteristic of the frequency shifts, therefore, may show the change in the magnitude of intermolecular interactions between different phases. It should be noted that the time duration for a significant change in frequencies to occur is in agreement with the time scale for detecting the anisotropy in the polarization intensities of Raman scattering.

The time evolution of the full width at half-maximum (FWHM) in a discontinuous fashion during the same time frame, as depicted in Figure 3, provides additional indirect evidence of a phase transition. A significant increase in peak width for a polymeric system is observed when the chain conformation changes from a well-defined ordered state to a random state. This occurs because the structure of disordered chains encompasses a broad distribution of chain conformations, and thus, their vibrational transitions have broad bandwidths. Therefore, the gradual decrease in

FWHM as evaporation proceeds can be rationalized by the fact that the interdigitating side chains force the P3HT backbone thiophene rings to be planar as the packing density increases via solvent evaporation. In contrast, in the dilute-solution state, internal twisting about ring-to-ring bonds may induce a deviation from planarity, thereby producing a structural disorder of the thiophene rings. This torsional mode may break up the long $\pi-\pi$ overlap[25] and broaden the bandwidth because of the large distribution of the extent of the width of the band. Therefore, the decreasing slopes observed upon solvent evaporation (Figures 2 and 3) represent a different state associated with the evolution of vibrational behavior with time, which characterizes a phase behavior distinct from that for either an isotropic solution or the crystalline state, namely, that of a liquid crystal.

These peak analyses, combined with the anisotropic nature of the peak intensity, provide firm evidence of a plausible model involving phase transitions from an isotropic solution to a liquid-crystalline phase and then to a polycrystalline phase via irreversible solvent evaporation. In order to evaluate the possibility that the system undergoes a phase transition to a lyotropic liquid-crystalline phase, we attempted to observe the perimeter area of a droplet under a polarized-light microscope, where we were able to detect the anisotropic nature in the polarized Raman spectra. It is well-known that when a drop of solution dries on a solid surface, the solute molecules are driven to the edge of the three-phase contact line, where the concentration of the solute increases,[26,27] and at a critical concentration, solutes with anisotropic shapes can form a liquid-crystalline phase.[28] Under crossed polarizers, one observes regions that display optical anisotropy, which may result from P3HT chain alignments, and this observation convinced us of the possibility that solution-processed P3HT can exhibit a liquid-crystalline phase (see the Supporting Information).

Liquid-crystalline ordering of P3HT chains during film formation may enable us to design improved materials having high charge mobility, since the liquid-crystalline phase possesses long-range orientational order and the capacity for self-healing (i.e., repair of structural defects), in contrast to the crystalline phase.[29,30] We are unaware of any study that has reported a lyotropic liquid-crystalline phase in the P3HT system at room temperature. Hence, our result will open a new paradigm for creating a long-range-ordered structure with fewer defects in a simple, controllable, and cost-effective manner via solvent-evaporation-induced self-assembly under external field to maintain the well ordered polymer chains even in a fully dried state. Despite the fact that we successfully detected the same trend of time evolution of peak shape and anisotropic nature in polarized Raman spectra from five separate trials, it should be noted that experimental factors such as the evaporation rate and the initial amount of solute in a given droplet of different volume may result in different time scales for the phase transition from one sample to the next. For instance, in the case of a higher evaporation rate under stronger air circulation, the isotropic solution may undergo the phase transition to the liquid crystalline phase earlier than 630 min, and the time duration when the sample exhibits the liquid crystalline phase may be shorter. In an effort to better understand these dynamic phenomena, systematic studies of the film formation mechanism and control of relevant experimental factors needs to be carried out.

In summary, we have used polarized Raman spectroscopy to demonstrate that P3HT can form a lyotropic liquid-crystalline phase beyond a critical concentration via solvent-evaporation-induced self-assembly. These phase transitions can be clearly understood by analyzing the vibrational frequency and bandwidth (FWHM) as the material changes from an isotropic solution to a solidified film. The gradually decreasing region in the evolution of the vibrational frequency and FWHM of the C=C stretching mode in the thiophene ring is attributed to the liquid crystalline phase intermediate between the isotropic solution and the solidified crystalline phase.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details concerning the sample preparations, in situ drain current mobility, polarized Raman spectra of P3HT in solution and their peak assignments, polarized optical microscopy images at the edge of the three-phase contact line of the droplet, and complete ref 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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