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The Evolution Study Of Thin Film Structure During The Film Formation

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Although it has been well known that the role of polymer relaxation in solvent plays a crucial role in the structural changes of conjugated polymer film^{1,2,3} [30,33,35], a coherent picture of film formation in the solution process is not complete. In this study, we report the behavior of conjugated polymer chains, poly(3-hexyl thiophene) (P3HT) in a solvent during film formation and the chain orientation of polymer chains on the deposition methodology using polarized Raman spectroscopy. We observed the time evolution of structural anisotropy of P3HT films with 1,2,4-trichlorobenzene as a solvent and found that directional preference of P3HT chain alignments changes as a function of time during solvent evaporation. It was found that no structural anisotropy was detected either before or after this duration. (Figure 1)

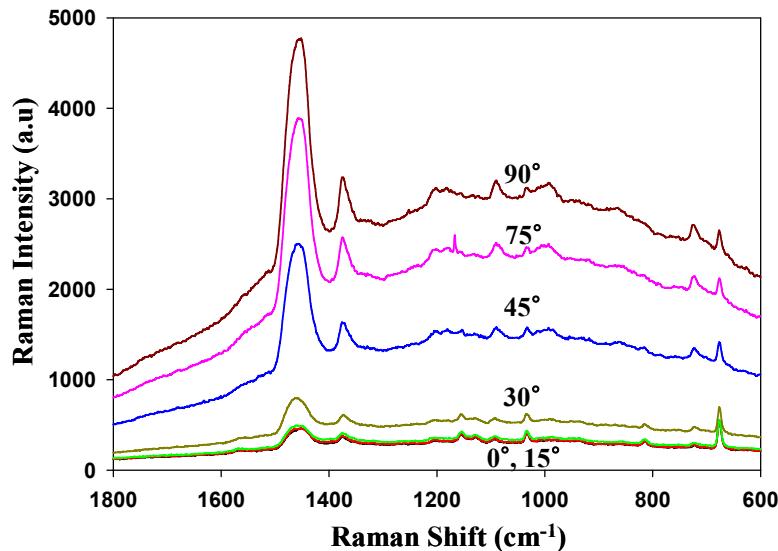


FIGURE 1. This Polarized Raman spectra measured after 10hours and 45minutes since we dropped solution. The spectra were taken as function of samole rotating angle angle between the incoming polarization and (100) direction of silicon wafer with 15° intervals.

This evolution of anisotropy of chain orientation indicates the possibility of a phase transition, likely to a liquid crystalline phase. Peak profile analysis of Raman spectra was performed to elucidate the phase behavior. The variation of peak frequency of the C=C stretching vibration in the thiophene ring is one of the indicators of the structural ordering of P3HT backbone chain. Remarkable characteristic of the frequency shifts was monitored, which indicates the evidence of the change of the conjugation length. Besides, the full width a half maximum (FWHM) changes in a discontinuous fashion during the same time frame when the stretching frequencies shift, indicative of a phase transition as well.

The information of conformational order in this study addresses the question of whether conjugated polymer film by solution-casting can have nematic ordering with non-separable anisotropic interactions where mean field theory predict ordering. As a result we propose a plausible mode of phase transition from isotropic solution to liquid crystalline phase followed to crystallization by dynamic-assembly via irreversible solvent evaporation for the first time.

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