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Exploiting interfacial polarization to detect phase transitions in dilute solutions: Crystallization and melting of P3HT in toluene down to ppm contents

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ABSTRACT

Determination of phase diagrams of polymer solutions with conventional techniques, like differential scanning calorimetry (DSC), is limited to sufficiently high concentrations due to a low signal/noise ratio. Controlling the nanoscale morphology formation upon solution processing of dilute conjugated polymer solutions however requires this information. In this work, we introduce an experimental methodology able to detect phase transitions in solutions over a wide concentration regime, by means of dielectric spectroscopy. We tested the validity of our method for solutions of poly(3-hexylthiophene) in toluene. Apart from providing crystallization and melting temperatures consistent with DSC data for the overlapping sample concentrations, our method turned out to be able to detect phase transition down to trace level mass fractions as low as 10 ppm.

1. Introduction

Poly(3-hexylthiophene) (P3HT) is a conjugated polymer widely used in the active layer of organic field effect transistors [1,2] and solar cells [3,4]. The final yield of these electronic devices strongly depends on the nanoscale morphology of the active layer [5], which is influenced by parameters like regioregularity [6] and molar mass [7] of its components as well as solvent of choice [8], and annealing conditions [9]. Increasing efficiently the performance of conjugated polymer electronics thus requires the knowledge of the phase behavior of the polymer in solution from the concentrated down to the dilute regime (~ 1 wt%), i.e. the starting point for layer deposition. Techniques like differential scanning calorimetry (DSC) and scattering methods fail at determining transition temperatures for mass fractions smaller than ~0.01 because of a low signal/noise ratio (SNR); on the contrary, due to saturation effects, optical methods encounter difficulties with more concentrated solutions [10–12].

In this Communication we introduce an experimental methodology able to detect phase transitions in solutions over a wide concentration regime by means of dielectric spectroscopy (DS). At the state of the art, this technique allows characterization of molecular relaxations and crystallization events in bulk melts [13–17], in concentrated solutions [18], under elevated pressures [19–21] and in confined geometries [22,23]. Our approach is based on the temperature dependence of localized fluctuations of the dielectric constant and the conductivity within the solution. Aggregation of molecules at distances exceeding the path over which mobile charges screen out the effects of external electric fields (Debye length, l_D) provokes interfacial polarization events affecting the apparent value of the dielectric constant.

Following Jonscher "universal" law [24,25], such a polarization grows with the inverse of the frequency, allowing an accurate detection of molecular reorganizations at crystalline contents lower than those detected by DSC.

2. Experimental section

2.1. Materials

Poly(3-hexylthiophene) (Plexcore OS1100, $M_w = 49800\ \mathrm{g\ mol^{-1}}$, PDI = 1.49 (GPC with PS standards in $CHCl_3$), RR = 96% (NMR), data

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as provided by the supplier, Plextronics) was mixed with toluene (HPLC grade 99.8%, Acros).

2.2. *Experimental methods*

Dielectric spectra in a frequency range from 10^6 Hz to 0.1 Hz were measured in isothermal conditions between 60 °C and −50 °C, at an effective scanning rate of 0.2 °C $\min^{-1}$, with an Alpha High Resolution Analyzer (Novocontrol Technologies). Solutions were sealed in a parallel plate cell for investigation of liquids to avoid evaporation during experiments.

Differential scanning calorimetry was performed with a DSC-7 (PerkinElmer) TAC 7/DX. Samples were placed in stainless steel capsules and subjected to the following temperature profile: isothermal 10 min at 80 °C, cooling ramp at −10 °C $\min^{-1}$ to −30 °C, isothermal 10 min and heating ramp to 80 °C. Crystallization (T_c) and melting temperatures (T_m) were respectively determined as the onset of the exothermic and end point of the endothermic peaks.

3. Results and discussion

The temperature dependence of the dielectric constant (ε') for solutions containing mass fractions of P3HT ranging from 0.05 to 10^{-5} is shown in Fig. 1. Blue and red lines correspond to values of ε' respectively obtained during cooling and subsequent heating scans; the response of pure toluene, appearing as a constant background over the whole temperature range investigated, is given in black.

Measurements on even more dilute solutions suffered from the increasing susceptibility to contaminations (e.g., from cell, sample preparation) that might alter the crystallization kinetics. We could promptly recognize contaminated samples, as the value of their dielectric constant at low and high temperatures deviated significantly from a flat response, see the lowest panel of Fig. 1. Nevertheless, regardless the reduction of the polarization intensity, analysis of isochronal plots at lower frequencies provides enough SNR to clearly observe transition phenomena at these extremely low concentrations.

During cooling, the temperature dependence of ε' shows a frequency independent maximum in correspondence to the onset of crystallization measured by DSC, T_C (blue rectangle in Fig. 1).

The reduction of ε' at lower temperatures could intuitively be ascribed to the immobilization of polymer chains and a decrease of the (mobile) dipole density in the samples, as expected during crystallization and observed in dry samples [14,22]. However, such a simplified picture cannot capture the enormous increase of the dielectric constant starting already 15 °C before the onset of the exothermic peak in the calorimetric runs. The increase of ε' preceding T_C suggests that this method is able to detect changes affecting the

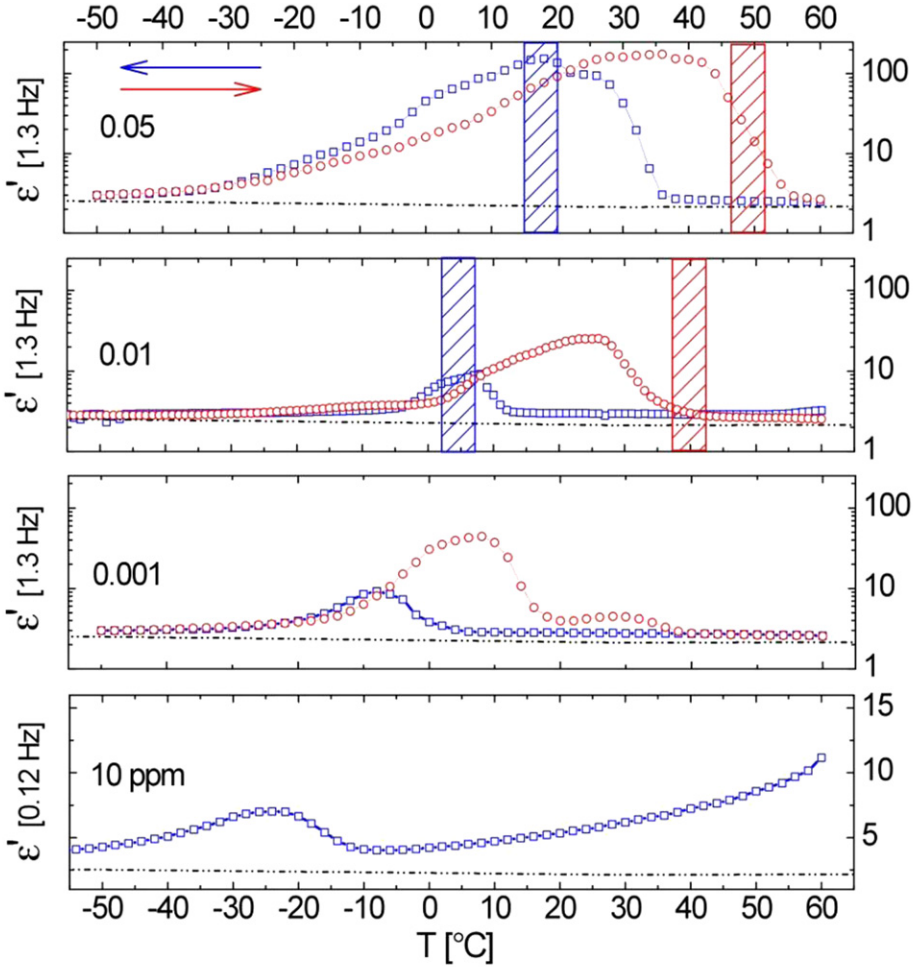

Fig. 1. Temperature dependence of the dielectric constant ε' for solutions containing different mass fractions of P3HT in toluene. Cooling runs are represented in blue while subsequent heating scans are plotted in red. The measured dielectric response of pure toluene is given as a black dashed line. Similar transition temperatures are observed in the temperature dependence of the conductivity and of the dielectric loss (see Supporting information). Dashed rectangles indicate the transition temperatures measured by DSC, and their width includes the uncertainty (±2.5 K) due to the different scanning rate used.