

Nanorheological approach for characterization of electroluminescent polymer thin films

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Shear-modulated scanning force microscopy (SM-SFM) is introduced as a nanorheological characterization method for the determination of optoelectronic properties of semiconducting polymer thin films (<100 nm). In this letter, the photoluminescence quantum efficiency of poly(*p*-phenylenevinylene) (PPV) was directly correlated to the glass transition property by SM-SFM. Conformational changes and chain packing were discussed as a function of the conversion temperature of the soluble PPV precursor. Compared to the bulk, very low glass transition temperature values in the range of 65 to 85 °C were found, which imply an increased molecular mobility in thin films of conjugated polymers. © 2003 American Institute of Physics.

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Over the past decade, advances in material synthesis have made conjugated polymer semiconductors very attractive for optoelectronic devices, such as light-emitting diodes (LEDs).¹ Conjugated polymers are attractive in part because of their unique mechanical and rheological properties compared to inorganic semiconductors. Polymers often exhibit unique rheological properties if spatially confined in thin films on the order of 10 to 100 nm thickness,^{2,3} which can lead to very unique optoelectronic properties (e.g., voltage-tunable reversible color changes in LEDs).^{4,5} Although the electronic, photonic, and electroluminescent (EL) properties of conjugated polymers, such as poly(*p*-phenylenevinylene) (PPV) have been extensively investigated, very little is currently known about their rheological and mechanical properties, particularly the relationship of these to the electronic and photonic properties.^{6–8} This is due to the inability of currently employed techniques, such as differential scanning calorimetry, to probe the nanoscale mobility in ultrathin films of EL materials. Because key processes in electroluminescence, such as exciton formation and charge carrier transport occur on a length scale of 10 nm,⁹ and are influenced by the molecular configuration and the supramolecular structures,^{8,10} the molecular mobility becomes particularly important for thin polymer films, where unique interfacial rheological properties are observed.^{3,11} In this letter, we investigate the molecular mobility using shear-modulated scanning force microscopy (SM-SFM). Local relaxation processes in thin films of PPV, in particular the glass transition values, are compared to the photoluminescence (PL) quantum efficiency.

Thin films (80–100 nm) of a PPV sulfonium precursor, which contain tetrahydrothiophenium leaving group, were

prepared by spin-coating at 1000 rpm. The substrate surfaces, 4-in. silicon wafers [(1,1,1)-oriented, Mitsubishi Silicon America], were prepared by rinsing sequentially with acetone and methanol. The spin-coated sulfonium precursor on silicon wafers yielded a series of samples, which were individually converted into PPV [see Fig. 1(a)] at different but constant conversion temperatures in a vacuum oven (Sun Fire 10Plus, J. M. Ney Co., <10 Torr). The temperature was changed at a rate of 10 °C/min starting from 100 °C. The conversion temperatures were kept for 25 min. A cooling rate of 40 °C/min was employed. To avoid photoinduced conversion and/or degradation, spin coating and conversion were performed in a dark room. The film thicknesses were determined by profilometry (Sloan Dektak 3030, Veeco Instruments, Inc.) at 0.1 N and a resolution of 0.1 nm for a 6500-nm-thick film.

Thermally induced rheological transitions (e.g., glass transitions) of PPV thin films were determined by the SM-SFM at ~10% relative humidity.^{12,13} The SM-SFM system involves a SFM system (Explorer, Veeco Instr.) in a non-scanning fashion with applied sinusoidal shear modulation provided by a digital function generator (DS345, Stanford Research Systems), a heating cooling system (K-20, MMR Technology), and an elaborate custom-designed control system written in LABVIEW (National Instrument). The SM-SFM method involves a nanometer sharp SFM cantilever tip (NanoSensors from NanoWorld GmbH, normal spring constant of 0.129 N/m) that is brought into contact with a polymer surface as sketched in Fig. 1(b). The SM-SFM system was calibrated on polystyrene prior to these experiments. The high accuracy of the method for glass transition (T_g) determination is well documented.^{12–14} The probing depth of the SM-SFM is on the order of 1 nm.

Constant loads of 150 nN were applied, and the probing

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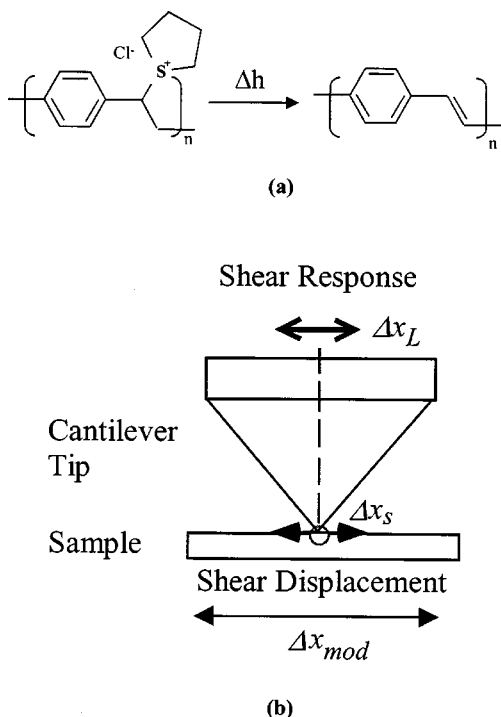


FIG. 1. (a) Thermal conversion of PPV from its sulfonium precursor. (b) Schematic of the SM-SFM. The sample is sinusoidally modulated (Δx_{mod}) relative to the probing cantilever tip. The shear response (Δx_L) is a qualitative measure of the contact stiffness (a convoluted expression of the combined shear modulus and the contact area). The contact stiffness is represented by the sample deformation Δx_S , and is directly obtained by the cantilever response Δx_L , with $\Delta x_{mod} = \Delta x_L + \Delta x_S$.

tip laterally modulated (with a nanometer sinusoidal amplitude that guarantees no relative probe-sample slippage), while the temperature was increased stepwise by 2 °C. At each temperature step the system was kept idle until thermal equilibrium was confirmed before any viscoelastic responses were recorded with a dual phase lock-in amplifier (Stanford Research Systems, SP830DSP). The recorded response amplitude, which is a measure of the contact stiffness,¹³ was then plotted versus the temperature. T_g values were determined from “kinks” in the response curve, as illustrated in Fig. 2 for a sulfonium precursor to PPV conversion at 175 °C.

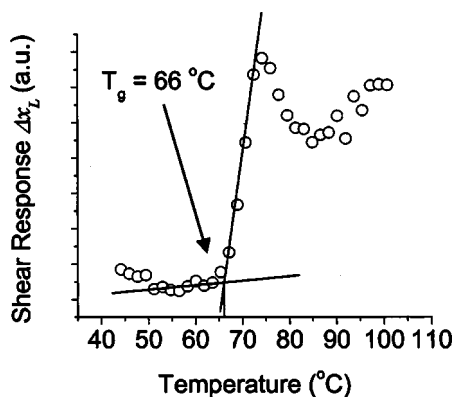


FIG. 2. Representative thermal-rheological SM-SFM plot of PPV at a conversion temperature T_{conv} of 175 °C. At T_g , the contact area increase dominates the modulus decrease of the polymer. Thus, the contact stiffness increases above T_g until the transition process is complete.

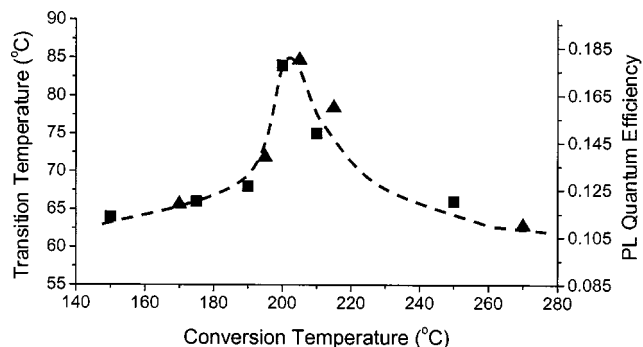


FIG. 3. Qualitative comparison of the PL efficiency (▲) (see Ref. 7) with the rheological transition (■) as function of the PPV conversion temperature. The rheological transitions were measured with the SM-SFM method. A dashed line has been added for trend enhancement.

Glass transition values, as determined in Fig. 2, are plotted in Fig. 3 as function of the conversion temperature T_{conv} . The T_g relaxation process is found to be strongly conversion-temperature dependent, which confirms the experiments by Wery *et al.*¹⁵ It is important to address the low transition values between 65 to 85 °C found in our thin-film experiments. Wery *et al.* also reported low transition temperature values at certain conversion temperatures,¹⁵ which are in contrast to the high transition values, of over 200 °C, found in PPV bulk systems.^{15,16} The implication of decreased transition values is an increased molecular mobility. In a system that is not well equilibrated, such as spin-cast thin films of “bulky” polymers, an increase in molecular mobility can lead to enhanced undesired conformational changes in the polymer matrix (e.g., π -stacking).¹⁷ Such conformational changes can result, for instance, in the loss of the spectral stability or, thus, in a decrease of the PL efficiency.¹⁸

The qualitative correspondence of the rheological relaxation process at T_g with the PL efficiency¹⁹ determined by Morgado *et al.*⁷ is also documented in Fig. 3. The optimum PL efficiency or maximum glass transition value, obtained at around 205 °C, divides the data set into two regimes.

In the lower temperature regime ($T_{conv} < 205$ °C) one could argue that it is the incomplete PPV conversion that is responsible for a low PL efficiency. Unconverted polymer chains shorten the conjugation length, and the residual byproduct, for instance, from the conversion reaction acts as quenching sites through a heavy-atom mechanism (spin-orbit coupling between exciton and sulfur atom), which in turn negatively impact the PL efficiency.^{20–22} It is also to be noted that the PPV conversion is complete in the bulk system at around 160 °C.²³

The rheological data suggest that with the improved conversion, significant conformational changes in the material occur. This is in correspondence to findings that significant geometrical rearrangements are required for the polymer chains to achieve a delocalized conjugated segment.²¹ The π -delocalization over adjacent aromatic rings, which increases the conjugation length and segmental stiffness, increases the activation energy for the T_g relaxation process. The degree of molecular rearrangement as function of the conversion temperature is also noticeable in the measured film thickness, Fig. 4. The thickness is found to steadily increase for $T_{conv} < 205$ °.

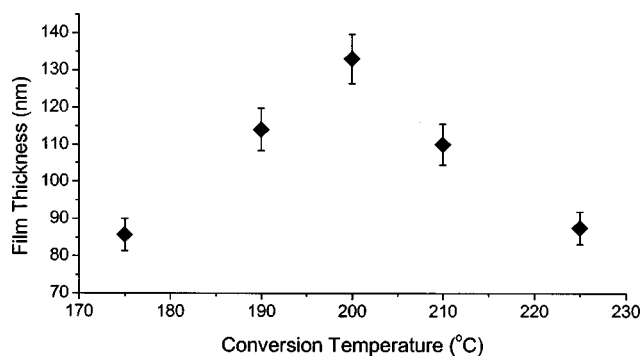


FIG. 4. PPV film thickness as a function of the conversion temperature determined by profilometry.

In the upper temperature regime ($T_{\text{conv}} > 205^\circ\text{C}$), oxidative degradation processes, such as the formation of carbonyl groups,^{7,24} and aggregation processes due to crystallization²⁵ reduce the PL efficiency. Since oxidative degradation occurs by breaking the vinylene π bond, it consequently increases the flexibility of the backbone chains, which is known to decrease the value of T_g .²⁶ Thus, the decrease in T_g with increasing T_{conv} above 205°C , can be interpreted as enhanced oxidation in the film. To what degree crystallization is impacting the T_g value is still unknown. The thickness-conversion temperature plot in Fig. 4, suggests that in the upper-conversion-temperature regime, significant reorganizations in the film occur that can be attributed to crystallization, which in turn depresses the PL efficiency.

In summary, we have introduced a thin-film characterization method, the SM-SFM technique, which provides fundamental insight into an EL polymer from a nanoscopic structural rheological perspective. Although this work focused on a very particular material and process, the SM-SFM method shows great potential wherever thin polymer films are used in optoelectronic devices. We showed that relaxation processes in PPV are strongly linked to the PL efficiency. Important material properties for the LED performance, such as polymer chain rearrangement, structuring, and oxidative degradation can be predetermined or fundamentally linked to the PL efficiency with the SM-SFM technique. In view of increasing advances in plastic optoelectronics with even thinner films or nonhomogeneous systems (e.g., blends), utilizing exotic mesoscale properties, a nanorheological technique that analyzes the actual system is important. To address quantitative relationship between rheological and optoelectronic properties, our ongoing effort involves spectrum analysis of the response signal of the SM-SFM method, which should provide critical barrier heights of rheological transitions.

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