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Supramolecular Aggregation in Bulk Poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene)

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Introduction. Electroluminescence (EL) properties of conjugated polymers have received widespread interest since 1990.[1] A vast amount of effort was made on modification of chemical structure for purposes of color tuning or improvement of device performance.[2] More recently, morphological effects in the light-emitting behavior of a representative conjugated polymer, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), have attracted some attention. This polymer has been considered as amorphous, with a glass transition (T_g) in the vicinity of 65 °C.[3,4] A growing number of evidences have generally suggested the presence of "aggregate emission" (at wavelength λ_{em} = ca. 640 nm) in solution-cast MEH-PPV films, which competes with single-chromophore exciton emission (λ_{em} = ca. 580 nm) and low-efficiency excimer emissions (λ_{em} = ca. 700 nm or higher).[4−11] The term "excimer" refers to a neutral excited state shared between multichain segments in the absence of ground-state electron orbital overlap whereas "aggregates" have both the ground state and the excited state delocalized between multichain segments. These "aggregates", already in existence in solutions above a moderate concentration threshold (on the order of 1% or less), may survive the film forming process (typically spin-coating) and affect significantly the light emission[4,7,8] by the generation of interchain species that compete with the single-chain exciton.[5−9] The "aggregation" in solution has previously been rationalized in terms of solvency power,[7] although its exact physical identity is still a subject of controversy.[11] Nevertheless, as emission from interchain species may be strongly enhanced after long-term annealing at an elevated temperature (i.e., several hours at 215 °C) *after* film formation,[6] there arises a distinct possibility for the existence of a thermodynamically favored way of molecular packing in the bulk state. This would also be consistent with recent observations of increased optical heterogeneity in the submicron scale and decreased hole mobility upon heat treatment.[10] Reported in this communication are our experimental findings that MEH-PPV is in fact mesomorphic in nature, with the tendency to form supramolecular assemblies with primitively layered structure (i.e., of smectic order) and yet maintaining its nematic-like optical texture upon heat treatment in the temperature range of 200−260 °C. Similarities in ultraviolet−visible light absorption and photoexcited emission behavior of heat-treated MEH-PPV as compared to reported aggregation effects in solution processed films appear to imply that the aggregates formed in solutions and the thermally induced supramolecular assemblies in the bulk state are structurally similar in terms of spatial arrangement of chain segments.

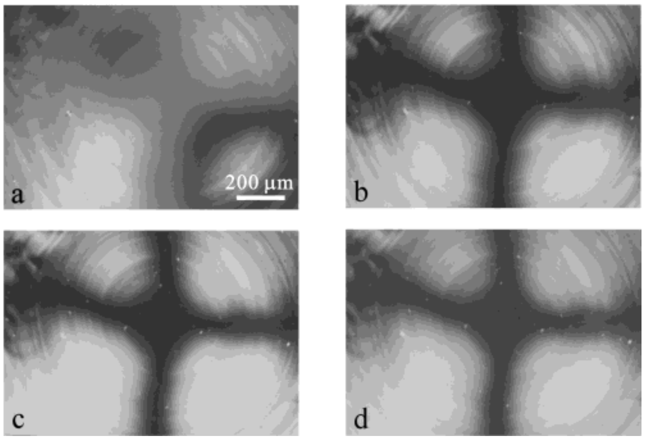

Figure 1. Polarized light micrographs of solution-cast MEH-PPV film at a fixed heating/cooling rate of 20 °C/min in the temperature range of ambient to 300 °C: (a) as-cast film at room temperature; (b) heated to 100 °C, (c) 180 °C, and (d) 260 °C before passing the isotropization temperature of 290 °C. During cooling from 300 °C, the optical texture and the thermochromism were reversibly observed.

Experimental Section. Poly(2-methoxy-5(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV, chemical structure given as inset in Figure 4a) was synthesized via the Gilch method following in general the procedure reported by Wudl et al.[12] Polarized light microscopic (PLM) observations were made by use of a Nikon Optiphot-Pol microscope equipped with a temperature-controlled stage. A Siemens D5000 diffractometer equipped with a copper target (Kα line, with wavelength λ = 0.154 nm), a graphite collimator, and a standard sample holder was used to obtain 1-D ("powder") X-ray diffraction (XRD) profiles at room temperature under a step-scan rate of 0.05° per 2 s in the scattering angle range of 2θ = 1°−41°. Transmission electron microscopic (TEM) studies were performed using a JEOL 3010 instrument under an acceleration voltage of 150 kV. Optical absorption (UV−vis) and photoluminescence (PL) spectra of the film specimens were obtained by use of a LabGuide USB2000 instrument.

Film specimens were drop-cast from toluene solutions on a quartz or glass substrate. Routine drying (ca. 4 h at 80 °C under vacuum) and heat-treatment (5 min at an elevated temperature under a protective stream of nitrogen, followed by fast cooling to room temperature) procedures were typically adopted to follow the thermally induced structural change or its effects on absorption/emission behavior. Oriented films were obtained via manual shearing at ca. 230 °C, followed by fast cooling to room temperature. For TEM studies, specimens were detached from the substrate using aqueous HF solutions and shadowed with platinum.

Results and Discussion. Given in Figure 1 is a series of optical micrographs taken during heating and subsequent cooling of MEH-PPV. The optical texture is clearly nematic-like, with reversible thermochromic changes (from orange-red to orange-yellow) upon heating toward or cooling from its isotropization temperature (T_i) around 290 °C. For poly(9,9-dihexyl- *2,7*-fluorene) (PdHF) with comparable level of side-chain

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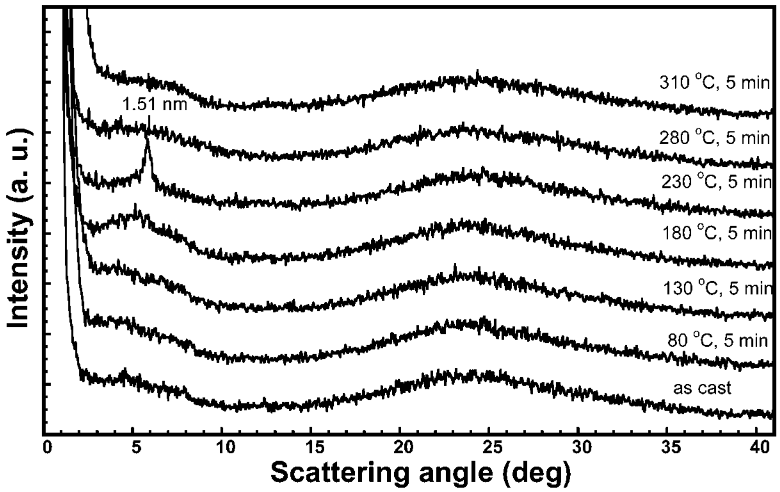

Figure 2. XRD profiles of solution-cast MEH-PPV film upon fast cooling to room temperature during a sequence of 5 min heat treatments at stepwise increased T_a.

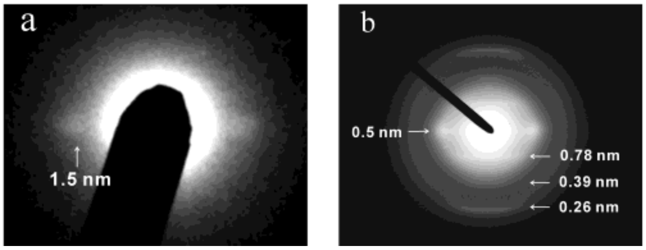

Figure 3. Selected-area electron diffraction patterns of shear-oriented specimens (with the shear direction parallel to the meridian) showing (a) equatorial first-order spots corresponding to layer spacing of 1.5 nm and (b) equatorial third-order spots of the layered structure and meridional streaks corresponding to dimeric registering in the direction of shear.

grafting (i.e., one hexyl substituent per backbone phenylene), a similar T_i range of 290−300 °C has been reported.[13] Note also the (reversible) change in the dark Maltese-cross pattern from room temperature to 100 °C, indicating effects of thermal stress. This is consistent with previously reported[3,4] T_g of 65 °C or the assignment of 80 °C (at the mid-transition point) from our own DSC analysis (not shown here).

Given in Figure 2 are XRD powder profiles of a piece of MEH-PPV film upon fast cooling to room temperature after short-term heat treatments under nitrogen protection at increasingly higher temperatures. The XRD profiles remain featureless for $T_a \leq 130$ °C, which explains for the earlier belief of MEH-PPV being amorphous. Interestingly, discernible changes may be identified in the scattering angle range of $2\theta = 4°-8°$ for $T_a = 180$ °C. After heat treatment at $T_a = 230$ °C, a clear peak emerges in the vicinity of $2\theta = 6°$ with a *d* spacing value of 1.51 nm, indicating some form of long-range nanoscale modulation. The ordered structure dissipates after annealing at 280 °C or above, consistent with our identification of $T_i =$ ca. 290 °C.

Given in Figure 3 are selected area diffraction patterns obtained from a sheared (right after the 5 min annealing at 230 °C before fast cooling to room temperature) TEM specimen, from which not only the main reflection at 1.5 nm (Figure 3a) but also the third-order reflection at 0.5 nm are identified along the equator. The structure is therefore consistent with layered morphology, in which in-plane backbones are aligned to give nematic-like texture under cross-polarized light. The meridional arcs of 0.78, 0.39, and 0.26 nm in *d* spacing suggest dimeric repeats (as the fully extended monomer size is only ca. 0.64 nm), which tilt from the mean direction of alignment by an angle of ca. arccos(0.78/1.28) = 52°. Note that the horizontal streaking of the first meridional arc implies the presence of stacking faults parallel to the mean backbone axis.[14] More detailed structural analysis is currently in progress, and results will be reported in a separate occasion. We emphasize here that the observed ordering is mesomorphic in nature, not to be confused with the previously proposed[15] crystalline order (orthorhombic, with lattice parameters $a = 0.712$ nm, $b = 1.605$ nm, and $c = 0.647$ nm, which is incommensurate with the present diffraction patterns) for a highly stretched (with a draw ratio of 5) MEH-PPV film, in which the backbone is fully extended in all-trans conformation along the *c*-axis. For unstretched films, a single reflection corresponding to a *d* spacing value of 1.8 nm was observed but not commented in terms of specific structural features.[15] We believe that this unidentified morphology is in better correspondence with the primitive smectic order reported here.[16] Similar observations of supramolecular assemblies of layered morphology have been reported for thin films of poly(*p*-phenylene ethynylene)s.[17]

As shown in Figure 4, both absorption and emission spectra are significantly affected by changes in molecular packing. There are no discernible changes in the absorption spectrum (cf. Figure 4a) with short-term annealing at $T_a \leq 180$ °C. However, for $T_a \geq 230$ °C, the wavelength at maximum absorption shifts from ca. 510 to 480 nm as the absorption edge shifts from ca. 590 to 570 nm, indicating shortened conjugation lengths with high-temperature heat treatment. In contrast, the emission spectrum (excitation wavelength = 500 nm) with two nearly equal-weighted emissions at ca. 600 and 640 nm remains unchanged for $T_a \leq 130$ °C; for $T_a \geq 180$ °C, however, the 640 nm emission becomes dominant until T_a approaches T_i (= ca. 290 °C). Upon heat treatment above T_i (i.e., at the highest T_a of 310 °C), the short-wavelength emission (now shifted slightly to ca. 590 nm, consistent with the blue shift in the corresponding UV−vis spectrum) becomes a major contributor to the emission spectrum. These changes correspond well to the emergence and the dissipation of structural order in the parallel XRD study shown in Figure 2. Previous luminescence studies via EL, PL, spatially resolved PL, and lifetime measurements have

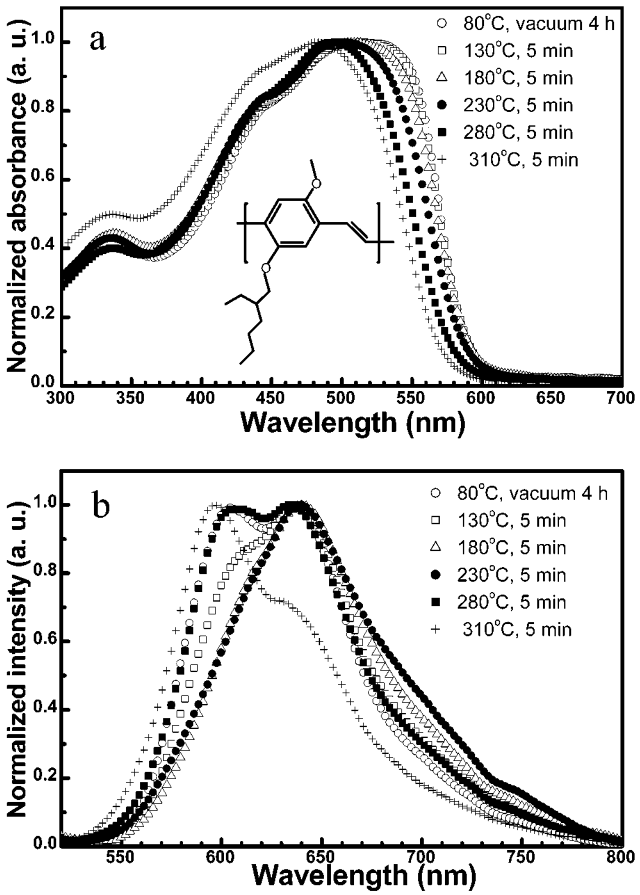

Figure 4. Normalized absorption and emission spectra of of solution-cast MEH-PPV film upon fast cooling to room temperature during a sequence of 5 min heat treatments at stepwise increased T_a. Note that the thermal history exactly parallels that of the XRD study in Figure 2.

clearly established that the 590 nm emission is due to single-chain chromophores and the 640 nm emission is due to interchain species in the aggregated state.[5−7,9] Our observation of stronger sensitivity of the emission spectrum (as compared to XRD and UV−vis results) toward heat treatment may therefore be attributed to biased representation of “aggregate emission” as a result of funneling of excitation energy to the ordered aggregates. The exact correspondence of relative contributions of the two emission paths with the formation and the dissipation of structural order implies that the aggregates formed in solutions and the supramolecular assemblies formed upon heat treatment in the bulk state are similar in the way of molecular arrangement[18] (as to have similar level of conjugation) and hence likely to be of the same thermodynamic origin, reminiscent partly of the similarity between micellar structure in solution and microdomain structure in the bulk state of block copolymers (i.e., effective repulsion between chemically different blocks) and partly of the duality of lyotropicity and thermotropicity in liquid-crystalline polymers (i.e., volume exclusion of the rigid mesogen).

As a final note, the formation of aggregates is not uncommon to conjugated polymers,[13,19−29] and the effects on the light-emitting properties can be dramatically different, most often resulting in quenching due to formation of excimers of low quantum efficiency[20−23,25,27] but sometimes effective color tuning via “aggregate emission” of fair efficiency at a red-shifted wavelength[5,7,27,29] or improved resistance[6] toward photobleaching in air. There are also reports on changes in carrier mobility[6,10] and the mode of carrier transport.[10,31] All these are believed to be closely related to molecular packing in the aggregated state.[29,30,32]

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