Aging of Poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene)/Toluene Solutions and Subsequent Effects on Luminescence Behavior of Cast Films

S. H. Chen,[†] A. C. Su,*[,†] C. S. Chang,[‡] H. L. Chen,*[,‡] Derek L. Ho,[§] C. S. Tsao,[||]
K. Y. Peng,[‡] and S. A. Chen[‡]

Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Institute of Nuclear Energy Research, Lungtan, Taoyuan 325, Taiwan

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Morphological effects in luminescence properties of a representative semiconducting polymer, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), has recently attracted much attention. Previous studies indicated that short-term heat treatment of solution-cast MEH-PPV *films* may result in the formation of mesomorphic order that is responsible for the "red" emission around 640 nm, in contrast to the single-chromophore "yellow" emission near 590 nm from the disordered matrix. On the basis of microscopic and spectroscopic evidence for films cast from freshly prepared and aged solutions, here we show that prolonged storage of MEHyellowPPV solutions at room temperature or lower may result in *retardation* of the thermally induced mesophase formation in the subsequently cast *films*. According to small-angle neutron scattering and differential scanning calorimetric observations over aged MEH-PPV/toluene solutions, we propose that the suppressed transformation into mesomorphic order is due to further development of nanocrystalline aggregates that serve as physical cross-links among MEH-PPV chains in the solution state upon long-term storage. These solvent-induced nanocrystalline aggregates, however, do not exhibit new spectroscopic features beyond the suppression of "red" emission at 640 nm from the mesomorphic phase.

Introduction

Poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) is one of the most extensively studied electroluminescent (EL) polymers.[1] The concept behind the molecular design of MEH-PPV is the use of asymmetric substitutions of methyloxyl and *branched* ethylhexyloxyl side chains to improve solubility in common solvents and minimize molecular aggregation via suppression of crystallinity.[2] Nevertheless, there still exists a significant tendency toward molecular aggregation, which in turn gives rise to strong morphological effects on its light emission properties.[3−11] The exact nature of such aggregates and corresponding details in molecular packing are not fully understood. By means of X-ray diffraction (XRD) and transmission electron microscopy (TEM), we have recently shown for MEH-PPV *films* the presence of molecular aggregation via formation of a biaxial nematic mesophase of sanidic nature upon short-term heat treatment at elevated temperatures, which is accompanied by a clear red shift of emission maximum from 590 to 640 nm.[12,13] The practical significance of such fundamental understanding in morphology effects is most clearly demonstrated by a recent study[14] on changes in emission wavelengths upon heat treatment (although in a more limited temperature range) and improved EL efficiencies, presumably as a result of more balanced electron/hole transport.[9,10,15]

Along the way of our morphological study of MEH-PPV films, some previously unreported effects of solution storage time came to our notice.[12,13] As an extension of our previous studies, here we present evidence from microscopic/spectroscopic/scattering observations and thermal analysis that there may exist another type of aggregate, formed in MEH-PPV *solutions* upon *long-term standing* at room temperature or lower. These "solvent-induced" aggregates, most likely nanocrystalline in nature, serve as physical cross-links among MEH-PPV chains that

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[†] National Sun Yat-Sen University.

[‡] National Tsing Hua University.

[§] National Institute of Standards and Technology.

[||] Institute of Nuclear Energy Research.

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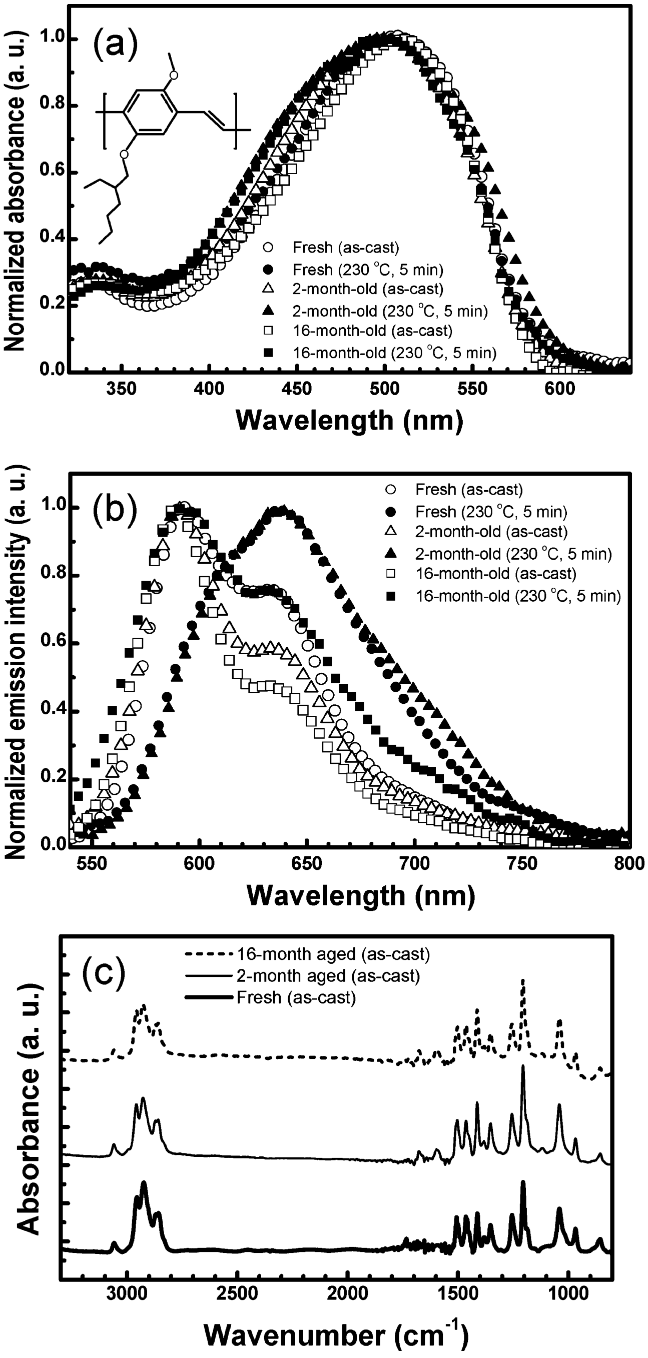

Figure 1. Normalized (a) absorption and (b) emission (excited at 480 nm) spectra of MEH-PPV films in the as-cast state (open symbols) and fast cooled to room temperature after 5 min of annealing at 230 °C (filled symbols). Circles correspond to film cast from freshly prepared 0.2 wt % MEH-PPV solution in toluene whereas triangles and squares correspond to films cast from solutions upon room-temperature storage of 2 and 16 months, respectively. (c) FTIR spectra of as-cast films from aged solutions after different periods of room-temperature storage demonstrate absence of photo- or thermo-oxidation.

retard or even inhibit the formation of the red-emitting mesomorphic phase in the subsequently cast film upon heat treatment.

Experimental Section

Material. Poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV, chemical structure given as insert in Figure 1a) was synthesized via the Gilch method following in general the procedure reported by Wudl et al.[16] The weight-average molecular mass and the polydispersity were ca. 400 kDa and 4.5, respectively, as determined via size exclusion chromatography (SEC) using polystyrene standards. Note that the SEC measurement was made using a *freshly prepared* 0.05 wt % solution of MEH-PPV in tetrahydrofuran, which is free from the aging effects in toluene solutions described in this study.

Microscopic/Spectroscopic Characterization. TEM studies were performed using a JEOL 3010 instrument under an acceleration voltage of 200 kV. Polarized light microscopy (PLM) observations were made by use of a Nikon Eclipse E400-POL microscope equipped with a nitrogen-protected heating stage (Linkam THMS-600) and a temperature controller (Linkam TMS-91). Optical absorption (UV−vis) and photoluminescence (PL) spectra of the film specimens were obtained by use of a Hong-Ming MFS-230 instrument. Fourier transform infrared (FTIR) spectra of cast films were obtained by use of a DigiLab FTS-40 spectrometer at a resolution of 2 cm^{-1}.

Scattering/Thermal Measurements. Small angle neutron scattering (SANS) experiments over a scattering vector ($q \equiv 4\pi \sin(\theta/2)/\lambda$ where θ is the scattering angle and λ the wavelength) range of ca. 0.03−4.0 nm^{-1} were carried out using the 30-m SANS instrument at the Center for Neutron Research, National Institute of Standards and Technology.[17] The incident neutron beam was 0.8 nm in wavelength, with resolution $\Delta\lambda/\lambda = 0.15$. The scattering intensity was corrected for background and parasitic scattering, placed on an absolute level using a calibrated secondary standard, and circularly averaged to yield the scattering intensity $I(q)$.[18] The incoherent background from the pure solvent was measured, corrected for the volume fraction of MEH-PPV, and subtracted from the reduced SANS data. Temperature (calibrated and controlled within ±0.1 °C) of the solution during SANS measurement was achieved by use of a 10-piston heating/cooling block connected to a circulating bath containing 50/50 mixture of water and ethylene glycol. For the measurement at each temperature, the sample was first held at the prescribed temperature for 30 min followed by data acquisition for another 30 min. Thermal transition of the (presumably) nanocrystalline clusters formed in a 1 wt % MEH-PPV/toluene solution after room-temperature aging for 24 days was examined by use of a TA DSC-2000 differential scanning calorimeter operated under a stream of protective nitrogen and routinely calibrated with indium standard. The sample was sealed in an aluminum hermetic pan, and the thermogram was recorded at a heating rate of 20 °C/min from 0 to 100 °C.

Solution/Film Preparation. Dilute solutions (ca. 0.1 wt % for TEM, 0.2 wt % for FTIR, and 1 wt % for SANS studies) of MEH-PPV in toluene were prepared via warming in a water bath up to ca. 90 °C, followed by room-temperature storage in dark for different periods of time in nitrogen-flushed glass vials. Paraffin wax films were used to wrap around the cap for minimized oxidation as well as solvent evaporation. Deuterated toluene was used for the SANS study. Film specimens were periodically drop-cast on quartz or glass substrates from these solutions; routine drying (in excess of 24 h under vacuum at ambient temperature) and heat-treatment (5 min at 230 °C under a nitrogen atmosphere, followed by fast cooling to room temperature) procedures were generally adopted to follow the thermally induced structural change or its effects on absorption/emission behavior.

Results and Discussion

Spectroscopic/Microscopic Evidence. Given in Figure 1a are normalized absorption spectra of MEH-PPV films in the as-cast state and fast cooled to room temperature after 5 min of annealing at 230 °C, respectively. Differences in room-temperature storage time of the solutions used for film preparation result in small changes in the UV−vis spectra whereas short-term heat treatment at 230 °C does result in some red shift of the absorption

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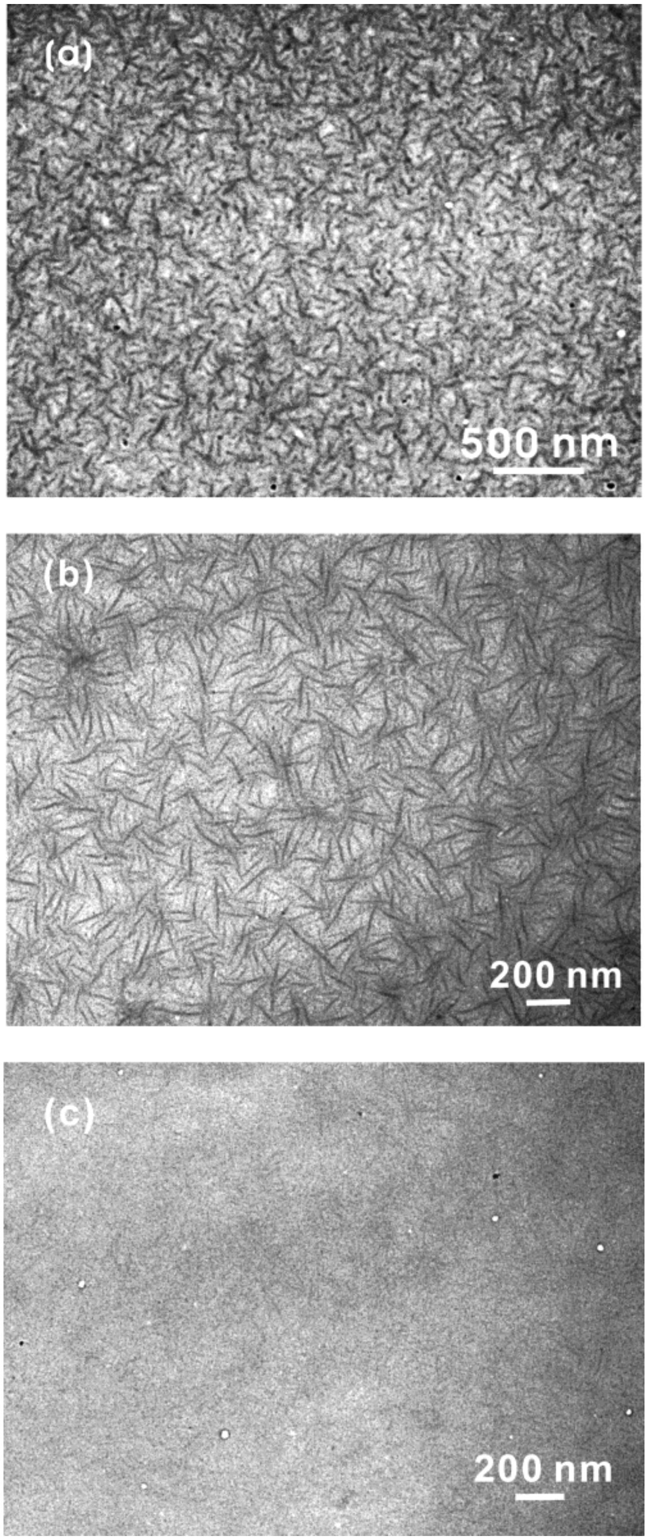

Figure 2. Representative TEM bright field images of annealed (5 min at 230 °C, followed by fast cooling to room temperature) films cast from 0.1 wt % MEH-PPV solution in toluene (a) right after fresh preparation, (b) upon room-temperature storage for 2 months, and (c) after room-temperature storage for 16 months.

edge as reported[13] previously. In contrast, the effect of room temperature storage is clearly demonstrated (particularly for heat-treated films) by the corresponding emission spectra in Figure 1b. For the *as-cast films*, the emission spectra are composed of a main emission at 590 nm (16950 cm^{-1}) and a sideband-like emission at 640 nm (15630 cm^{-1}). Note that the relative intensity of the latter emission decreases with room-temperature storage time.

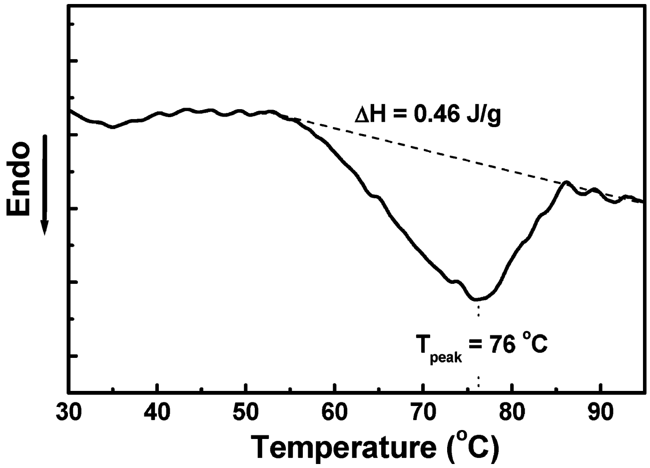

Figure 3. DSC heating thermogram of the 1 wt % MEH-PPV/toluene gel formed during aging at room temperature for 24 days. The corresponding trace of a freshly prepared reference showed only a flat baseline.

As reported[13] previously, the short-term heat treatment at 230 °C results in red-shifted (from 590 to 640 nm) emission maximum for the specimen cast from the freshly prepared solution. This dramatic shift in emission maximum has been attributed to the formation of mesomorphic aggregates[13] as shown by the TEM micrograph in Figure 2a. The red shift in emission maximum upon heat treatment is also observed for the film cast from the 2-month-old solution (cf. Figure 1b); the corresponding development of the mesomorphic aggregate, however, is more limited in extent (cf. Figure 2b). In contrast, this characteristic shift in emission maximum upon heat treatment (which has been *reproducibly* observed in various occasions[12−14]) is strongly suppressed for the specimen cast from the 16-month-old solution. This suggests *inhibited transformation into the mesomorphic phase* as clearly supported by the corresponding TEM micrograph in Figure 2c. For this particular case, we note that the intensity of the weak emission at 640 nm (as compared to two other as-cast films) is still increased upon heat treatment. This is consistent with our previous interpretation that emission at this wavelength is composed of contributions from both the phonon sideband of the single-chromophore emission at 590 nm as well as the emission from mesomorphic aggregates. The suppression of the mesomorphic aggregation cannot be attributed to unruly oxidation upon long-term standing: FTIR spectra (cf. Figure 1c) of films cast from aged solutions after different periods of room-temperature storage and those upon short-term heat treatments (cf. Figure 8d in ref 13) demonstrate general absence of photo- or thermo-oxidation in our carefully protected specimens. The suppressed transformation is therefore more likely a result of physical changes that occurred during the long-term room-temperature standing in the solution state.

Thermal Transition. To identify "physical changes" that occurred during aging, a more concentrated solution of 1 wt % MEH-PPV was prepared. This resulted in formation of *soft gels* after prolonged storage at room temperature or lower, suggesting formation of physical cross-links in the form of interchain clusters. The gel structure is easily dissipated upon heating above 90 °C. This is accompanied by an endothermic heat flow in the temperature range of 55−85 °C, as indicated by the DSC heating trace in Figure 3 for the gel formed by aging the 1 wt % MEH-PPV solution at room temperature. The corresponding DSC scan of the freshly prepared solution

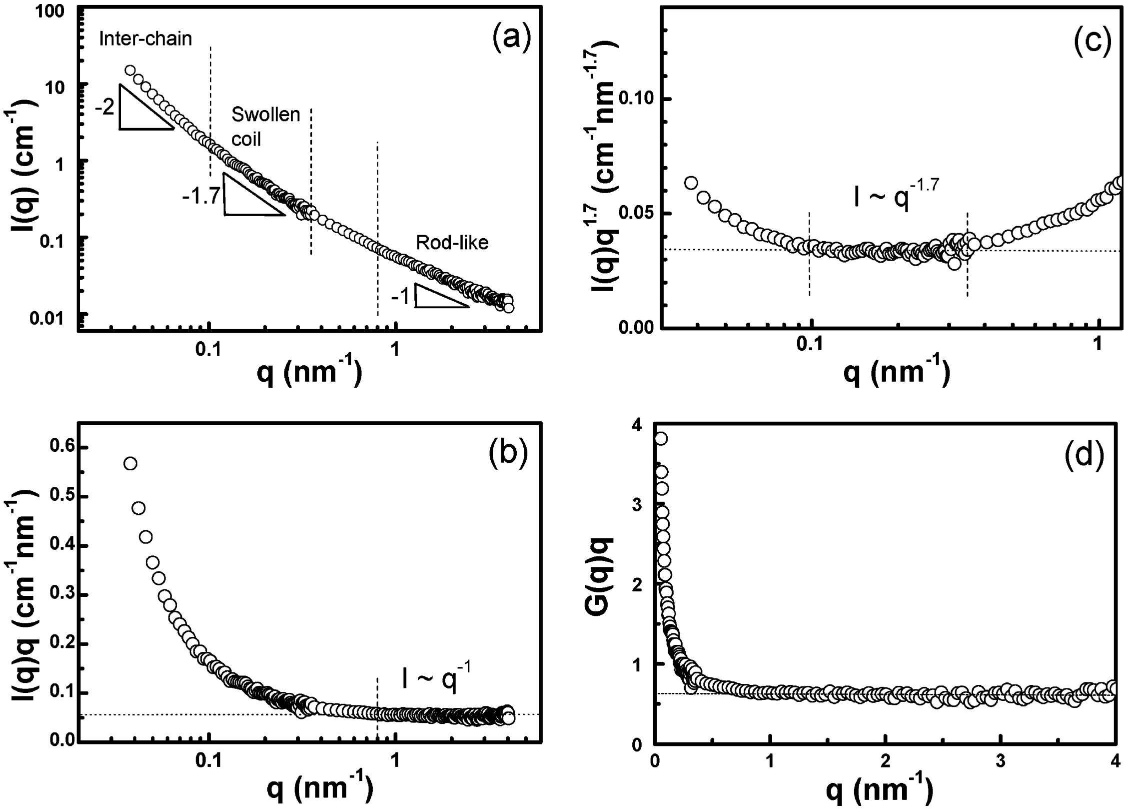

Figure 4. High-temperature SANS pattern of 1.0 wt % MEH-PPV/toluene solution collected at 85 °C: (a) the absolute intensity profile; (b) Kratky plot of $I(q)q$ to demonstrate the power law of $I(q) \sim q^{-1}$ in the high-q region; (c) Kratky plot of $I(q)q^{1.7}$ to demonstrate the power law of $I(q) \sim q^{-1.7}$ in the intermediate-q regions. (d) Plot of $G(q)q$ vs q for the determination of the mass per unit length (M_L) of rodlike MEH-PPV segments using the high-q SANS intensity.

shows only a flat baseline. The measured enthalpy of melting of the gel is 120 J/mol repeating unit of MEH-PPV, which falls in the expected range of low-crystallinity polymers. We therefore attribute the interchain clusters that serve as physical cross-links in the gel of aged solution to a solvent-induced crystalline phase. The formation of such physical gels has in fact been reported[19] to occur during synthesis of MEH-PPV using the original[16] Wudl procedure. It is well-known that physical gels[20,21] may form in polymer solutions of limited crystallinity development, where "microcrystallites" or nanocrystalline clusters are believed to function as physical cross-links. As MEH-PPV is a polymer capable of developing a limited extent of crystallinity,[22] it is more likely that the physical cross-links in the gel correspond to a crystalline structure, whose formation is kinetically assisted by the presence of a solvent for nominally *amorphous* polymers such as aromatic polycarbonates[23,24] and poly(2,6-dimethyl-1,4-phenylene oxide)[25,26] that are difficult to crystallize in the bulk state.

It should be emphasize here that this *solvent-induced* aggregation (due to formation of nanocrystalline clusters) of MEH-PPV *solutions* in toluene should not be confused with the *thermally induced* aggregation (due to formation mesomorphic phase) in MEH-PPV *films*. The characteristic emission at 640 nm of the latter (mesomorphic phase) in the bulk state is clearly suppressed (cf. Figure 1b) in the presence of the former (nanocrystalline clusters) aggregates. This is taken as an (admittedly tentative) operational definition to differentiate the two types of clusters. In this respect, structural development in the solution state as manifested by SANS profiles may provide further insights to the solvent-induced aggregation process. A hierarchy of structural features, ranging from single chains viewed in short length scales to physically cross-linked network structure at greater length scales of observation, are nevertheless expected in this semidilute case of swollen gel: Hence, for clarity of discussion, we present first high-temperature SANS features associated predominantly with the dissolved chains, followed by room-temperature SANS profiles of aged solutions showing significant effects from interchain aggregation; comparison among SANS profiles of solutions with different thermal histories are then made to elucidate the nature of the aggregates formed.

Scattering Mainly from Dissolved MEH-PPV Chains. In view of the observed melting of nanocrystalline clusters at 85 °C, the scattering pattern primarily associated with molecularly dissolved MEH-PPV chains was obtained by SANS measurements at this temperature. Given in Figure 4a is a logarithmic plot of the SANS profile of a 1.0 wt % MEH-PPV solution in deuterated toluene that was collected at 85 °C. Power-law relationships of $I(q) \sim q^{-1}$ for $q > 0.8$ nm^{-1} and $I(q) \sim q^{-1.7}$ for $0.1 < q < 0.3$ nm^{-1} may be observed. These are as further verified by Kratky plots (i.e., plots of $I(q)q$ and $I(q)q^{1.7}$ versus

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logarithmic q) shown in parts b and c of Figure 4, where horizontal regions in the corresponding high-q and intermediate-q ranges may be identified.

The power law of $I(q) \sim q^{-1.7}$ in the intermediate-q region corresponds to swollen coils.[27,28] The scattering at larger q is governed by the behavior of sections of semirigid MEH-PPV chains, and the intensity curve shows indeed the q^{-1} behavior of thin rods.[27,29] The mass per unit length (M_L) of the rod can be determined from the intensity in this region via the dimensionless scattering function[27,30]

$$G(q) = \frac{I(q)M_u}{cN_{av}\Delta\rho^2 {v_u}^2} = \frac{\pi M_L}{M_u}\frac{1}{q} \qquad (1)$$

where $I(q)$ is the scattering intensity in the unit of cm^{-1}, c is the polymer concentration in g/mL, $\Delta\rho$ is the scattering length density (SLD)[27,29] contrast between the solvent and MEH-PPV ($\rho_{MEH-PPV} = 7.91 \times 10^{-5}$ nm $^{-2}$ and $\rho_{d-toluene} = 5.20 \times 10^{-4}$ nm^{-2}), v_u is the volume of a MEH-PPV monomer unit ($v_u = 0.441$ nm^3), M_u is the molecular weight of the monomer unit (M_u = 260 Da), and N_{av} denotes Avogadro's number. Equation 1 prescribes that the product of $G(q)$ and q would reach an asymptotic value given by $\pi M_L/M_u$, as shown by Figure 4d. M_L determined from the plateau in the $G(q)q$ vs q plot is 4.8 ± 0.5 g mol^{-1} nm $^{-1}$, which compares reasonably with the mass per unit length of the monomer unit calculated by M_u/(length[13] of a repeating unit = 0.67 nm) = 3.9 g mol^{-1} nm $^{-1}$ and certainly much lower than multiples of the latter. The rod character probed at the high-q region may hence be associated with *molecularly dissolved* segments of MEH-PPV instead of any form of multichain aggregate in rodlike geometry. Therefore, the semirigid MEH-PPV chain may be represented by the successive connection of rodlike segments but globally behaves as a swollen coil.

We note that the SANS intensity exhibits an upturn in the low-q region ($q < 0.1$ nm^{-1}), signifying that presence of some *interchain interaction* even in this case of presumably dissipated nanocrystalline order. The exact nature of the interchain interaction, however, is not yet clear. We would naturally expect the contribution from interchain meshing in the semidilute state should follow the Ornstein−Zernike expression,[27−29] which dictates an asymptotic power-law behavior of $I \sim q^{-2}$ in the high-q range. At the low-q limit, a plateau value $I(0)$ is determined by composition. This, however, is at variance with the experimental observation in Figure 4a where the SANS intensity shows stronger q-dependence, indicating additional contributions from interchain correlations not yet identified.

Room-Temperature SANS Profiles. Compared in Figure 5 are room-temperature SANS profiles of 1 wt % MEH-PPV/deuterated toluene solutions in the freshly prepared state and after "accelerated" aging at −4 °C for 2 days, respectively. This "accelerated" aging generally results in gels similar in appearance to those obtained upon long-term aging at room temperature. The accelerated gelation of the 1 wt % toluene solution at a *lowered* temperature is also consistent with our attribution of gelation to formation of nanocrystalline clusters.

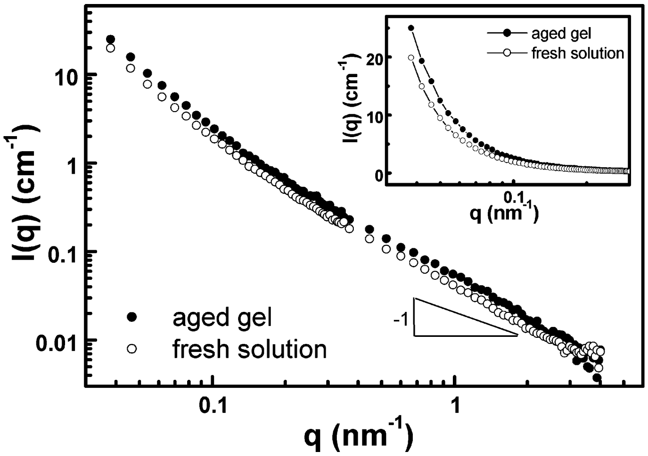

Figure 5. Room-temperature SANS profiles of 1 wt % MEH-PPV solutions in deuterated toluene in the freshly prepared state (open circles) and after "accelerated" aging at −4 °C for 2 days (filled circles). The semilogarithmic curves in the inset demonstrate more clearly the enhanced low-q scattering upon aging.

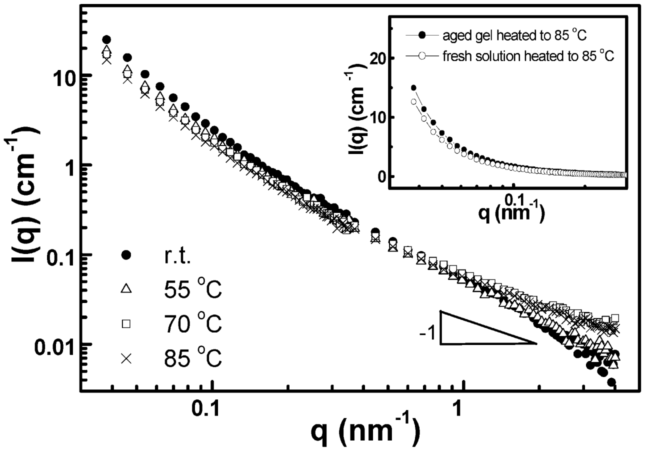

Figure 6. High-temperature SANS profiles collected during stepwise heating of the 1 wt % MEH-PPV/deuterated toluene gel obtained via aging at −4 °C for 2 days. The inset shows high-temperature SANS patterns obtained at 85 °C for both the aged gel and a freshly prepared solution: the two scattering curves match rather well with each other (cf. inset of Figure 5 for comparison), indicating that the aggregates developed upon aging have mostly dissipated at this temperature.

For the freshly prepared solution, the scattering intensity exhibits a slope more negative than −1 in the high-q region. As a matter of fact, room-temperature SANS profiles in logarithmic plots of the freshly prepared solutions normalized by the corresponding polymer concentration, $I(q)/c$, did not fall into a single curve. Instead, they varied with concentration in terms of both the magnitude and the slope in different q regions.[31] These observations imply the presence of (concentration-dependent) contributions arising from interchain aggregates, which have perturbed the power-law dependence (cf. Figure 4) of scattering from molecularly dissolved chain segments even in the freshly prepared solution. Nevertheless, the general increase of scattering intensity (except at the experimentally accessed high-q end) attests to further aggregation of the MEH-PPV chains in this 1 wt % solution upon aging.

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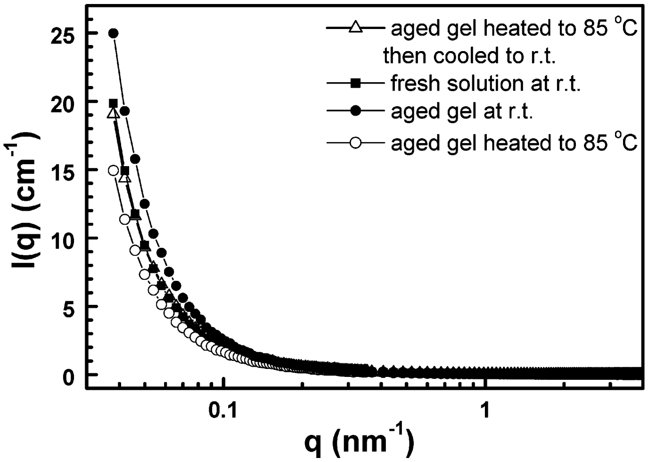

Figure 7. SANS profile (open triangles) of the solution studied in Figure 6 immediately after cooling to room temperature. For comparison purposes, scattering profiles of the as-aged gel at room temperature (i.e., before being heated to high temperatures, filled circles), the freshly prepared solution at room temperature (filled squares), and the aged solution heated to and maintained at 85 °C (open circles) are also shown. The scattering intensity is displayed in linear scale to demonstrate more clearly the differences in the low-q region.

Temperature Dependence of Solution Structure. Shown in Figure 6a are a series of SANS profiles of the aged MEH-PPV/toluene solution collected in situ during a sequence of stepwise increases in temperature. It can be seen that the improved solvent quality with increasing temperature results in systematic decreases of the scattering intensity in the low-q ($q < 0.2$ nm^{-1}) region. This is accompanied by corresponding increases in scattering intensity in the high-q ($q > 1.0$ nm^{-1}) region where the slope of the intensity profile also becomes less negative with increasing temperature and approaches the rigid-rod value of -1 at temperatures above 70 °C. The decrease in low-q intensity is attributed to the decrease of aggregate concentration with increasing temperature. This declustering process should then result in increased concentration of dissolved chains and is hence expected to enhance the high-q intensity contributed by the form factor of dissolved chains, as is indeed observed. It is also noteworthy that the scattering curve of the aged gel heated to 85 °C approaches that of the freshly prepared solution heated to the same temperature (cf. insets of Figures 5 and 6), indicating that the aggregates formed *during* aging have mostly dissipated at this temperature.

At the end of the high-temperature measurements discussed above, the sample was allowed to cool back to room temperature, at which an additional SANS profile was taken. This is given in Figure 7, along with profiles of the aged solution when heated to and maintained at 85 °C, the as-aged gel at room temperature (i.e., before being heated to higher temperatures), and the freshly prepared solution at room temperature for comparison purposes. We note first that cooling from 85 °C to room temperature results in an obvious increase of the low-q intensity, indicating *immediate reclustering* of MEH-PPV chains. The reaggregated solution structure is similar to that of the freshly prepared solution, as the corresponding SANS profiles match well with each other. Effects of aging, as demonstrated by the clearly stronger low-q intensity of aged gel, are therefore efficiently washed away by an increase in temperature above 85 °C. In other words, the rapid reclustering process upon cooling to room temperature recovers only the “preexisting” aggregates in the freshly prepared solution.

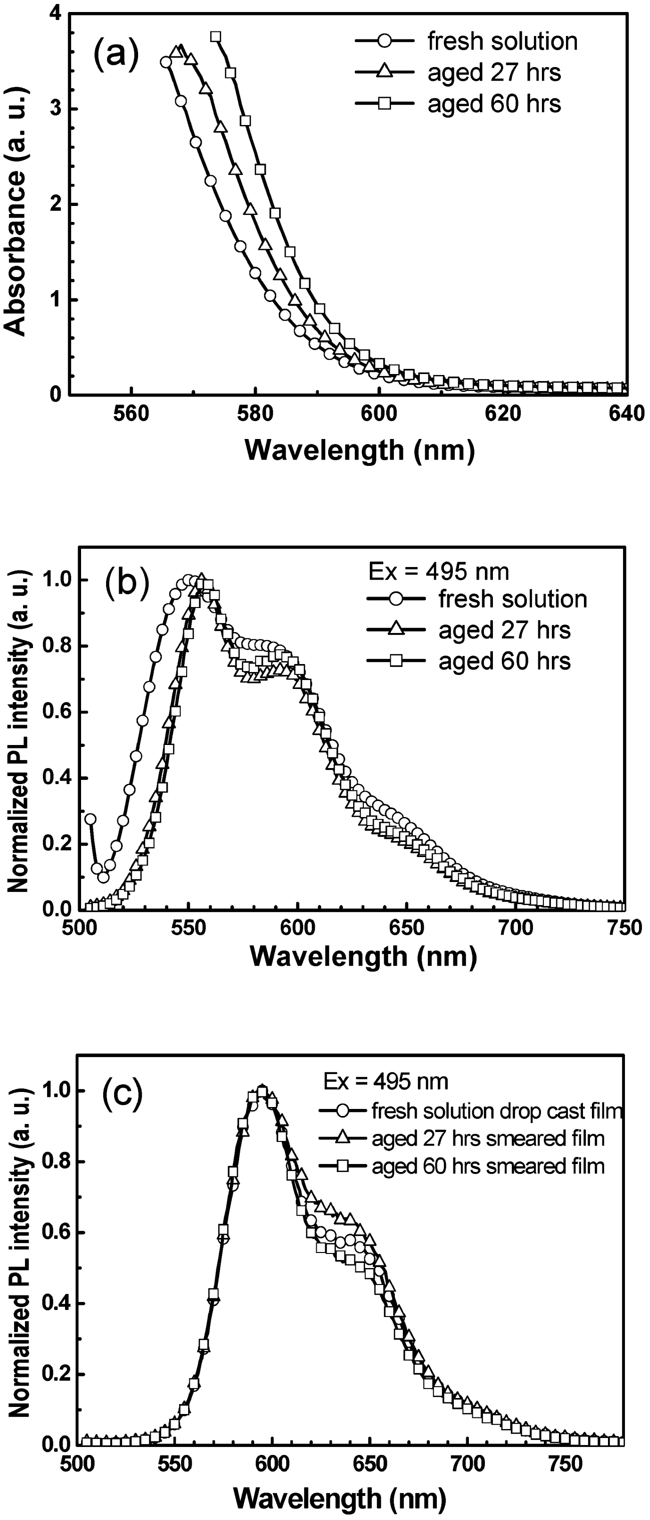

Figure 8. (a) Absorption and (b) normalized emission spectra (excited at 495 nm) of 1 wt % MEH-PPV/toluene solution after different periods of accelerated aging at −4 °C. (c) Normalized emission spectra of films prepared from corresponding gels.

The molecular origin of this low-barrier process may possibly be related to the decrease in solvency power upon cooling to room temperature: within the framework of Flory’s classical lyotropic polymer solution theory,[32] thermodynamic solubility of semirigid chains such as MEH-PPV is expectedly low *even in good solvents*, showing a chimney-like phase diagram in which an incipient

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nematic phase (slightly more concentrated in rods) may coexist with the dilute (and isotropic) mother phase. It should be noted that formation of this type of aggregate is amplified in the present case of a rather high concentration (as compared to those adopted for our microscopic and spectroscopic studies or in typical device fabrication processes) of 1 wt % MEH-PPV in deuterated toluene for the purpose of stronger SANS signals. By contrast, the formation of physical cross-links responsible for gelation is rather slow and requires either extended storage time at room temperature or a decrease in storage temperature, implying a high nucleation barrier. This is consistent with the proposed nanocrystalline nature for this type of aggregate.

Spectroscopic Behavior of Gels during Accelerated Aging. For comparison with SANS results obtained during accelerated aging at −4 °C, evolution of absorption and emission spectra of the 1 wt % solution is given in Figure 8. Also included are the emission spectra of films obtained from the aged gels. The absorption spectra in Figure 8a are limited by the strong absorption due to the high concentration used. They nevertheless indicate a red-shifted absorption edge with aging time, consistent with the clustering process observed via SANS. In comparison, the corresponding emission spectra in Figure 8b are largely unaltered in emission wavelengths. These observations indicate that, although the nanocrystalline clusters are more extensively conjugated, they do not constitute as effective emitting species: although not identifiable in the normalized spectra, the total intensity actually decreased with aging time. It is therefore reaffirmed that these nanocrystalline clusters are photophysically different from the thermally induced mesomorphic aggregates (which exhibits predominant emission at 640 nm, cf. Figure 1b). This characteristic emission is also absent in the normalized emission spectra of films prepared from the gels after accelerated aging (cf. Figure 8c), reassuring the necessity of high-temperature heat treatment for its emergence.

Conclusion

Previous studies[12,13] have indicated that short-term *heat treatment* of solution-cast MEH-PPV *films* may result in the formation of mesomorphic order that is responsible for the “red” emission around 640 nm, in contrast to the single-chromophore “yellow” emission near 590 nm from the disordered matrix. In the present work, we have shown via spectroscopic and microscopic evidence that prolonged storage of MEH-PPV solutions at room temperature may result in *retardation of such transformation* in cast films. On the basis of DSC and SANS observations on aged MEH-PPV/toluene solutions, we propose that the suppressed transformation into mesomorphic order in *films* is due to development of interchain aggregates (most likely nanocrystalline in nature) that serve as physical cross-links among MEH-PPV chains in the *solution* state upon long-term room-temperature storage. As a final remark, we add that these solvent-induced nanocrystalline aggregates do *not* exhibit new spectroscopic features beyond the suppression of “red” emission at 640 nm from the thermally induced mesomorphic phase in the bulk state by inhibiting its formation.

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