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Neutron reflection study on soluble and insoluble poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] films

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Neutron reflection (NR) has been utilized to study the physical structure of the light-emitting polymer poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEHPPV). Films of soluble MEHPPV (S-MEHPPV) and insoluble MEHPPV (I-MEHPPV) prepared via a chloro precursor polymer were investigated. For S-MEHPPV spin-coated films were found to contain two layers, one of low-density and thickness of ≈ 1360 Å with the second layer being thinner, ≈ 240 Å, but denser. The thicker layer only covered about 30% of the substrate surface. In contrast, I-MEHPPV formed uniform films across the substrate. We found that during the thermal conversion of the chloro precursor polymer the film thickness was maintained and it was only on cooling that the films contracted. Importantly, the thermal expansion and contraction of I-MEHPPV was reversible. NR showed that thermal annealing of I-MEHPPV had little effect on the films physical structure while for S-MEHPPV only the thinner layer was changed and became more dense. Photoluminescence spectra of S-MEHPPV before and after annealing showed that the densification observed in the neutron reflection measurements was mirrored in the emission properties of the polymer film. © 2002 American Institute of Physics. [DOI: 10.1063/1.1468902]

I. INTRODUCTION

Morphology has become an important topic of investigation for light-emitting conjugated polymers.¹⁻⁶ It has now been clearly demonstrated that the morphology of the polymer can directly affect the device performance of such materials in light-emitting diodes (LEDs).^{1,3,4} The light-emitting polymers used in LEDs fall essentially into two main classes.^{7,8} The first group are polymers that are soluble in the conjugated form with the solubility imparted by the addition of long lipophilic groups. The soluble polymers can be further divided into two main classes, namely poly(1,4-phenylenevinylene) (PPV) and poly(flourene) based materials. The second type of polymers are those which are insoluble in the conjugated form and prepared via soluble precursor polymers. These latter polymers are essentially poly(arylenevinylene)s. Although considerable effort has gone into the development of soluble conjugated polymers it is not clear that these will be used to the exclusion of insoluble polymers produced via the precursor route. Indeed, insoluble polymers could have distinct advantages over soluble polymers in the areas of patterning, robustness, density of film, and the development of multilayer devices. The main studies linking polymer morphology to the photophysical and device properties have been carried

out on soluble poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEHPPV).¹⁻⁶ For soluble MEHPPV it has been shown that solvent, polymer concentration, spin-coating speed, and annealing can affect the surface morphology of the films, their photoluminescence properties, charge injection and mobility, and device performance. Although the effects of different film preparation can be "seen" in the properties of the films, in most cases the actual physical structure of the polymer films has not been investigated. The limitation of optical and device techniques is that they do not reveal the morphology or macromolecular structure directly. In fact there are few reports where the physical structure of an MEHPPV film has been studied. In one case x-ray diffraction was used⁹ while in a second study electron diffraction was utilized.¹⁰ Two powerful techniques that can be applied to determining the physical structure of polymer films directly are neutron reflection (NR) and small angle neutron scattering. In this article we describe our results in determining the physical structures of films of MEHPPV by neutron reflection. We have studied two types of films, first where the MEHPPV films were prepared via a chloro precursor polymer (I-MEHPPV) and secondly from MEHPPV soluble in the conjugated form (S-MEHPPV).

II. EXPERIMENT

To gain the required sensitivity for the NR experiments the deuterated MEHPPV derivatives illustrated in Fig. 1

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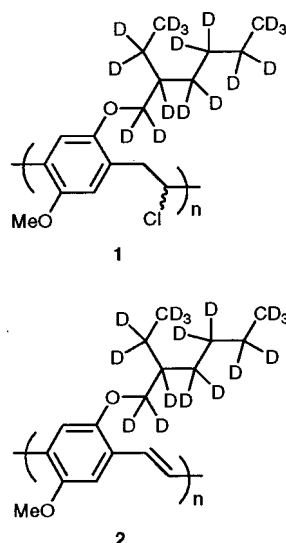


FIG. 1. Polymer structures: **2** can either be soluble (S-MEHPPV) or insoluble (I-MEHPPV) if formed from **1**.

were prepared. The syntheses of **1** and **2** followed the literature procedures^{11,12} but with the protonated 2-ethylhexyl chain being replaced by the perdeuterated equivalent. The weight average molecular weight, \bar{M}_w , of the chloro precursor **1** used in these experiments was determined by gel permeation chromatography (against polystyrene standards in tetrahydrofuran) and was found to be greater than 1×10^6 before disaggregation.¹³ The bulk material of S-MEHPPV **2** contained material that swelled but did not dissolve in tetrahydrofuran (THF) even with ultrasonication or ultrasonication combined with mild heating. The measurements on S-MEHPPV **2** were therefore carried out on the ultrasonicated or heated and ultrasonicated, filtered soluble fraction. The infrared spectra of I-MEHPPV (converted from **1** at 170 °C under vacuum) and S-MEHPPV were similar but with some differences observed in the relative intensities of the absorptions. The UV-visible spectra of I-MEHPPV, S-MEHPPV **2**, and protonated I-MEHPPV films are shown in Fig. 2 and indicate that the optical properties of the deuterated and protonated materials are similar. For the NR experiments the chloro precursor films were spin-coated onto silicon wafers, of 2 or 3 in. diameter, from tetrahydrofuran at a polymer concentration of around 10 mg/ml at 2000 rpm for 60 s. Thin films of **1** were also prepared on quartz, under the same spin-coating conditions, and KBr disks to follow the properties of the films during the NR experiments carried out under vacuum. The S-MEHPPV film was formed on the silicon substrate by spin-coating a saturated solution of polymer in tetrahydrofuran at 2000 rpm for 60 s. Samples of **2** on quartz and KBr were also prepared. In both cases the samples were filtered through cotton wool to remove dust particles and any insoluble polymeric material to leave what appeared to be homogeneous solutions. Photoluminescence spectra were measured following excitation at 500 nm in an Instruments S.A. Fluoromax-2 fluorimeter.

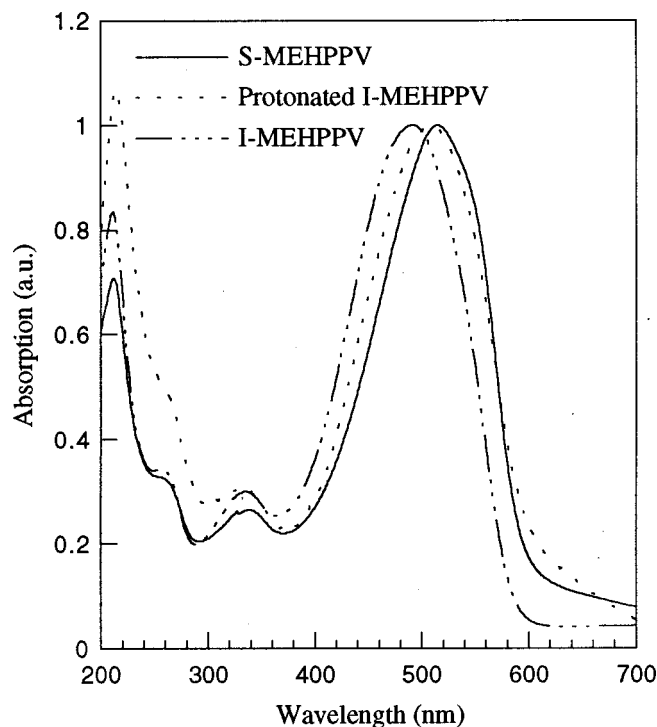


FIG. 2. UV-visible spectra of I-MEHPPV, S-MEHPPV, and protonated I-MEHPPV.

III. RESULTS AND DISCUSSION

A neutron reflectivity (NR) profile is a measure of the specular reflectivity as a function of momentum transfer Q [$Q = (4\pi \sin \theta)/\lambda$ where θ is the grazing angle of incidence and λ is the wavelength of the neutron]. It can be measured either by varying the wavelength of the neutrons at a fixed angle or by varying the angle of reflection at a fixed incident wavelength. We used both methods. Some measurements were made on the reflectometer CRISP at the Rutherford-Appleton Laboratory, ISIS, Didcot,¹⁴ where the reflectivity profile is measured at a fixed angle using a white neutron beam, and others were made on the long wavelength diffractometer D16 where a monochromatic neutron beam is incident on the sample and the angle of incidence is varied, or the dedicated reflectometer, D17, at the Institut Laue-Langevin, Grenoble.¹⁵

The NR profile is determined by the profile of the scattering length density, ρ , across the interface, which depends on the number density of each atomic species, n_i , and its known scattering length, b_i :¹⁶

$$\rho = \sum_i n_i b_i.$$

Since the stoichiometry and isotopic composition of the polymers is already known this equation can be rewritten in terms of the segment density, ρ_s , of the film:

$$\rho = b_s \rho_s,$$

where b_s is the scattering length of a monomer unit. In the simplest case of a uniform film of polymer the NR profile consists of a series of fringes whose spacing is directly re-

lated to the thickness of the film. The segment density of the film can be determined either from the amplitude of the fringes or, if the scattering length density of the film is greater than that of the substrate and the film thickness is greater than about 40 nm, from the critical angle for total reflection. In our case the partial deuteration of the polymer ensures that the scattering length density of the film is greater than the substrate. This is important because the reflectivity profile is likely to be complicated by factors such as roughness in such a way that the amplitude of the fringes is not easily related to the film density. As the roughness of a film increases the interference fringes become progressively more damped and, under these circumstances the behavior of the amplitude of the fringes gives more information about the roughness than about the density of the film. For more complex film structures the reflectivity is fitted by comparison of the observed reflectivity with profiles calculated using the optical matrix method, for which a detailed description has been given by Born and Wolf¹⁷ and Lekner.¹⁸ In the optical matrix method the reflectivity can be calculated exactly for any chosen distribution of scattering length density normal to the interface. The procedure that we have followed uses the minimum number of subdivisions of the film structure required to obtain the best fit to the data. For the films being studied here the structure is generally that of a single layer with roughness. The two key parameters that can be extracted from the NR data are then the film thickness (D) and the scattering length density (SLD), and in addition some qualitative information about the nature of the roughness can be gained.

A. I-MEHPPV

We first examined the formation of I-MEHPPV from chloro precursor **1** under two different conditions, namely argon and vacuum. We found that there were differences in the film structure when the precursor was converted under either argon or vacuum. In both cases the spin-coated precursor polymer films were reasonably uniform as evidenced by the presence of interference fringes in the reflectivity (in nonuniform films the variation in thickness between different parts of the film severely damps any interference effects).

B. I-MEHPPV formed under Ar

When **1** was converted under argon the following cycle was used. The film was analyzed at room temperature, 70 °C [above the glass transition temperature (T_g) measured for **1** in the bulk], 180 °C, 50 °C, and then 180 °C. To a first approximation, thermal conversion of **1** to I-MEHPPV should lead to no change in the scattering length density because both the thickness of the film and the number of atoms will decrease. At room temperature under argon the film of **1** was found to have $D = 670 \text{ \AA} \pm 8\%$ and $\text{SLD} = (4.75 \pm 0.35) \times 10^{-6} \text{ \AA}^{-2}$. On heating to 70 °C the thickness of the film was found to increase ($D = 700 \text{ \AA}$) and the SLD to decrease to $4.45 \times 10^{-6} \text{ \AA}^{-2}$. The two changes in D and SLD suggest that the film has expanded by 4%–8%. Note that the quoted error here refers to the absolute error, which includes possible deficiencies in the fitted model. The relative errors, especially in D , are much smaller because they are determined

simply by examination of changes in the position of the fringes or the critical angle for total reflection. The film of **1** was then heated to 180 °C for 2 h to give I-MEHPPV **2**. The neutron reflectivity of I-MEHPPV **2** was then measured at 180 °C. The SLD and film thickness of I-MEHPPV **2** at $4.37 \times 10^{-6} \text{ \AA}^{-2}$ and 700 Å at 180 °C were essentially the same as the film at 70 °C. On cooling to 50 °C the SLD of I-MEHPPV **2** increased to $4.8 \times 10^{-6} \text{ \AA}^{-2}$ but the film thickness decreased to give $D = 610 \text{ \AA}$. This is an increase of 12% in the SLD and a decrease of 13% in thickness on cooling from 180 to 50 °C. A final important observation was that on heating the film of the I-MEHPPV **2** sample back to 180 °C the reflectivity profile of the film was essentially the same as the profile recorded at that temperature after the thermal conversion.

The NR results can be explained in the following manner. When the film of **1** was heated to 70 °C it expanded slightly due to either residual tetrahydrofuran being removed and/or there being some thermal expansion of the polymer film at a temperature above the T_g of **1**. It has previously usually been assumed that the films contract during the thermal conversion as the leaving group is removed. This is not what we have observed and we found that the film of the converted I-MEHPPV **2** at 180 °C is actually thicker than the precursor film at room temperature. The fact that the film of I-MEHPPV **2** at 180 °C was not thicker than the precursor film at 70 °C suggests that after the thermal expansion in going from room temperature to 70 °C any further thermal expansion at 180 °C was offset by loss of the hydrogen chloride. The expanded form of the film of I-MEHPPV **2** would, interestingly, have the consequence that it would have pathways for the hydrogen chloride to escape. That there is no residual hydrogen chloride in voids after conversion is confirmed by the final SLD and film thickness. If hydrogen chloride remained in the film the SLD would decrease significantly due to the voids caused by the relatively large molecular volume of hydrogen chloride and the thickness of the film would also probably increase. Neither of these effects was observed. The combination of film thickness of 610 Å and SLD of $4.8 \times 10^{-6} \text{ \AA}^{-2}$ means that the cooled film of I-MEHPPV **2** is about 9% more dense than the precursor film of **1**. None of this arises from the elimination (conversion) itself because the estimated loss of volume caused by the elimination of hydrogen chloride is about 4%, which would lead to a decrease of 4% in the thickness but should have a negligible effect on the atomic density of the film, which is what determines the SLD. Most importantly, we found that the thermal expansion and contraction of the film of I-MEHPPV **2** was reversible which suggests that the films are effectively annealed postconversion. This is not unreasonable as the precursor **1** has a T_g around 50 °C in the bulk. However, it is interesting to note that the coefficient of expansion of 9% for **2** is similar to that of polystyrene heated above its T_g (8%).¹⁹ Finally, the reflectivity profiles indicated that the conversion process resulted in more uniform films which is also indicative of an annealing process. In fact, we found that it was possible to form relatively uniform films of I-MEHPPV (interference fringes) from nonuniform precursor films (little or no interference fringes) (Fig. 3).

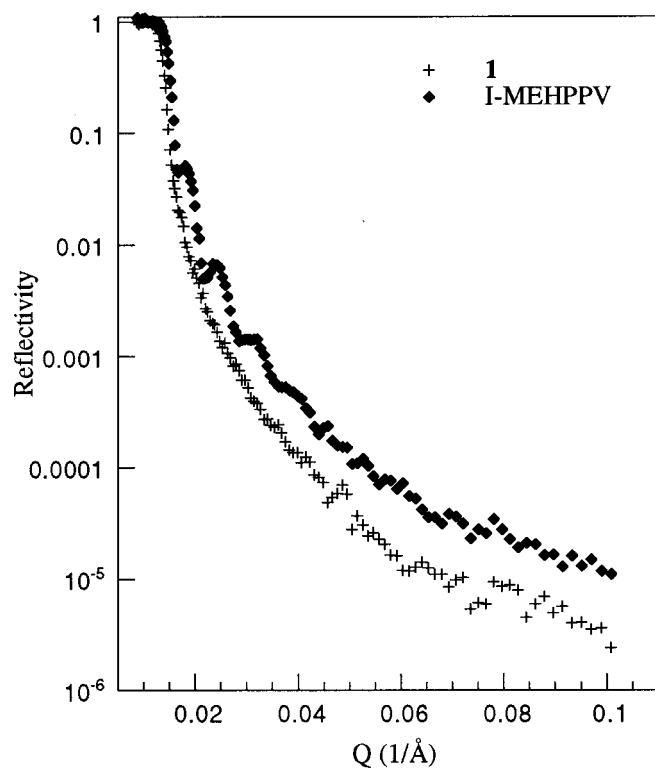


FIG. 3. Reflectivity profiles of an initially poor film of **1** at 25 °C and subsequent I-MEHPPV film at 50 °C showing improved uniformity. The film of I-MEHPPV was formed and measurements carried out under Ar.

C. I-MEHPPV formed under vacuum

A similar study was carried out on the conversion of **1** to I-MEHPPV **2** but this time under vacuum. The thermal cycle that was used in this experiment involved collecting the reflectivity profiles at room temperature, 180 °C, room temperature, then 180 °C, and finally room temperature again. The SLD and D were found from the reflectivity profile of **1** under vacuum to be $4.04 \times 10^{-6} \text{ \AA}^{-2}$ and 1610 Å, respectively. After conversion at 180 °C the film of I-MEHPPV **2** was found not to have expanded with the thickness and SLD of the film being the same as the film of **1**. One possibility for the lack of film expansion on heating is that any remaining tetrahydrofuran is removed more effectively from the film under vacuum at room temperature. As in the first experiment the film did not shrink at 180 °C by the amount expected for the loss of the hydrogen chloride. This again indicates that the films stay thermally expanded during the conversion process allowing the loss of the eliminated by-products. Only on cooling did the film of I-MEHPPV **2** finally shrink. The film of I-MEHPPV **2** at room temperature had a thickness $D = 1470 \text{ \AA}$ and a $\text{SLD} = 4.3 \times 10^{-6} \text{ \AA}^{-2}$, corresponding to a 9% decrease in film thickness and 6% increase in SLD. As for the first experiment, this strongly suggests that there are no voids in the converted film. On heating reversible expansion of the converted film was again observed with only a slight change in the film thickness and scattering length density on cooling in comparison with the newly converted film of I-MEHPPV **2**.

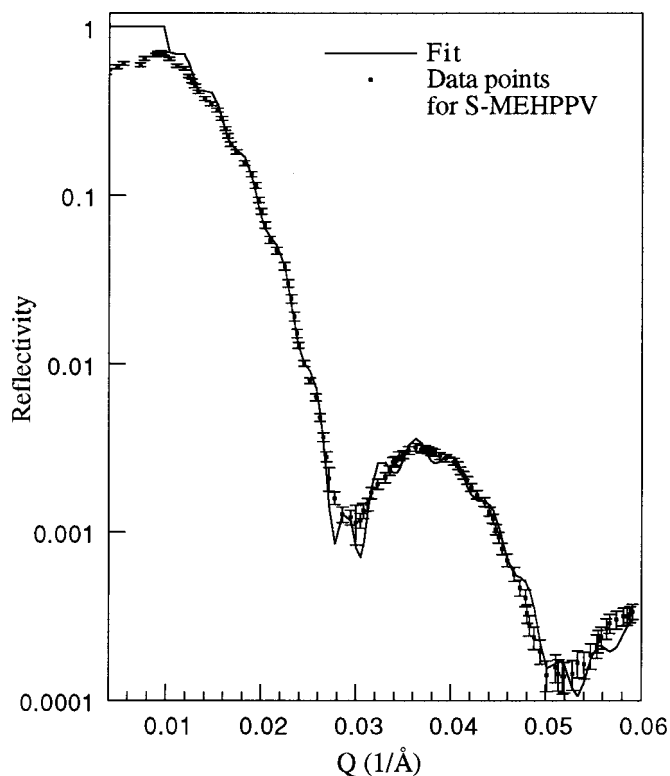


FIG. 4. Reflectivity profile of S-MEHPPV showing the two overlaid interference patterns with the fitted profile.

D. S-MEHPPV

We found that there was a distinct difference in the film forming properties of samples of S-MEHPPV when compared with I-MEHPPV formed from **1**. While I-MEHPPV formed uniform films reproducibly the reflectivity profile of the spin-coated films of S-MEHPPV were particularly sensitive to the preparation conditions. The reflectivity profile of the first film studied (in which only ultrasonication was used to prepare the solution for spin-coating) indicated that the film was comprised of two different but well-defined layers. Careful examination of the reflectivity profile (Fig. 4) shows two distinct length scales for the interference. These could be fitted with structures consisting of either a thin dense layer next to the silicon substrate and a thick low density layer on top of the thin layer or with the two layers the other way around. The parameters of the two layers were $\text{SLD} = (4.0\text{--}4.5) \times 10^{-6} \text{ \AA}^{-2}$ and thickness $D \approx 240 \text{ \AA}$ for the dense layer and $\text{SLD} = (0.9\text{--}1.5) \times 10^{-6} \text{ \AA}^{-2}$ and $D \approx 1360 \text{ \AA}$ for the second layer. We have only given approximate fits here because the alternative positions with respect to the silicon substrate of the two layers result in slightly different fitting parameters. However, the key point is that there are two well defined thicknesses with the thin layer particularly well defined. The value of the SLD for the thin layer is consistent with a complete coating of S-MEHPPV but the SLD of the thick layer shows that the mean density of this layer is approximately one-third of that of the thin layer. In principle, this low density could result either from a spongy layer, i.e., uniform on a lateral length scale of greater than a few hundred nm, or it could result from a small num-

ber of patches of normal density. These two models have quite different effects on the reflectivity profile, and although we cannot be very precise about the exact lateral length scale, the observed reflectivity is only consistent with a spongy thick layer. This result from the neutron reflectivity may help to explain a scanning force microscopy study of S-MEHPPV spin-coated from THF. The latter study showed that the S-MEHPPV films had topographic features in the film, which were assigned to polymer aggregates.⁵ We believe that the topographic features observed by scanning force microscopy may correspond to the thicker spongy layer observed by neutron reflectivity in our sample of S-MEHPPV. This would then suggest that the spongy layer is on the outside of the film. The topographic features are believed to arise from aggregates in solution being transferred to the film during spin-coating. If this is the case then what is remarkable is that, given the range of sizes possible for such aggregates, the width of our thick layer is so well defined. One would expect a range of thickness in this layer which would lead to a complete absence of any interference fringes in contrast to our observation of a very well defined thickness. This suggests that there may be an alternative explanation for the formation of the topographic features, for example, that they arise from a competition between the polymer-substrate surface interactions versus polymer-polymer interactions. That is, a homogeneous solution is deposited but with the film organizing itself to minimize its energy. Such an organization would be expected to be uniform over the whole film and could give rise to two distinct but uniform layers. Such an organization would be clearly sensitive to the environmental conditions and solution concentration from which the sample was processed.

To determine the effect of annealing on this peculiar structure the film was heated to 180 °C under vacuum and then cooled back to room temperature. There was little change on heating up to 180 °C but, on cooling, the thickness of the thinner layer decreased by about $10 \pm 5\%$ while there was no change in the thicker layer. The lack of change in the spongy layer, if at the air-polymer interface, is different from the scanning force microscopy experiment which showed some apparent annealing of the surface of MEHPPV films. The differences in the observations of the effect of annealing will have to be studied further.⁵ However, the change in thickness of the thin layer shows that it has been annealed. The T_g of S-MEHPPV 2 has been reported to be in the region of 216 °C.⁵ We have measured a broad T_g for our sample of S-MEHPPV, in the bulk, centered at 205 °C. Therefore we prepared a second film of S-MEHPPV and annealed it at 220 °C before allowing it to cool. In this second film the thicker layer was not clearly observable reflecting that slight differences in polymer solution preparation can affect the formed spin-coated film. Nevertheless, the thinner layer was well defined and similarly to the earlier sample the thin layer decreased in thickness by around 6% and scattering length density increased by around 10%. This clearly shows that there is a densification of the S-MEHPPV on annealing which could effect the photophysical properties of the film. The fact that subtle differences in processing conditions can give rise to interesting structures within

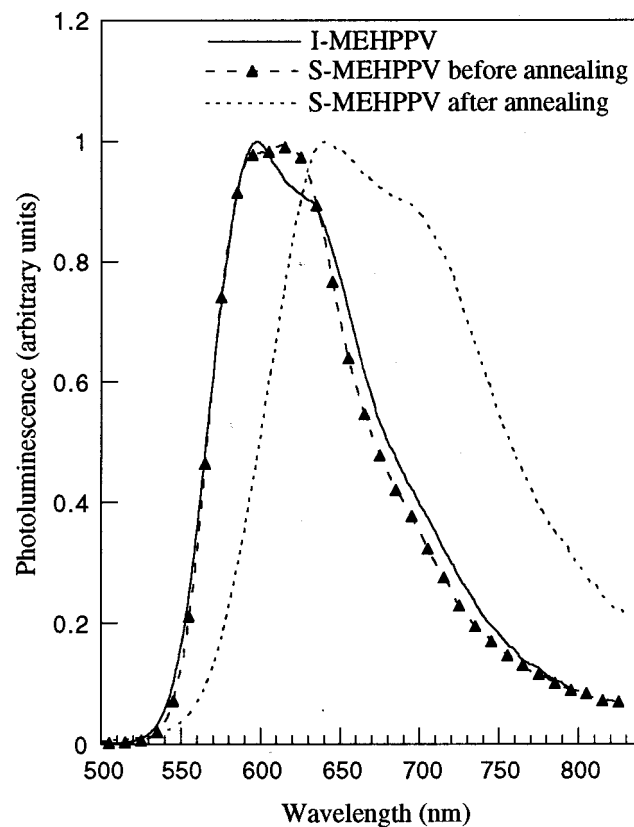


FIG. 5. PL spectra of I-MEHPPV and S-MEHPPV before and after annealing.

S-MEHPPV 2 films shows that there is a need for further investigation of the deposition process.

E. Photoluminescence spectra

It is important to relate the physical properties observed in the reflectivity measurements to the optical properties of the polymers. Therefore we have measured the photoluminescence (PL) spectra of I-MEHPPV and S-MEHPPV with the latter measured before and after annealing. The PL properties of conjugated polymers are particularly sensitive to intermolecular interactions. Close packing of conjugated chains can lead to excimer emission, which is observed as a broad red tail on the PL spectra. The PL spectra of I-MEHPPV and S-MEHPPV on quartz before and after annealing are shown in Fig. 5. The I-MEHPPV was prepared by heating **1** under vacuum for 10 h at 220 °C, i.e., at a similar temperature as the T_g measured for S-MEHPPV. S-MEHPPV was measured before and after annealing at 220 °C for 1 h. A slightly lower molecular weight S-MEHPPV was used for the PL measurements to ensure the films were of good optical density. Two important observations can be made; first, for S-MEHPPV there was a redshift of the peak maximum and onset of absorption, and broadening of the PL spectra after annealing. The redshift in the absorption maxima suggests that there is better intramolecular order in the film and the broadening and slightly longer red tail is indicative of increased intermolecular interactions. These two results are consistent with the densification observed from the reflectivity profiles for S-MEHPPV after an-

nealing and a previous PL measurement.⁵ The second observation is that the PL spectra of I-MEHPPV and unannealed S-MEHPPV are very similar. The NR reflectivity results show that the I-MEHPPV films are annealed after the conversion process. This suggests that I-MEHPPV and annealed S-MEHPPV form films of different morphology.

IV. CONCLUSION

We have shown that neutron reflectivity is a powerful technique for probing the physical structure of conjugated polymers. We have shown that S-MEHPPV can form two component films when spin-coated from tetrahydrofuran, and that the thinner layer can be annealed by thermal cycling. In contrast, the films of I-MEHPPV formed from a chloro precursor polymer were uniform and effectively annealed during the conversion process. On thermal annealing there was little change to the physical structure of the film although I-MEHPPV does have a large coefficient of expansion. The reflectivity data suggests that the amount of available hydrogen chloride in a converted film, which may react with the underlying electrode material,²⁰ is low. Finally, the PL spectrum of S-MEHPPV shows a distinct redshift and broadening after annealing which corresponds to the densification observed from the reflectivity measurements. We are continuing to study this and other conjugated polymer systems by NR in an effort to relate the physical structure to the optoelectronic properties of the conjugated polymers.

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