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Microstructure of gel-processed blends of conjugated polymer and ultrahigh molecular weight polyethylene

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Abstract

Blends of conjugated polymers with ultrahigh molecular weight polyethylene (UHMW-PE) containing up to 30% (w/w) of poly(2-butyl, 5-(2′-ethyl-hexyl)-1,4-phenylene vinylene) (BuEH-PPV) have been prepared by gel processing. The microstructure of both pristine and oriented (tensile drawn) films were studied using optical microscopy (365 nm ultraviolet illumination), X-ray diffraction and transmission electron microscopy. The results show that in pristine films, phase separation results in bicontinuous interpenetrating networks. After tensile drawing to a draw ratio $\lambda = 100$, the structure develops into nematically oriented microfibers comprising oriented macromolecules interspersed within similar (partially) crystalline microfibers of UHMW-PE. The photoluminescence emission from the oriented blends (30% (w/w) BuEH-PPV) is polarized with a polarization ratio of 50:1 (parallel to perpendicular with respect to the draw axis).

Keywords: Microstructure; Conjugated polymer blend films

1. Introduction

Although the method of gel processing has been successfully used to chain extend and orient the macromolecules of conjugated polymers in ultrahigh molecular weight polyethylene (UMHW-PE) [1–10], the microstructure of the blends is not yet clear. Mesoepitaxy (epitaxial orientation of the conjugated polymer on the internal surfaces of the gel-processed PE) was initially proposed as the mechanism for orientation of the conjugated polymer macromolecules [2]. Weder et al. subsequently commented that the blend appears to be a molecular dispersion of the conjugated polymer in the host UHMW-PE [7].

Highly polarized photoluminescence (PL) emission (polarization ratio parallel to perpendicular with respect to the draw axis of 60:1 [2] and 72:1 [7]) was reported from dilute (1–2% (w/w)) blends of the conjugated polymer in UHMW-PE. Weder et al. found, however, that the polarization ratio was reduced at high concentrations (25% (w/w)) of the conjugated polymer component [7].

With a goal of improving the optical quality of the oriented films, we have prepared and characterized the microstructure of blends of BuEH-PPV in UHMW-PE at concentrations up to 30% (w/w). PL polarization ratios as high as approximately 50:1 were achieved even at these high concentrations of conjugated polymer. We summarize here the results of optical microscopy (365 nm ultraviolet illumination), X-ray diffraction and transmission electron microscopy (TEM) studies which together lead to a model for the microstructure of both pristine films and drawn films of the BuEH-PPV/UHMW-PE blends. In pristine films, phase separation results in bicontinuous interpenetrating networks of the BuEH-PPV and UHMW-PE components. After tensile drawing to draw ratio $\lambda = 100$, the networks develop into nematically oriented micro-fibrils comprising oriented macromolecules of the conjugated polymer interspersed within similar (partially) crystalline microfibers of UHMW-PE.

2. Experimental

The BuEH-PPV was prepared as described by Andersson [11]. The molecular weight data, as determined by gel permeation chromatography (GPC), were as follows: $M_n = 95097\ \mathrm{g\ mol^{-1}}$, $M_w = 142387\ \mathrm{g\ mol^{-1}}$ with polydispersity index equal to 1.5. The glass transition temperature (T_g), as determined by dynamic mechanical analysis (DMA) with a

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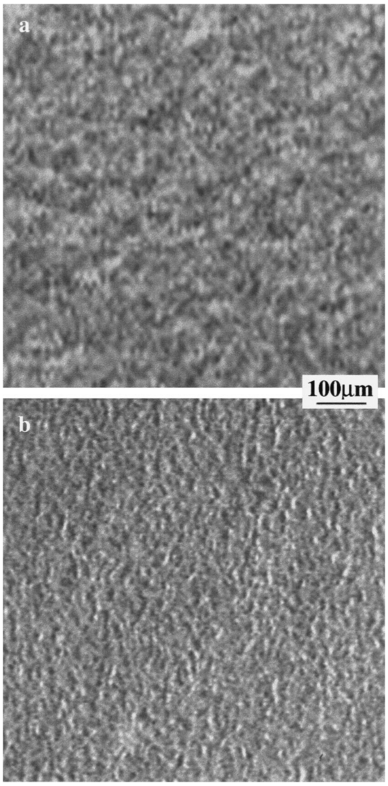

Fig. 1. UV optical micrographs of 17% (w/w) BuEH-PPV (a), and 30% (w/w) BuEH-PPV (b) in pristine blend film with UHMW-PE, showing continue network morphology of BuEH-PPV.

PERKIN ELMER 7, is approximately 65°C. By visual observation under an optical microscope equipped with a hot stage, no melting point was observed at temperatures up to 200°C.

For preparing and gel-processing the blend, 60 mg of UHMW-PE (Aldrich, $M_w = (4 - 6) \times 10^6$ g mol^{-1}) and 26 mg of BuEH-PPV were mixed with 7.5 ml of *p*-xylene in a closed vial, thereby making a solution with a concentration of ~1.1% (g/v). The mixture was put into an oil bath at 80–90°C and stirred vigorously to make a uniformly dispersed colloidal solution prior to the dissolving temperature of PE (after the PE begins to dissolve, the solution becomes too viscous for effective stirring). After bringing the temperature up to 100°C, the cap of the vial was removed for about a minute to allow any residual water vapor to escape. The UHMW-PE began to dissolve when the solution was at approximately 114°C. When the temperature reached 125–128°C, the UHMW-PE was completely dissolved, and the solution became clear and fluid. The clear solution was poured out and cast onto a glass surface (at room temperature). After drying in a fumehood for about 24 h, the cast film was pumped in a desiccator (for more than 24 h) until the solvent was completely extracted. A homogeneous gel film with thickness of about 30 μm was obtained. The film was then tensile drawn to a draw ratio of $\lambda = 100$ in nitrogen atmosphere at temperatures in the range of 90°–105°C. The thickness of the drawn film was typically 1–2 μm.

To obtain samples sufficiently thin (thickness of several hundred nm) for TEM, thinner pristine films were prepared by diluting the initial solution. One drawn BuEH-PPV/UHMW-PE blend film was studied “as prepared” by TEM. Another TEM sample was prepared from the same drawn blend film; however in this case, the film was stored in *p*-xylene for about one week to extract the BuEH-PPV (after which the green color of the BuEH-PPV could no longer be seen). This fully extracted sample was carbon coated (thickness of carbon film about 10 nm) to avoid charging by the electron beam of the TEM.

A Nikon optical microscope equipped with a CCD camera was used to study the morphology of the blend film. The light source was a UV lamp (365 nm); under 365 excitation the BuEH-PPV component is highy luminescent while the UHMW-PE is dark. X-ray diffraction studies of the pristine and drawn blend films used a Siemens Smart X-ray diffractometer equipped with CCD camera and rotation stage. A Philips X’pert diffractometer was used for neat single component films. TEM studies were performed with a JEOL 100 CX, operated at 100 kev accelerating voltage.

3. Result and discussion

3.1. Microstructure of pristine films

In order to study the microstructure of the blend films we chose BuEH-PPV, a typical conjugated polymer, as the guest for mixing with UHMW-PE as host, because the luminescent polymer can be specifically identified in the blend by UV optical microscopy and X-ray diffraction (see below). It is reasonable to expect that that the structural aspects of other UHMW-PE blends with conjugated polymers will be similar.

3.1.1. Optical observation

As noted above, that UHMW-PE is dark, while BuEH-PPV is highly fluorescent under UV illumination by 365 nm light. Thus, one can observe the morphology of the BuEH-PPV in the blend directly. Fig. 1a and b are optical micrographs of blends with concentrations of 17% (w/w) and 30% (w/w) of BuEH-PPV respectively. The BuEH-PPV exhibits a continuous network in the pristine blend film; phase separation results in bicontinuous interpenetrating networks of BuEH-PPV and UHMW-PE. Fig. 1 also shows that higher the concentration of the conjugated polymer, higher the density of the interpenetrating network. Unfortunately, when the concentration is lower than 10% (w/w) of the BuEH-PPV, the optical density of the BuEH-PPV component is too low to be detected by the CCD camera.

3.1.2. X-ray diffraction

Using X-ray diffraction to look at the bicontinuous interpenetrating networks of the pristine film on molecular

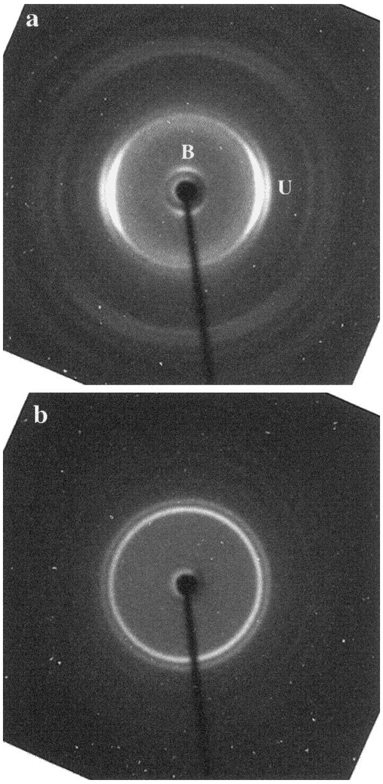

Fig. 2. X-ray diffraction patterns of 30% (w/w) BuEH-PPV pristine blend film with UHMW-PE for setting of X-ray beam parallel (a) and perpendicular (b) to the film plane. The diffraction arcs, indicated by B and U in (a) arise from the BuEH-PPV and UHMW-PE crystalline phases, respectively.

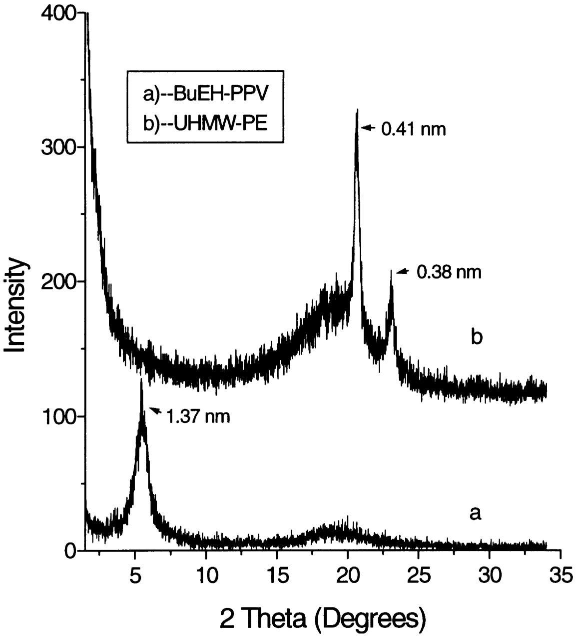

Fig. 3. The diffraction patterns of the neat BuEH-PPV (a) and the neat UHMW-PE (b) films, respectively.

length scale, we found that there are crystalline phases in both the BuEH-PPV and the UHMW-PE networks. Fig. 2a and b are X-ray diffraction patterns from the 30% (w/w) BuEH-PPV/UHMW-PE pristine film, obtained by setting the film parallel and perpendicular to the X-ray beam respectively (the small spots in the patterns of Fig. 2a and b are artifacts). Fig. 2a shows that there are reflections (in the shape of arcs) in both the meridional and equatorial directions, indicated by B and U, respectively. For comparison, Fig. 3a and b are diffraction patterns of neat BuEH-PPV and neat UHMW-PE films, respectively. BuEH-PPV has a strong characteristic peak at low angle corresponding to a *d*-spacing of 1.37 nm, while UHMW-PE has peaks at higher angles corresponding to *d*-spacing of 0.41 and 0.38 nm. These characteristic peaks match the positions of the diffraction arcs in the meridional (B) and equatorial (U) directions in Fig. 2a, respectively. The characteristic *d*-spacings of 0.41 and 0.38 nm correspond to the positions of the strong rings in Fig. 2b as well. Based upon these *d*-spacings, the diffraction features in Fig. 2a and b can be identified as reflections from the crystalline phases of the BuEH-PPV and the UHMW-PE components, respectively. Thus, phase separation is definitively observed by characterization of the crystalline phases of the individual components.

The arc-shaped diffraction features in Fig. 2a indicate anisotropy in the diffraction pattern and hence imply anisotropic alignment of the crystalline phases (crystalline planes) in each network of the pristine film. The arcs occur in the meridional direction, as indicated by B in Fig. 2a (but not in Fig. 2b). This means that the crystalline planes of BuEH-PPV are predominantly parallel to the plane of the film. The intermolecular distance of the BuEH-PPV along the side chain direction (perpendicular to the main chain) is estimated to be 1.37 nm. Thus, the 1.37 nm *d*-spacing in-plane structure corresponds to ordering of the side-chains of the BuEH-PPV molecules. The aliphatic character of the side chains of the molecules in *p*-xylene makes such side-chain ordering favorable. Similar results were obtained from dMOM-PPV films solution cast from *p*-xylene [12], where a laminated structure was inferred in which the benzene ring plane was orthogonal to the film plane.

A schematic drawing of the molecular structure of BuEH-PPV in the pristine blend is shown in Fig. 4a. The lamellae and the lines are, respectively, the crystallites and the amorphous parts of the network.

There is also anisotropy in the diffraction features of the UHMW-PE, as indicated by U in Fig. 2a. However, there is a difference in crystalline alignment of the UHMW-PE from that of the BuEH-PPV. The crystalline planes of UHMW-PE are mostly perpendicular to the film plane, while the lamellae of BuEH-PPV are parallel to the film plane. The rings indicate that the crystalline planes of the UHMW-PE are not only perpendicular to the plane of the film, but also randomly distributed with respect to the azimuth of the film,

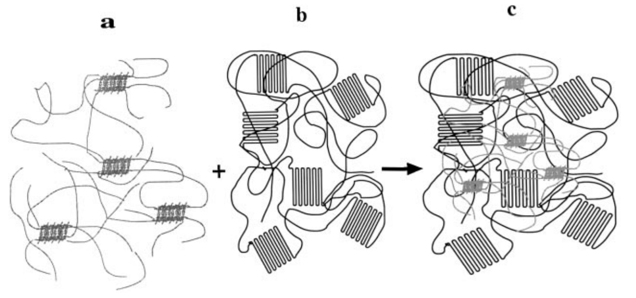

Fig. 4. The schematic drawings of the bicontinuous network morphology of the blend. (a) BuEH-PPV as lamellas and lines (representing the crystalline and the amorphous regions, respectively); (b) UHMW-PE as the folded and the non-folded black lines (representing the crystalline and the amorphous regions, respectively); (c) Mixture of BuEH-PPV with UHMW-PE, as in the blend.

as shown in the schematic drawing of the molecular structure of UHMW-PE (Fig. 4b). The parallel folded lines and random lines refer to the crystalline planes and amorphous parts, respectively.

The molecular model of the pristine blend film shown in Fig. 4c indicates a mixture of two interpenetrating continuous networks; the gray color for BuEH-PPV and the black color for UHMW-PE. The crystalline domain size can be estimated as 20 nm and 40 nm for BuEH-PPV and UHMW-PE by using Scherrer formula [13] and the data from the strongest peaks in Fig. 3a and b.

The UV optical microscopy and the X-ray diffraction data are consistent and show that the microstructure of the pristine gel film can be described as a bicontinuous interpenetrating network that results from phase separation. Note that the network structure can be exhibited both on the μm-scale (Fig. 1) and on the nm-scale (Fig. 4).

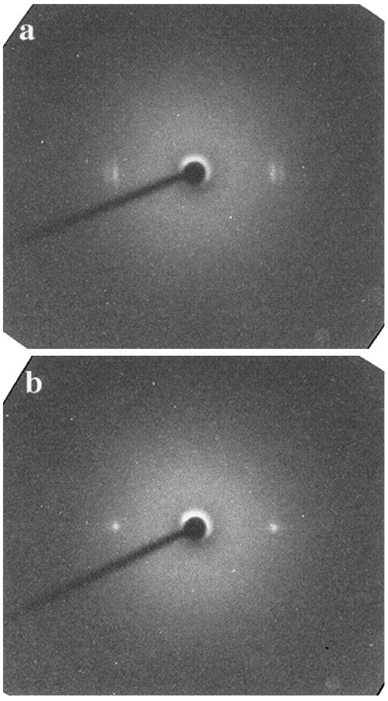

Fig. 5. X-ray diffraction patterns of 30% (w/w) oriented BuEH-PPV blend film with UHMW-PE, showing only reflections (spots) from oriented UHMW-PE (no reflections from BuEH-PPV). Fig. 5a, and b are the patterns obtained by setting X-ray beam parallel to the film plane and perpendicular to the draw direction, and perpendicular to the film plane, respectively.

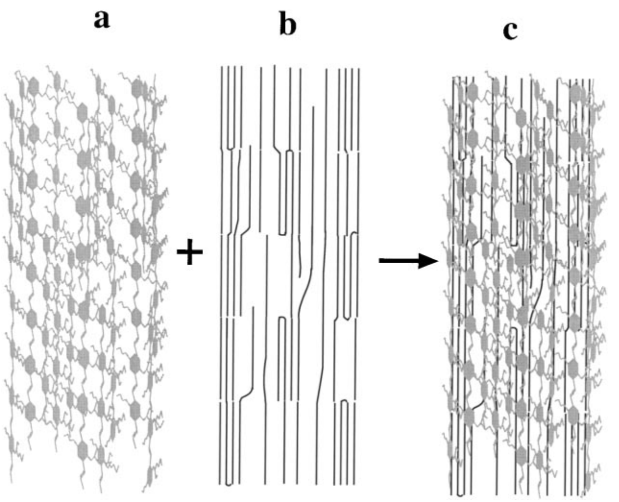

Fig. 6. The schematic drawings of the oriented BuEH-PPV macromolecules (a); and UHMW-PE (b); and their mixture (c) showing the interstitial microfiber structure.

3.2. The microstructure of the oriented films

Based on the microstructure of the pristine film, one anticipates that by tensile drawing, the macromolecules of conjugated polymer in the blend film will orient by stretching the bicontinuous interpenetrating networks. As a result, as shown in the following paragraphs, the morphology of the oriented macromolecules in the drawn blend films can be described as interspersed microfibers, as revealed by X-ray diffraction and TEM.

3.2.1. X-ray diffraction

Fig. 5 is the X-ray diffraction pattern obtained from an oriented 30% (w/w) BuEH-PPV blend film by the setting X-ray beam parallel to the film plane and perpendicular to the draw direction (Fig. 5a), and perpendicular to the film plane (Fig. 5b). Only reflections from the crystalline phase of UHMW-PE can be seen; there are no reflections from the BuEH-PPV component. This means that the crystalline phase in the BuEH-PPV network is destroyed by tensile drawing. Thus, the BuEH-PPV macromolecules are chain extended and oriented along the draw direction, but they are randomly shifted and rotated along and about the chain axes, forming a nematically oriented microfiber structure, as shown in schematic drawing in Fig. 6a. The crystalline phase, actually the interchain order, of the UHMW-PE in the stretched blend film gives the reflections shown as spots in equatorial direction in the diffraction patterns of Fig. 5. The corresponding molecular model of the UHMW-PE in the blend is shown in Fig. 6b where the UHMW-PE

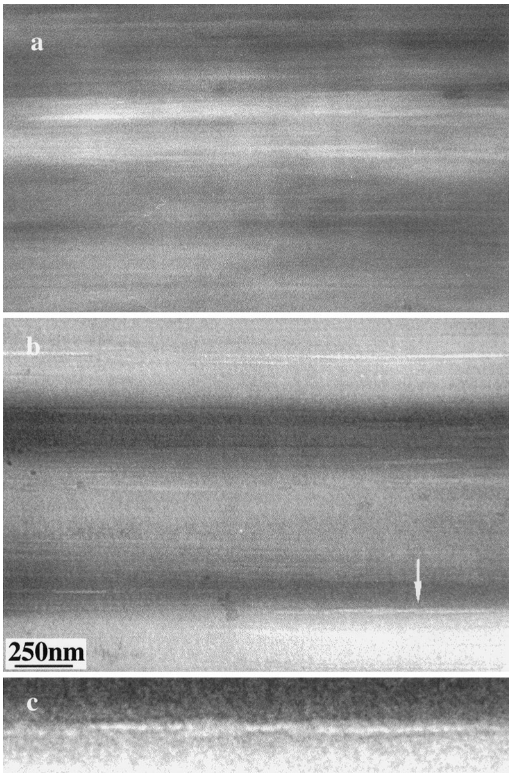

Fig. 7. TEM micrographs of the oriented blend films. (a) Drawn sample (the contrast is blurred), and (b) Sample without the BuEH-PPV component, showing clear microfiber structure, (c) An enlarged entanglement, indicated by an arrow in (b).

macromolecules are sketched by black lines. The interspersed oriented microfibers of BuEH-PPV and UHMW-PE are shown schematically in Fig. 6c. Thus, the bicontinuous interpenetrating networks of the pristine film (Figs. 1 and 4) evolve to an interspersed array of phase separated microfibers in the stretched blend film.

3.2.2. TEM observation

The microfiber structure, inferred from X-ray diffraction data, can be imaged directly via TEM. Two TEM samples are examined for comparison: an “as drawn” blend film and an identical drawn blend film from which the BuEH-PPV component has been extracted. Fig. 7a is an electron micrograph (bright field image) of the drawn blend film containing BuEH-PPV. The contrast is quite blurred, though μm-scale brighter and darker horizontal strip-like area and some nano-scale brighter and darker horizontal lines can be seen. Fig. 7b is the electron micrograph (bright field image) of the film with the BuEH-PPV component removed; the contrast is significantly improved and more fine lines are observed in the brighter and in the darker strips of the film.

According to image contrast theory in TEM for such polymer object [14], the brighter and the darker contrast in the shape of the μm-scale strips and the nano-scale lines correspond to thinner and thicker areas of the film, respectively. These lines are images of the microfibers. Oriented BuEH-PPV microfibers are interspersed within similar microfibers of (partially) crystalline UHMW-PE. The fine lines are more clear (the contrast is better) in Fig. 7b after extraction of the BuEH-PPV. The characteristic width of the microfibers is approximately 20–30 nm (Fig. 7b). These microfibers are entangled, but aligned; one typical entanglement is shown in Fig. 7c where the feature indicated with an arrow in Fig. 7b has been enlarged by a factor of four.

These interspersed BuEH-PPV microfibers give the PL polarization ratio as high as approximately 50:1.

4. Conclusion

The X-ray and TEM data show that the bicontinuous interpenetrating network structure of the pristine film develops into a microfiber structure during the tensile drawing. The microfiber structure of the drawn films originates from the bicontinuous interpenetrating network of the pristine film. The driving force for forming the microfiber structure is obviously the tensile drawing. Entanglement of the BuEH-PPV and UHMW-PE components in the network structure is an important factor that causes the two components to align and restructure, resulting in the stretched and oriented microfibers in the oriented film. Thus, the mechanism of the orientation is not mesoepitaxy [2], nor is it molecular scale dispersion of the guest in the host [7]. The mechanism relies on the nature of the phase separation into bicontinuous networks in the pristine film. The order in the conjugated polymer microfibers is nematic; the BuEH-PPV macromolecules are chain extended and oriented, but with no observed interchain order. The microfibers of the UHMW-PE component on the other hand, exhibit a relatively high degree of interchain order.

Acknowledgements

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