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Branched Polyethylene as a Plasticizing Additive to Modulate the Mechanical Properties of π-Conjugated Polymers

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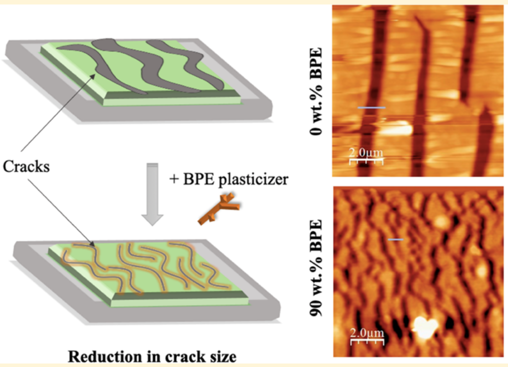
Supporting Information

ABSTRACT: A new approach for improving the mechanical properties of semiconducting polymers was established via physical combination of a diketopyrrolopyrrole-based conjugated polymer with a low-molecular-weight branched polyethylene (BPE). The influence of the BPE additive on the stretchability and mechanical properties of the conjugated polymer was studied at different scales, using various characterization techniques, including atomic force microscopy, UV−vis spectroscopy, and grazing incidence X-ray diffraction. At the micron scale, the BPE additive acts as a plasticizer and significantly reduces Young's modulus of the conjugated polymer and increases the crack onset strain, reaching a maximum of a 75% strain elongation when 90 wt % of BPE is blended with the conjugated polymer. The introduction of BPE to the blended systems decreases the crack propagation of polymer thin films, making them softer and more ductile, with Young's modulus of 112 MPa at 25 wt % of BPE before thermal annealing. At the nanoscale, the improvement of stretchability is shown by the reduction of the crack size under a 100% strain, going from 3100 to 600 nm at 0 and 90 wt % of BPE, respectively. The results obtained in this investigation confirm that an improvement in the mechanical properties and a modulation of the solid-state morphology of the semiconducting materials can be enabled by the physical mixing of conjugated polymers with a nontoxic, low-molecular-weight branched polyethylene, particularly favorable for the solution deposition of organic semiconductors.



1. INTRODUCTION

The expanding field of flexible organic electronics has driven the development of soft and stretchable electronic materials with better performance and enhanced thermophysical properties.[1−3] One of the biggest challenges for the design and preparation of flexible and stretchable electronics is to maintain their good performance while applying physical and mechanical stimuli as both properties are in competition.[4,5] To address this challenge, organic electronics are particularly promising as their fabrication involves materials that possess both good electronic and mechanical properties, particularly desirable for the production of new stretchable electronics.[6−9] Among other, semiconducting π-conjugated polymers are remarkable candidates to develop intrinsically stretchable organic electronics.[7,10] More specifically, conjugated polymers possess the advantages of being potentially low cost, lightweight, and easily processable through large-scale solution deposition, thus providing an interesting route to stretchable electronics.[11,12] As a result, an important scope of research has been focused on the development of novel strategies to enhance mechanical properties of conjugated polymers while maintaining their good electronic properties with stretching.[13−15]

One common approach to achieve mechanically robust and stretchable conjugated polymers is through physical blending of the rigid-rod materials with soft elastomeric materials.[16−19] Poly(dimethylsiloxane) (PDMS) has become one of the most commonly used elastomers for fabricating stretchable devices, being used either as a substrate, dielectric materials, or directly as a component of semiconducting polymer/elastomer blends.[20] In recent years, Reichmanis et al. reported the utilization of PDMS with conjugated polymers, which resulted in improved electronic and thermomechanical properties of the semiconductor.[21−23] Interestingly, organic field-effect transistor (OFET) devices, using PDMS and poly(3-hexylthiophene, P3HT) blends as semiconducting materials, were fabricated and shown good electronic properties under strain.[22] In

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addition to PDMS, other soft polymers such as polystyrene (PS) and polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene were used to improve electronic properties and mechanical compliance of semiconducting polymers.[24−26] Despite promising results, the impossibility of removing the soft polymer from the semiconducting layer upon thermal annealing can potentially have an effect on the overall performance as a significant amount of insulating material has to be used. Therefore, additives that can be removed during device fabrication have been developed recently and have been shown to enhance the charge transport of conjugated polymers by promoting aggregation between polymer chains.[27−29] Reported by Jeong et al., the utilization of dichlorobenzene as a solvent additive in the processing of P3HT for thin-film transistor was shown to be particularly interesting.[30] As a result, the charge transport mobility in OFETs was enhanced from 0.017 $cm^2 V^{-1} s^{-1}$ for the pure conjugated polymer to 0.082 $cm^2 V^{-1} s^{-1}$ with solvent additive, due to the effect of the small molecules on the morphology of the semicrystalline polymer. Despite the promises for control and fine tuning of thin-film morphology, and potential positive impact on the charge carrier properties of rigid semiconducting materials, low boiling point additives and their impact on the thermomechanical and physical properties of semiconducting polymers have not been fully investigated.

Recently, our group reported the combination of a low-molecular-weight branched polyethylene (BPE) with a poly(diketopyrrolopyrrole-*co*-thienovinylthiophene) P(DPPTVT) conjugated polymer for controlling the morphology in the solid state.[31] The branched polyethylene, when mixed to a π-conjugated polymer, was found to increase aggregation, decrease crystallinity, and help maintain good charge transport (hole mobility of 0.3 $cm^2 V^{-1} s^{-1}$ in top-contact bottom-gate OFETs) even though the amount of polymer was reduced to 0.05 wt %. This is especially attractive for the large-scale processing of organic semiconductors via solution deposition.

Herein, we report the effect of BPE on the mechanical properties of conjugated polymers in thin films and its impact on the solid-state morphology of the conjugated polymer. Multiple techniques were utilized to characterize the impact of BPE on the thermomechanical properties of the semiconducting polymer before and after blending. Among others, grazing incidence X-ray diffraction (GIXRD), atomic force microscopy (AFM), and film-on-water tensile pull testing were utilized to examine the effect of the additive on the semiconducting conjugated polymer morphology in thin films before and after removing the additive via thermal treatment. Based on the obtained results without thermal annealing, BPE was found to act as a plasticizer (Figure 1), making the polymer thin films more amorphous, which is beneficial for mechanical properties. More specifically, the addition of BPE to a rigid conjugated polymer showed a reduction in crack propagation and crack size upon strain, and a moderate decrease in Young's modulus was also observed. The influence of this new additive on the thermomechanical properties can be attributed to a nanophase separation in the polymer blend, which helps to reduce Young's modulus and crack onset strain. The BPE additive is, therefore, particularly promising for the design of stretchable electronic devices and the development of innovative technologies based on organic polymer blends.

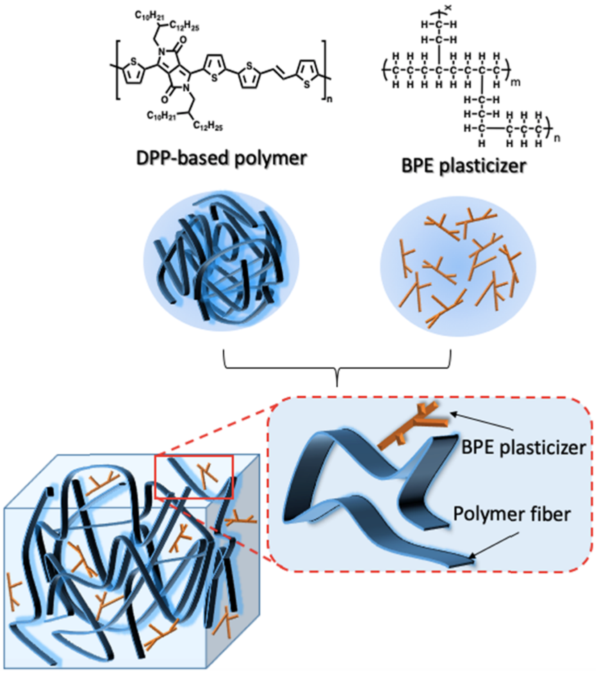

Figure 1. Plasticizing effect of a branched polyethylene (BPE) additive physically blended with a DPP-based polymer for the fine tuning of the thermomechanical properties of the semiconducting polymer.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial reactants were used without further purification unless stated otherwise. All of the solvents used in these reactions were distilled prior to use. Low-molecular-weight branched polyethylene (BPE, ~500 Da) was purchased from PolyAnalytik (London, Ontario) and used as is. Tris(dibenzylideneacetone)-dipalladium(0)-chloroform adduct ($Pd_2(dba)_3 \cdot CHCl_3$) was purchased from Sigma-Aldrich and recrystallized following a reported procedure.[32] (*E*)-1,2-bis(5-(Trimethylstannyl)thiophen-2-yl)ethene (TVT) and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione were synthesized according to the literature.[33]

2.2. Measurements and Characterization. High-temperature gel permeation chromatography was utilized to examine number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index and was performed on an EcoSEC HLC-8321GPC/HT (Tosoh Bioscience) equipped with a single TSKgel GPC column (GMH_{HR}-H; 300 × 7.8 mm^2) calibrated with monodisperse polystyrene standards in 1,2,4-trichlorobenzene. UV−visible spectroscopy was performed on a Varian UV/visible Cary 50 spectrophotometer. A multimode atomic force microscope (AFM, Digital Instruments) operated in the tapping mode at room temperature was used to probe the surface structure of polymer films. Images were collected using Nanoscope 6 software and processed using WSxM 5.0 Develop 8.0 software. Grazing incidence X-ray diffraction (GIXRD) experiments were realized at the Canadian Light source (beamline HXMA) at an X-ray wavelength of 0.9758 Å, corresponding to a beam energy of 12.7 keV. The incidence angle of the X-ray was set at 0.12. The sample-to-detector distance was fixed at 150 mm. Numerical integration of the diffraction peak areas was performed using the software fit2d. Grazing incidence wide-angle X-ray scattering (GIWAXS) under strain was performed on a Xenocs Xeuss 2.0 beamline with an X-ray wavelength of 1.54 Å at a sample-to-detector distance of 150 mm. The scattering signal is collected by a Pilatus 1 M detector and later processed using Igor 8 software combined with Nika package and WAXSTools. X-ray diffraction was performed on a Proto AXRD benchtop powder diffractometer with a Cu source (λ = 1.5406 Å). Film thickness was evaluated by AFM. The chemical topographies of the polymer films were mapped using a Bruker Anasys nanoIR3 equipped with a Daylight Solutions MIRcat-QT IR laser and Anasys PR-EX-TnIR-A cantilever tip. A wavelength of 1664 cm^{-1} was used to measure the relative wavelength absorption of the DPP domains, and 5 μm^2 images were collected using Analysis Studio software at a scan rate of 0.5 Hz using a 512 × 512 point raster resolution. Dynamic mechanical analysis (DMA) measurements were performed on a TA Q800 instrument.

2.3. Sample Preparation. The polymer mixtures were prepared by dissolving the conjugated polymer and branched polyethylene with selected weight ratios in chlorobenzene (3 mg/mL in total), at 80 °C overnight. To prepare a stock solution, the BPE (75 mg) was dissolved in 10 mL of diethyl ether. Depending on the selected weight percent of BPE required (from 0 to 90 wt %), a certain amount of BPE (stock solution) was transferred in a scintillation vial and evaporated. Then, a selected quantity of the semiconducting polymer was added to the mixture and stirred overnight in chlorobenzene at 80 °C. The obtained solutions were spin-coated onto the silicon substrate with native oxides for further characterization. To remove BPE, thin films are placed on a hot plate and thermally annealed for 30 min at 170°C. The samples for DMA were prepared by drop-casting the polymer solution to a rectangular-shaped mold and left in the vacuum oven at 170 °C for half an hour. The samples were then left at 60 °C overnight before the experiment.

3. RESULTS AND DISCUSSION

To determine the influence of BPE on the mechanical compliance of conjugated polymers, a diketopyrrolopyrrole-based (DPP) semiconducting polymer was directly combined with BPE at different weight ratios. The DPP-based conjugated polymer used in this investigation was prepared according to a previously reported procedure.[34] Known to typically lead to good charge transport mobility, a DPP-based monomer was copolymerized with bis(trimethyltin)thienovinylthiophene (TVT) via Stille polymerization.[35] Subsequently, the material was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, and hexane. The purified polymer was collected in chlorobenzene, followed by precipitation in methanol, and dried under vacuum. Among other additives, BPE was selected due to unique features, which include nontoxicity, low viscosity, and, most interestingly, low boiling point (135 °C) and low molecular weight (500 Da), which allows for the additive to be removed after thermal annealing. Due to its hyperbranched structure, BPE also strongly promotes molecular aggregation of the conjugated polymer and phase-segregated solid-state morphology. Previously reported results of organic field-effect transistor characterization of nonannealed BPE/polymer blends are summarized in Table S1, showing a relatively stable charge transport mobility (average mobility around 0.3 $cm^2\ V^{-1}\ s^{-1}$) regardless of the amount of BPE added to the mixture.[31] After annealing, the annealed devices showed increased charge carrier mobility, going from 0.3 to 1.0 $cm^2\ V^{-1}\ s^{-1}$ (75 wt % BPE/DPP-based polymer).[31] Devices were also fabricated with diluted solutions of semiconducting polymers (with and without the BPE) to minimize the quantity of the semiconductor required. Interestingly, no working devices were obtained without annealing for a solution of conjugated polymer (0.05 wt %) in chlorobenzene, due to a suboptimal thin-film quality. A 98 wt % BPE/semiconducting polymer mixture showed enhanced performance before thermal annealing, reaching a charge transport mobility of 0.054 $cm^2\ V^{-1}\ s^{-1}$.

To investigate the plasticizing effect of BPE, the conjugated polymer was combined with various amounts of BPE additives (0−90 wt %). The effect of BPE on the mechanical properties of conjugated polymers was investigated by lamination on soft substrates.[15,36] Briefly, the blended solutions were spin-coated on top of a glass slide precoated with polystyrene sulfonate (PSS). Then, a PDMS slab was placed on top of the blended materials. By dissolving the PSS sacrificial layer with water, the blended film was transferred on PDMS and the resulting transferred films were directly stretched on PDMS at certain predetermined strain. Finally, to help with material characterization and device fabrication, the stretched thin films were transferred back onto a silicon wafer, functionalized with a monolayer of octadecyltrichlorosilane. The complete procedure of lamination on soft substrates is detailed in the Supporting Information (Figure S1). To gain insight on the thermomechanical properties of P(DPPTVT) upon the addition of BPE at the micron scale, the crack onset strain before thermal annealing of blends containing 0−90 wt % of BPE was measured by optical microscopy. Crack onset strain is defined as the minimum strain at which cracks start to propagate at the microscale. As shown in Figure 2a, for the blended system containing 0 wt % BPE, micron-scaled cracks are observed at a 23% strain, while the incorporation of 90 wt % BPE to the conjugated polymer led to an increase in crack onset strain, reaching a maximum of a 77% strain, as shown in Figure 2b. The progressive incorporation of BPE to the conjugated polymer increases its tolerance to strain, demonstrated by an increase in crack onset strain at the micron scale. This phenomenon is directly due to the effect of BPE on the solid-state morphology and softness of the blend (Figure S2).

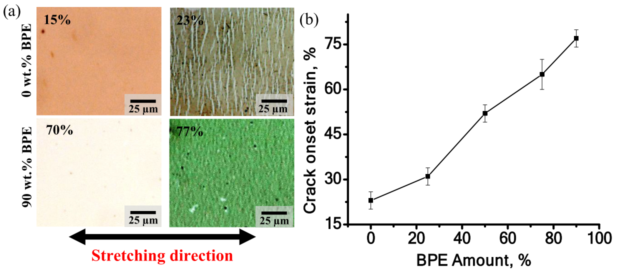

Figure 2. Mechanical properties of the semiconducting polymer with and without the BPE additive at the micron scale. (a) Crack onset strain of P(DPPTVT)/BPE blends containing 0 and 90 wt % of BPE before (left) and after (right) the formation of cracks, as observed by optical microscopy. Scale bars are 25 μm; and (b) crack onset strain versus the amount of BPE as determined by optical microscopy before thermal annealing. Results are averaged from three different samples.

Because phase separation is a key parameter for promoting deformability in conjugated polymer blends, atomic force microscopy coupled with Fourier transform infrared spectroscopy was performed to probe the nanoscale morphology of the blended films.[37] Samples composed of branched polyethylene (BPE) and the DPP-based conjugated polymer were measured as a function of the DPP-based polymer content. The results are summarized in Figure 3, and the parameters used for the experiment are listed in Table S2. All images were measured on a 5 μm^2 scale. As one would predict, as the BPE concentration increases in the blends (going from 25 to 90 wt %), the area occupied by the DPP-based polymer (colored in yellow-red) phase decreases significantly, and an increase in blue domains, associated with BPE-rich domains, can be observed. This observation confirms that the addition of BPE causes a phase

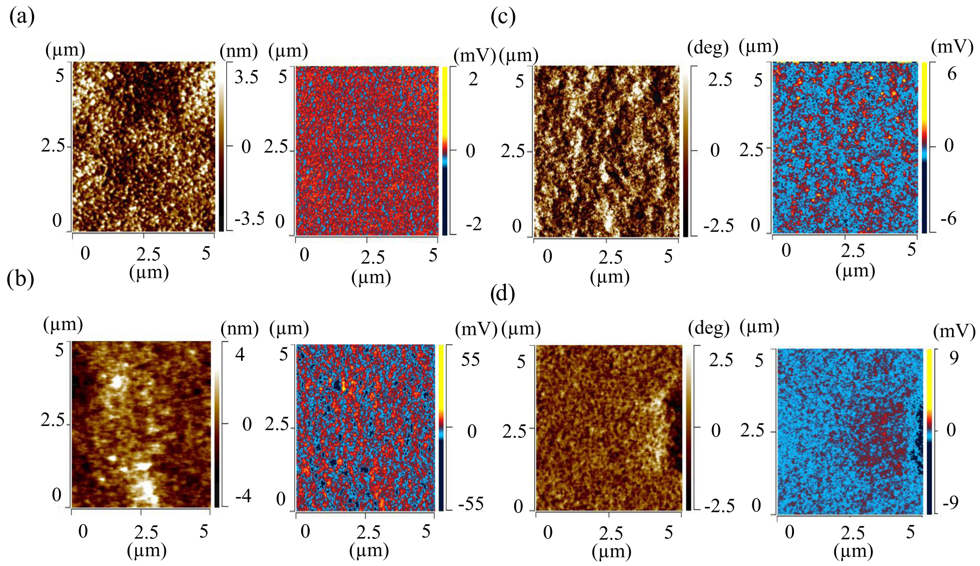

Figure 3. Atomic force microscopy—Fourier transform infrared spectroscopy analysis of polymer blends prepared with (a) 25 wt %, (b) 50 wt %, (c) 75 wt %, and (d) 90 wt % of BPE before annealing. DPP-based polymer is depicted in red/yellow and BPE is depicted in blue.

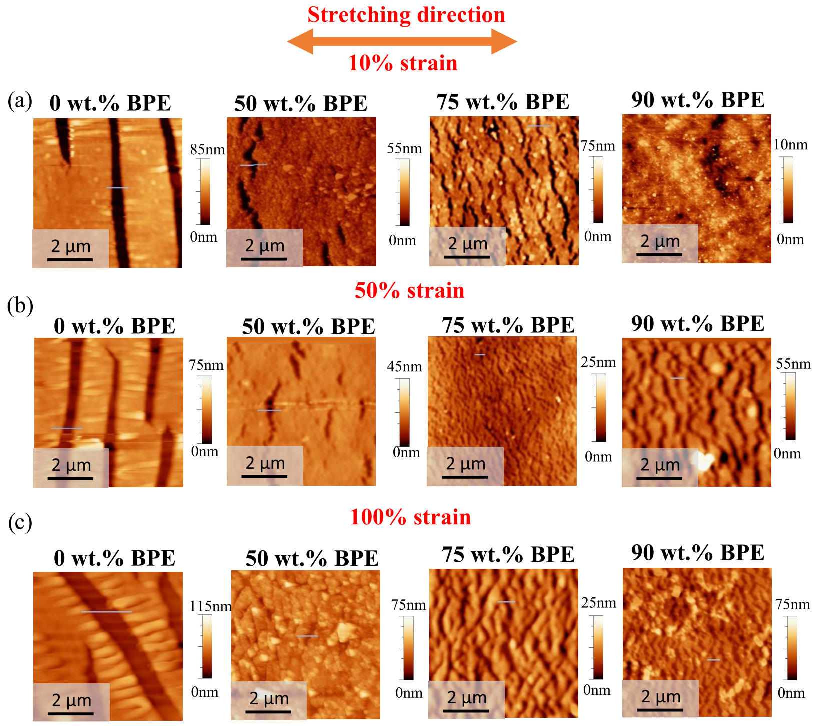

Figure 4. Atomic force microscopy images (height) of BPE/P(DPPTVT) blends containing 0−90 wt % BPE at (a) 10, (b) 50, and (c) 100% strain before thermal annealing. Scale bar is 2.0 *μ*m.

separation, which ultimately can impact the mechanical properties of the polymer blends.

To fully elucidate the plasticizing effect of BPE before thermal annealing at the nanoscale, the characterization of BPE/P(DPPTVT) blends containing 0−90 wt % of BPE under strain was performed using atomic force microscopy (AFM). Based on the obtained results, the number of cracks and their size has been drastically decreased when BPE is added to the semicrystalline polymer. As shown in Figure 4, at 0 wt % BPE (pure conjugated polymer), the thin film mostly consists of long, large nanoscale cracks. Upon the addition of BPE, the nanoscale cracks significantly decrease in size, independent of the strain applied to the materials. The important influence of BPE on crack size and propagation indicates that the additive can act as a plasticizer, improving the mechanical properties of conjugated polymers by reducing their ductility and helping in stress dissipation. The detailed AFM analysis with height profiles is summarized in the Supporting Information (Figures S3−S7). Interestingly, at 90 wt % of BPE, no nanoscale crack was observed at a 10% strain. This finding is also supported by optical microscope observations, resulting in the highest crack onset strain for 90 wt % of BPE compared to the other ratios. Moreover, for 90 wt % BPE/DPP-based polymer blends stretched at a 100% strain elongation, the number of cracks is decreased when compared to the pure P(DPPTVT), as shown in Figure 4c. Since the BPE additive is easily removed upon thermal treatment, the AFM images of P(DPPTVT)/BPE blends containing 0, 50, and 90 wt % at a 50% strain were recorded after annealing (Figure S8). Based on the observed AFM images, the same trend of increased stretchability was observed even without the presence of BPE in the final thin film. Finally, independent of the strain or blending ratio, the addition of BPE promotes a uniform distribution of smaller cracks as opposed to the native conjugated polymer, which showed localized larger cracks.

Crack size analysis at the nanoscale for different blended systems under strain is summarized in Figure 5. At a 25% strain, the crack size was reduced from 1500 nm for P(DPPTVT) to 300 nm for the 90 wt % BPE/polymer blended system. Moreover, a thin film of P(DPPTVT), without introducing any amount of the BPE additive, reached a crack size of 3100 nm at a 100% strain, followed by an abrupt decrease to 300 nm upon the incorporation of 90 wt % BPE to the system. The same trend is observed for BPE/polymer thin-film blends at a 50% strain. Interestingly, the combination of the rigid semiconducting polymer and BPE at various ratios tends to prevent crack propagation, as observed in Figure 5. In all cases, the crack size remains fairly stable upon various strains in contrast to the pure conjugated polymer, which undergoes significant crack propagation and increased nanoscale crack sizes. To confirm the effect of BPE on crack propagation and its plasticizing effect, crack size analysis at the nanoscale was also performed with BPE additives blended with polyisoindigo-*co*-thienovinylthiophene (P(iITVT)), as this polymer is another semiconducting polymer commonly used for the fabrication of high-performance organic field-effect transistors. This analysis was performed using AFM, and the results are depicted in the Supporting Information (Figures S9 and S10). As observed for P(DPPTVT), BPE was shown to significantly influence crack propagation and crack size upon strain when blended at various ratios with P(iITVT). This confirms the trend observed initially and also demonstrates the versatility of our approach to fine-tune the mechanical properties of semiconducting polymers. Similar to what was observed for the initial polymer amalgams, the combination of P(iITVT) with various ratios of BPE tends to prevent crack propagation. Moreover, in all cases, the crack size remains fairly stable upon various strains in contrast to the pure conjugated polymer, which undergoes significant crack propagation and increased nanoscale crack sizes.

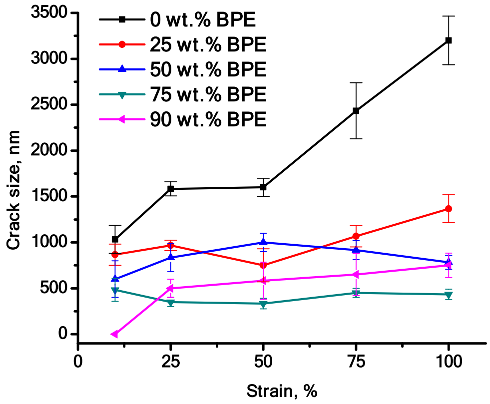

Figure 5. Thin-film crack size versus the different percent strains at 0−90 wt % of the BPE additive as determined by atomic force microscopy (AFM) before annealing. Results are averaged from five different cracks on three different samples.

As demonstrated by AFM analysis, the BPE behaves as a plasticizer, affecting the thermomechanical properties of conjugated polymers. To gain insight into the influence of BPE on the stretchability of conjugated polymers, strain-induced alignment of the polymer chains was quantified with polarized UV−vis spectroscopy by determining the dichroic ratio. The dichroic ratio is defined as $\alpha_{\parallel}/\alpha_{\perp}$, where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the absorption of light polarized parallel and perpendicular to the stretching direction, respectively. A schematic diagram of polarized UV−vis characterization on stretched polymer blend films is illustrated in Figure S11. The measurements were performed with all of the BPE/P(DPPTVT) blending systems to demonstrate the influence of BPE on the chain alignment, which is critical for the mechanical properties (Figures S12−S16). The value of the dichroic ratio is expected to steadily increase upon chain alignment.[38,39] Once cracks are formed, the dichroic ratio becomes smaller meaning that the chain alignment is disrupted. For the pure conjugated polymer (0 wt % BPE), the dichroic ratio increased to 1.9 upon a 25% strain, indicating a certain chain alignment (Figure S17a). However, upon further stress, the dichroic ratio was shown to decrease to 1.3 at a 100% strain, which means that the polymer chains can no longer align past 25% strain. This observation is consistent with the results obtained from AFM. In comparison, the dichroic ratio of BPE/P(DPPTVT) blends containing 50 wt % linearly increased up to 2.5 at a 100% strain, whereas BPE/P(DPPTVT) blended systems containing 25 wt % linearly increased to 1.6 as the strain increased to 100% starting to reach a plateau (Figure S17b,c). The most linear trend of dichroic ratio in the function of strain was observed in the blended system of conjugated polymer and 75 wt % BPE, as shown in Figure S17d. Similarly, the blending system with 90 wt % BPE showed polymer chain alignment up to 100% strain, reaching a value of 3 (Figure S17e). These findings indicate that the conjugated polymer can withstand a 100% strain with aligned chains upon the incorporation of BPE to the system.

As previously reported for polymer blends, the incorporation of the soft component to the conjugated polymers strongly influences their elasticity.[25,26] The effect of the BPE additive on the conjugated polymers was studied using a pseudo freestanding thin-film tensile test.[40,41] Young's modulus was first measured for the BPE/polymer blends before thermal annealing to gain insight into the effect of BPE on the elastic modulus of the conjugated polymer before it has been removed. Young's modulus of the 25 wt % BPE/P(DPPTVT) blend was found to be 57 ± 15 MPa, which is more than three times lower than the elastic modulus of 201 ± 25 MPa for the pure conjugated polymer before thermal annealing (Figures 6a and S18). It is important to mention that it was impossible to measure the elastic modulus for the blended system above 25 wt % BPE in the conjugated polymer due to the brittleness of the freestanding thin films, as shown in Figure S19. The elastic modulus of BPE/conjugated polymer blends was also measured after thermal annealing. The elastic modulus of the pure conjugated polymer was determined to be 224 ± 46 MPa, while the elastic modulus of blended system containing 25 and 50 wt % of BPE remained mostly constant with a modulus of 275 ± 39 and 195±20 MPa, respectively (Figures 6b and S20). Young's modulus could not be measured at for DPP polymer

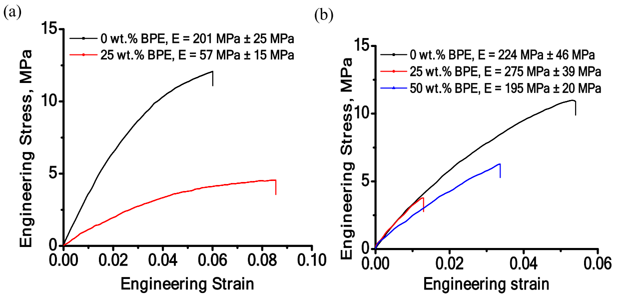

Figure 6. Elastic modulus of the polymer blends (a) before and (b) after thermal treatment as determined by film-on-water tensile pull test.

with 90 wt % of BPE even after thermal annealing due to the brittleness of the freestanding thin films. Interestingly, Young's modulus of the thin film at 25 wt % of BPE is more than 4 times lower before thermal annealing (57 MPa) compared to that of the thermally annealed film (275 MPa), which is another indirect proof of the BPE additive removal and increased crystallinity. This result indicates that the incorporation of BPE to the blended system reduced Young's modulus of the conjugated polymer even after its removal, which is in good agreement with a decrease in the crystallinity of BPE/polymer blends.

The influence of BPE on the thermomechanical properties of the conjugated polymer was also investigated by dynamic mechanical analysis (DMA). Figure S21 shows the results for DMA analysis performed on the different blends. Previously performed on similar conjugated polymer systems, DMA gives access to storage and loss moduli, and the analysis of the tan δ curve gives information on the glass-transition temperature (T_g) of both side chains and π-conjugated backbone. For P(DPPTVT), two peaks can be observed at around −37 and 6 °C, respectively, attributed to the T_g of the flexible alkyl side chains and backbone of the conjugated polymer. For the 50 wt % BPE/P(DPPTVT) blend, a backbone T_g was observed at −1.98 °C, which represent a significant reduction in comparison to the pristine polymer. On the contrary, the side-chain transition peak was observed at −35°C, which is almost similar to the pristine conjugated polymer. By incorporating more BPE to the conjugated polymer (90 wt %), the plasticizing effect of BPE became so pronounced that the peak associated with the π-conjugated backbone T_g completely disappeared, resulting in the observation of a single peak attributed to the T_g of the alkyl side chain at −39 °C. The reduction of the π-conjugated polymer backbone T_g upon the addition of BPE can be directly attributed to the effect of BPE and to its plasticizing effect.

To further investigate the solid-state morphology of BPE/polymer blends and gain insight into the thin films' crystallinity, grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were performed on the different polymer mixtures after annealing. The BPE additive was found to disrupt the thin-film morphology and prevented large crystalline phases to form. The diffraction peak intensity progressively decreased upon the incorporation of 90 wt % BPE to the conjugated polymer, as shown in Figure S22. Interestingly, the additive did not significantly impact the edge-on orientation of the polymer chains relative to the substrate, despite a decreased crystallinity at 50 wt % BPE (Figure S22b). GIWAXS was also performed to study the microstructure of the thin film under different degrees of strain. Specifically, GIWAXS experiments were performed on three annealed samples (pure conjugated polymer, 50 and 90% wt % mixtures) under different degrees of strain (from 0 and 100%) along two directions, parallel and perpendicular to the incident X-ray. Results are presented in Figures S23−S28. In the parallel direction, the lamellar packing for samples with an increasing percentage of BPE was less influenced, as demonstrated by a slightly weaker (300) lamellar peak intensity in the out-of-plane direction. In the meantime, the film adopts a mostly edge-on packing structure, as evidenced by the increase in the intensity of the (010) peak along the in-plane direction. On the other hand, along the perpendicular direction, while pure P(DPPTVT) still exhibits good lamellar packing, the 50% BPE and 100% BPE systems show the disappearance of lamellar packing and π−π stacking peaks with an increasing degree of strain. Such behavior results from the alignment of crystallites under strain in the parallel direction and confirms that the disruption of BPE in P(DPPTVT) packing is more pronounced for strained samples.

4. CONCLUSIONS

In conclusion, this study demonstrates a useful way to improve the mechanical properties of conjugated polymers via physical blending with a branched polyethylene additive. Incorporation of the BPE additive at different ratios drastically decreased the crystallinity of a DPP-based material, which is beneficial for flexibility and stretchability. At the micron scale, the BPE additive acts as a plasticizer and significantly reduces Young's modulus of the conjugated polymer (112 MPa at 25 wt % BPE before thermal annealing) and largely increases the crack onset strain, reaching a maximum of a 77% strain elongation when blended with 90 wt % BPE. The stretchability of BPE/P(DPPTVT) thin films is significantly improved upon introducing more BPE additive to the system. At the nanoscale, cracks can be observed at various strains, but the crack size was reduced from 3100 to 600 nm at 0 and 90 wt % of BPE, respectively, under a 100% strain. The addition of BPE promotes a uniform distribution of numerous smaller cracks across the thin film compared to that of the pure conjugated polymer thin film, which showed few localized larger cracks. Interestingly, following the removal of blended BPE, the thin films showed the same trend with improved stretchability. Additionally, the BPE additive influences the chain alignment of conjugated polymers, showing the chain alignment of polymer chains even above 100% strain at 90 wt % BPE while the pure conjugated polymer stops aligning at a 25% strain. With the growth of flexible and stretchable electronics, the BPE additive is a promising candidate to enhance the mechanical properties of conjugated polymers. We believe that this work will advance the research and development of new flexible and stretchable electronic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b01697.

General procedure and materials; procedures for sample preparation and film-on-water method; synthetic methods and NMR spectra; crack onset strain of P(DPPTVT)/BPE blends containing from 25 to 75 wt

% of BPE obtained by observing the formation of cracks under optical microscope and before the appearance of cracks; atomic force microscopy images (height) of BPE/P(DPPTVT) blends containing 0−90 wt % BPE at 10, 25, 50, 75, and 100% strains before thermal annealing; atomic force microscopy images (height) of BPE/P(DPPTVT) blends containing 0−90 wt % BPE at 50% strain after thermal annealing; dichroic ratios of the BPE/P(DPPTVT) blends containing (a) 0 wt %; (b) 25 wt %; (c) 50 wt %; (d) 75 wt %; and (e) 90 wt % of BPE in the function of strain determined by polarized UV−vis spectroscopy; polarized UV−vis spectra of BPE/P(DPPTVT) blended system with 0, 25, 50, 75, and 90 wt % BPE stretched at different percent strains, with the polarization direction of light parallel (0°) and perpendicular (90°) to the stretching direction; observations of a brittle freestanding thin film above 25 wt % BPE obtained by film-on-water tensile test; viscoelastic property of P(DPPTVT), 50 wt % BPE/P(DPPTVT), and 90 wt % BPE/P(DPPTVT) as measured by dynamic mechanical analysis; wide-angle grazing incident X-ray diffractogram (GIXRD) of (a) P(DPPTVT), (b) P(DPPTVT) + 50 wt % BPE, and (c) P(DPPTVT) + 90 wt % BPE; GIWAXS two-dimensional images for annealed BPE/P(DPPTVT) blend films under strain parallel and perpendicular to the incident X-ray direction (PDF)

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Notes

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