Solution-Assembled Blends of Regioregularity-Controlled Polythiophenes for Coexistence of Mechanical Resilience and Electronic Performance

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ABSTRACT: Considering all the potential applications of organic electronics in portable, wearable, and implantable devices, it is of great importance to develop electroactive materials that possess mechanical reliability along with excellent electronic performance. The coexistence of these two attributes, however, is very difficult to achieve because there is an inverse relationship between the electrical properties and the mechanical flexibility, both of which are associated with the conjugation length and intermolecular ordering of the polymers. Herein, we demonstrate a simple and robust approach based on solution assembly of two different poly(3-hexylthiophene)s (P3HTs) with regioregularity (RR) contents of 97% and 66% to impart both electrical and mechanical properties to films for organic electronic applications. The 97% RR P3HT exhibits high electronic performance but poor mechanical resilience, and vice versa for the 66% RR P3HT. Selective crystallization of high RR P3HT induced by solution assembly allows the use of a one-step process to construct percolated networks of high RR P3HT nanowires (NWs) in a low RR P3HT matrix. Only 5 wt % of high RR P3HT NWs in a 95 wt % low RR P3HT matrix was required to produce hole mobilities comparable to that of pure high RR P3HT, and this blend film exhibited improvements by factors of 20 and 60 in elongation at break and toughness, respectively. Selective self-assembly of RR-controlled polymers allowed us to overcome the fragile nature of highly crystalline conjugated polymer films without sacrificing their electronic properties.

KEYWORDS: regioregularity, solution assembly, nanowire, mechanical stability, stretchable organic electronics

1. INTRODUCTION

Despite notable advances in the performance of organic electronics during the past decade, there has been a growing concern regarding the mechanical reliability of organic semiconducting materials.1−4 While the common perception is that organic electronic materials, especially polymeric materials, are already highly flexible and elastic, recent studies revealed that most highly efficient, electroactive conjugated polymers are rather stiff and brittle,5−7 resulting in critical mechanical failure of the devices during field tests.8 Such mechanical instability of conjugated polymers critically limits the long-term stability and reliability of organic electronics, which are subjected to a variety of mechanical stresses during device fabrication and subsequent operation.9−11 In addition, considering all of the attractive potential applications of organic electronics in portable, wearable, and bioimplantable devices, where mechanical resilience against extreme physical deformation is an operational requirement,12,13 it is urgent and of great importance to develop high-performance electroactive conjugated polymers that permit significant tensile deformation.

Designing conjugated polymer films that provide both mechanical resilience and good electronic performance is not a trivial endeavor, because there is a fundamental trade-off between the two properties.1,4,14−16 Electronic properties are strongly associated with a high degree of intermolecular ordering between conjugated polymer chains, which allows efficient delocalization of π-electrons across the aligned polymer chains. However, highly ordered polymer domains also cause significant stiffness and brittleness of the films. This is because the high rigidity and sharp grain boundaries of the crystalline domains cannot effectively dissipate local stress, resulting in mechanical failure even under very small strains. For example, incorporation of thienothiophene units in the
backbone of poly(3-alkylthiophene) (P3AT), which represents one of the most extensively studied conjugated polymer systems in various organic electronics, leads to a higher degree of crystallinity and significantly enhanced transistor mobility, but the fragility of the polymer was also greatly amplified.\textsuperscript{16} Similarly, when the length of the alkyl side chains of P3AT was increased from hexyl (n = 6, P3HT) to dodecyl (n = 12, P3DDT), the ductility and elasticity of the polymer were notably enhanced due to the reduced crystallinity;\textsuperscript{14} however, these characteristics were accompanied by serious degradation of the field-effect transistor mobility and photovoltaic efficiency.\textsuperscript{17,18} A few research groups have attempted to overcome such fundamental incompatibilities by synthesizing copolymers,\textsuperscript{19} optimizing alkyl chain length,\textsuperscript{19} and exploring new molecular structures.\textsuperscript{5} In most cases, however, the enhancement of mechanical stability generally led to the degradation of electronic performance.

In an effort to surmount the inverse relationship between the electrical and mechanical properties of conducting polymers, several blending approaches have been adopted for producing a continuous phase of conjugated polymer in mechanically robust, insulating polymer matrices. One method involving templating of conducting polymers, which is generally applicable to most conjugated polymers including those with low crystallinity, was developed to produce polymer films with both excellent electrical and mechanical properties.\textsuperscript{20–22} The use of well-designed templates, i.e., colloids or polymeric nanoparticles, allowed fabrication of a continuous conducting phase of conjugated polymers at low volume fractions within insulating matrices, resulting in enhanced stability of the conducting film.\textsuperscript{23–25} Another approach involved the use of solution-assembled, one-dimensional crystalline nanowires (NWs) from highly crystalline conjugated polymers.\textsuperscript{26–33} The high aspect ratio of NWs provides a unique opportunity to achieve percolated networks of conducting polymers in mechanically stable polymer matrices.\textsuperscript{34–38} For example, the percolation threshold of conducting P3HT polymers in an insulating polystyrene matrix can be dramatically reduced by using a solvent conducive to the formation of NWs.\textsuperscript{34} The proper choice of the matrix can bring important properties, such as ambient stability,\textsuperscript{34} high processability,\textsuperscript{35,39} and mechanical stability,\textsuperscript{37,40} which are typically inaccessible with single-component conjugated polymer systems. To date, however, most efforts have focused on the use of insulating/conjugated binary polymer systems,\textsuperscript{41–44} whereas conjugated polymer blends remain less explored.\textsuperscript{45} Recently, Chu et al.\textsuperscript{46} reported an elegantly designed conjugated polymer blend system comprised of regioregular and regiorandom P3HTs. In this blend system, vertically segregated, UV-irradiated regioregular P3HT\textsuperscript{47} formed efficient charge transport pathways in relatively flexible regiorandom P3HT domains, leading to the successful fabrication of high-performance, flexible transistors. While this work reported the concept of blending regioregular and regiorandom P3HTs, we anticipated that precise control of the regioregularity (RR) would allow for different combinations of blends for further optimization of electrical and mechanical properties to meet the various requirements of different organic electronic applications. In addition, direct evaluation of stress–strain curves of the constituent P3HTs and blend films is required to provide further insight on these materials to yield an optimal combination of electrical and mechanical properties.

Our group recently developed a synthetic methodology for producing P3HTs with a wide range of control over RR value.\textsuperscript{48} This work also showed the effect of RR on mechanical properties through novel, direct tensile tests performed on films floating on water. The inherent properties of P3HT were found to be readily regulated by tuning the RR: higher RR P3HT exhibited high electrical performance, while lower RR P3HTs had excellent mechanical properties, including low tensile modulus and high elongation at break. Despite these advances by our group and others, simultaneous optimization of both electrical performance and mechanical stability remains a challenge.

Herein, we demonstrate the fabrication of conjugated polymer composites consisting of two different P3HTs with controlled RR (RR-97 and RR-66, containing 97% and 66% controlled RR P3HT, respectively) possessing either good electronic performance (RR-97) or mechanical stability (RR-66). Importantly, both polymers were synthesized from the same well-defined polymerization method to yield similar, high molecular weight P3HTs with low dispersity (D) and different RR contents, thus producing a model system for investigation of the effects of RR content on the electrical and mechanical properties of composite films. The large differences in the degree of crystallinity between RR-97 and RR-66 allowed selective formation of long, continuous NWs from the high RR P3HT by solution-assembly, leading to a one-step construction of percolated networks of the NWs embedded in a mechanically stable, low RR P3HT matrix (Scheme 1). These experiments showed that 5 wt % high RR P3HT was sufficient to obtain a hole mobility comparable to that of the pure high RR P3HT film. Furthermore, films of high RR NWs embedded in a low RR matrix exhibited 20 times longer elongation at break and 60 times higher toughness, according to direct tensile tests of the films performed using a free-standing tensile method.\textsuperscript{49} The percolated NW structure preserved the efficient hole-transporting pathways within the surrounding low RR P3HT matrix, which alleviated extensive external mechanical stress. Thus, this work provides important design guidelines for
producing highly stretchable, conjugated polymer films that exhibit stable electronic operation under extreme deformation.

2. RESULTS AND DISCUSSION

RR-controlled P3HTs were synthesized following our previously reported method.48 The key synthetic feature is that the regioslective head-to-head (H–H) coupled 3,4′-dihexyl[2,2′]-bithiophene was copolymerized with 3-hexylthiophene using modified Grignard metathesis (GRIM) polymerization. By changing the feed ratios, the RR can be systematically tuned while high molecular weight (Mn) and D are maintained. We prepared two P3HT samples with different RR contents: one with a high RR, which led to excellent electronic performance and high crystallinity, and the other with a sufficiently low RR for great mechanical resilience, with a low tensile modulus and high elongation at break. The RR values of the two different P3HTs were determined to be 97.1 ± 0.9% and 65.8 ± 1.3% by comparing the 1H NMR-integrated peaks corresponding to head-to-tail (H–T) versus H–H linkages at δ 2.81 and 2.58 ppm, respectively [Figure S1, Table S1, Supporting Information (SI)]. For convenience, P3HT samples with 97% and 66% RR content are denoted as RR-97 and RR-66, respectively. The polymerization conditions were optimized to yield relatively high Mn values of over 20 kg mol⁻¹, which is essential for producing P3HT with high electronic and mechanical performance.7,50 The Mn values were determined to be 27.1 kg mol⁻¹ for RR-97 (D = 1.14) and 20.1 kg mol⁻¹ for RR-66 (D = 1.44) by size exclusion chromatography (SEC) (Figure S2, SI). The effect of RR content on the crystalline behavior of the P3HT was evaluated quantitatively by differential scanning calorimetry (DSC) (Figure S3, SI). RR-97 exhibited prominent thermogram peaks associated with the melting temperature (Tm) at 233 °C and the crystallization temperature (Tc) at 199 °C. The degree of crystallinity of RR-97 was calculated to be 41% by comparing the melting enthalpy (ΔHm) value with that of ideal P3HT crystallites (ΔHm° = 37 J g⁻¹).51,52 These values were well-matched with those typically obtained from high RR and high Mn P3HT.38,51,52 By contrast, no crystallization peak was observed in the DSC thermogram of RR-66, indicating that the crystallization was greatly suppressed by the high loading of regio-defective units. Interestingly, the glass transition temperature (Tg) was independent of the RR; both RR-97 and RR-66 showed similar Tg values at around −20 to 0 °C. Therefore, we successfully produced two P3HT samples with similar Mn and relatively low D with significantly different crystalline properties; i.e., RR-97 exhibited strong crystallinity, whereas no crystalline peaks were observed for RR-66.

Selective solution assembly of RR-97 into NWs was performed by the whisker method53,54 using o-xylene as the processing solvent to take advantage of the significantly different crystallization behavior of RR-97 and RR-66 in o-xylene. Xylene has been widely used to produce NWs from high-RR P3HTs because it provides sufficient solubility at elevated temperature, while causing aggregation of high-RR P3HT at room temperature.53,54 In these experiments, both RR-97 and RR-66 were dissolved in o-xylene (4 mg mL⁻¹) at high temperature (>60 °C), and then the solutions were cooled to room temperature (20 °C) at an average rate of 5 °C min⁻¹. Initially, both RR-97 and RR-66 were well-dissolved in the solution, with single absorption bands at around λmax = 460 nm (RR-97) and λmax = 438 nm (RR-66), which are typical indicators of the π−π* transition of well-dissolved P3HT chains. Note that RR-66 appeared to have a lower wavelength transition peak in the dissolved state due to the presence of regio-defective units reducing the effective conjugation length along the polymer chain. As the aging time of the P3HTs in solution at room temperature increased, clear differences were evident between the two solutions. For RR-97, the intensities of the vibronic bands at 558 and 608 nm progressively increased, indicating that the delocalization of the π-electrons occurred with the formation of NWs (Figure 1a).56 In contrast, the absorption peak of the dissolved RR-66 P3HT was unchanged with extended aging time (Figure 1b). The steric hindrance caused by the randomly oriented side chains in the regio-defective units resulted in twisted polymer chains and suppression of crystallization in the solution state. To visualize the solution assembly of the P3HTs with two different RR contents, we performed transmission electron microscopy (TEM) on samples prepared by casting dilute solutions (0.1 mg mL⁻¹) on thin carbon-supported grids. After sufficient aging time (>6 h), RR-97 formed well-defined NWs with lateral dimensions of 18–20 nm and lengths of over several micrometers (Figure 1c), while no distinct structures were formed from RR-66 (Figure 1d). It is noteworthy that we observed only featureless, amorphous morphologies for RR-66, even at high concentrations (70 mg mL⁻¹) and low temperatures (−10 °C). The weak crystallization behavior of the RR-66 prohibited the growth of the NW structure in the o-xylene solvent, whereas RR-97 formed well-defined NWs under the same conditions. This finding opens a new window for processing RR-97/RR-66 blend systems, in which the selective formation of RR-97 NWs leads to a one-step construction of interconnected networks of RR-97 NWs embedded in a noncrystalline RR-66 matrix.

To examine the effect of the formation of RR-97 NWs on the electrical properties of RR-97/RR-66 blend films, hole carrier mobilities (μh) as a function of RR-97 content were measured with organic thin-film transistors (OTFTs) (Figure 2a).
series of blend solutions were prepared using either \( \alpha \)-xylene or chlorobenzene (CB). CB was chosen as a reference because both RR-97 and RR-66 are highly soluble in CB, and it has a boiling point close to that of \( \alpha \)-xylene (\( \alpha \)-xylene = \( 144^\circ \text{C} \), CB = \( 131^\circ \text{C} \)), which is a critical factor affecting polymer morphology during the film deposition process. CB, however, does not induce the formation of RR-97 NWs, and therefore, comparing with CB-processed blend films allows us to understand the effect of the presence of RR-97 NWs on the electrical properties of the blend films. The blend solutions (4 mg mL\(^{-1}\)) were spin-coated on a highly n-doped Si wafer with a thermally grown SiO\(_2\) layer (thickness \( \approx \) 300 nm, \( C_i = \text{ca.} \ 10 \ \text{nF cm}^{-2} \)). Gold electrodes were then deposited on top of the film with a channel length and width of 50 \( \mu \text{m} \) and 1000 \( \mu \text{m} \), respectively. The dielectric surface was not modified with organosilanes, such as \( n \)-octadecyltrimethoxysilane (OTS). When the OTFTs were fabricated with CB, the \( \mu_h \) of RR-97 was measured to be \( 3.31 \pm 1.30 \times 10^{-3} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1} \), which agreed well with previously reported values for high RR P3HT without dielectric surface modification.\(^{57,58}\) As the content of RR-97 decreased, a linear decrease in the values of \( \mu_h \) was observed (Figure 2a and Table S2a, SI), eventually reaching \( 1.58 \pm 1.42 \times 10^{-6} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1} \). This can be attributed to the incorporation of a higher content of RR-66 impeding the formation of \( \pi-\pi \) intermolecular assemblies and ordered crystalline domains, giving rise to a significant decrease in the \( \mu_h \) values of the blend films. This trend was similar to that observed for pristine films of RR-controlled P3HT, where the \( \mu_h \) decreased monotonically with the RR of the P3HT.\(^{58}\) Thus, simple blending of RR-97 and RR-66 polymers with different contents of RR-97 produced similar effects to those achieved by tuning the RR during the synthesis of P3HT. In stark contrast to the monotonic decrease of the \( \mu_h \) as a function of RR-66 content observed in the CB-processed blend films, using \( \alpha \)-xylene as the processing solvent resulted in \( \mu_h \) values that essentially plateaued at a very small content of RR-97 (~5 wt %) (Figure 2a and Table S2b, SI). First, the RR-97 NW film exhibited a higher \( \mu_h \) \( \approx (2.14 \pm 0.90) \times 10^{-2} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1} \) than the pristine RR-97 film prepared from CB, which was attributed to the formation of highly ordered intermolecular NW structures. More importantly, the highly anisotropic features of the RR-97 NWs generated effective percolated networks of RR-97 NWs in the blend films, resulting in high \( \mu_h \) values comparable to that of the pure RR-97 films even at RR-97 contents as low as 5 wt %. Figure 2b compares transfer characteristics of OTFT devices (\( V_{DS} = -100 \ V \)) with 10 wt % RR-97 processed from two different solvents, i.e., CB and \( \alpha \)-xylene. The device processed from \( \alpha \)-xylene showed enhanced transistor characteristics, with a higher on/off current ratio (~10\(^4\)) and \( \mu_h \) \( \approx (6.42 \pm 3.96) \times 10^{-3} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1} \) than the device processed from CB. Output characteristics of the blend devices are shown in the Supporting Information (Figure S4).

To investigate the morphology of RR-97 in the OTFT devices, we selectively removed the RR-66 phase by immersing the devices in dichloromethane (DCM), which is a good solvent for RR-66, but not for RR-97, at room temperature. The remaining RR-97 phases between the Au electrodes of the devices were observed using scanning electron microscopy (SEM) (Figure 3). Figure 3a–c shows the morphology of the devices processed from \( \alpha \)-xylene. Images of the device

![Figure 2](image-url)

Figure 2. (a) Hole mobilities of RR-97/RR-66 blend OTFT devices as a function of the RR-97 P3HT content. The use of \( \alpha \)-xylene induced the formation of RR-97 NWs from mixed solutions of RR-97/RR-66, whereas the use of chlorobenzene (CB) resulted in homogeneous films from RR-97/RR-66 mixtures. (b) Transfer characteristics (\( V_{DS} = -100 \ V \)) of transistor devices based on 10/90 wt % RR-97/RR-66 blends processed from \( \alpha \)-xylene and CB, respectively.

![Figure 3](image-url)

Figure 3. SEM images of OTFT devices processed from \( \alpha \)-xylene with (a) 100 wt %, (b) 20 wt %, and (c) 10 wt % RR-97. (d) SEM image of the OTFT device processed from CB with 10 wt % RR-97. For all images, RR-66 was selectively removed by rinsing with DCM for clear visualization of the NW structures.
fabricated with 100 wt % RR-97 showed highly connected networks of NWs with lengths of several micrometers (Figure 3a). Although the density of NWs decreased as the content of RR-97 was reduced, the interconnected networks of NWs were still observed, even at low RR-97 contents (Figure 3b,c). The formation of RR-97 NWs in o-xylene solutions with different contents of RR-97 was also confirmed by UV–vis spectroscopy (Figure S5, SI). Such percolated networks of the RR-97 NWs ensure the presence of efficient conducting channels between the Au electrodes in the OTFT devices, maintaining high electronic performance even at very low RR-97 contents. In contrast, when CB was used as the processing solvent, homogeneous blend films with no NW structures were obtained (Figure 3d). It is worthwhile to note that this intermixed morphology from RR-97/RR-66 blends is very different from the massively phase-separated morphology observed from blends of insulating and conducting/conjugated polymers, which impose large enthalpic penalties due to their chemical incompatibility.

A deeper insight into the polymer packing structure in the different blends was obtained by grazing incidence wide-angle X-ray scattering (GI-WAXS) measurements (Figures S6 and S7, SI). All samples were prepared under the identical conditions employed for preparing the OTFT devices. GI-WAXS of the RR-97 film revealed P3HT crystals with edge-on geometry, showing highly ordered (h00) scattering peaks and a strong (010) peak, which corresponded to lamellar stacks in the out-of-plane direction (q_\parallel) and θ-π stacking in the in-plane direction (q_\perp), respectively. In contrast, the preferential face-on structure was observed in the RR-66 films. This is consistent with our previous finding that the reduced planarity of low RR P3HT disturbed the formation of edge-on-oriented crystallites. When 10 wt % RR-97 was mixed with RR-66 using CB as the processing solvent, the face-on crystalline orientation of RR-66 was relatively dominant. On the contrary, when the blend film was processed from o-xylene, the 10 wt % RR-97/RR-66 blend film exhibited highly ordered (h00) and (010) scattering peaks in the q_\parallel and q_\perp directions, suggesting that the well-developed crystalline structures of the RR-97 NWs with edge-on geometry were preserved in the blend films, which is beneficial to charge transport in OTFT devices.

In order to examine the mechanical properties of RR-97 NW-embedded RR-66 blend films, free-standing tensile tests were conducted on films floating on the surface of water. Despite the great importance of measuring the intrinsic mechanical properties of conjugated polymers, direct tensile testing of the conjugated polymer films in electronic devices has remained a significant challenge. This is because the thickness of the active layers in the devices is typically less than a few hundred nanometers, which makes it very difficult to prepare and handle free-standing specimens without sample damage and wrinkling. We adopted free-standing tensile tests that utilize the water–air surface as a friction-free, underlying support, thereby enabling the direct measurement of intrinsic mechanical properties of P3HT thin films without sample damage. The blend solutions, 10/90 wt % RR-97/RR-66 and 20/80 wt % RR-97/RR-66 in o-xylene, were spin-coated on poly(styrenesulfonate) (PSS)-coated glass substrates into films with dimensions of 5 mm × 25 mm and a thickness of approximately 100 nm. Additionally, the pristine RR-97 film spin-cast from CB was prepared as a reference because the pristine RR-97 film processed from o-xylene was too brittle to produce a defect-free film on water. The samples were floated on water upon dissolution of the PSS sacrificial layer. Specimen gripping and tensile tests were performed following our previously reported conditions. Figure 4a shows representative stress–strain curves of the pristine RR-97 film, as well as the 10/90 wt % RR-97/RR-66 and 20/80 wt % RR-97/RR-66 blend films. The tensile modulus of the pristine RR-97 film was measured to be 300 MPa, which was in good agreement with previously reported values (287 ± 19 MPa) for high-RP3HT. In addition, elongation at break, defined by the strain (\varepsilon) at which cracks first appear in the specimen, was measured to be 0.55%. The high content of crystalline domains with strong rigidity and sharp grain boundaries of the pristine RR-97 film resisted elastic deformation, resulting in high modulus and mechanical failure of the films at very low applied \varepsilon (Figure 4c). However, when RR-97 NWs were embedded in the RR-66 matrix, a dramatic enhancement was observed in the
mechanical properties. The tensile moduli of 10/90 wt % RR-97/RR-66 and 20/80 wt % RR-97/RR-66 blend films were measured to be 64 and 55 MPa, with greatly enhanced elongation at break of 5.3% and 10.6%, respectively, both of which provide critical advantages for flexible and/or stretchable devices. The amorphous, mechanically resilient RR-66 domain extended efficiently under applied force along the strain axis, leading to higher mechanical stability at much higher $\varepsilon$. The excellent mechanical properties of the composite films were further confirmed by the calculation of toughness (U_t) by integrating the stress–strain curves (Figure 4b). The U_t of the pristine RR-97 film was found out to be 4.4 $J \cdot m^{-3}$, whereas the 20/80 wt % RR-97/RR-66 and 10/90 wt % RR-97/RR-66 blend films had greatly enhanced U_t values of 84.0 and 268.7 $J \cdot m^{-3}$, respectively. We note that the 10/90 wt % RR-97/RR-66 films exhibited almost 20 times higher elongation at break and 60-fold enhanced U_t than the pristine RR-97 film, even though they had similar hole mobilities. Therefore, we successfully demonstrated the coexistence of excellent electronic properties and mechanical reliability in the composite P3HT films by constructing high-RR P3HT NWs in low-RR P3HT matrix using one-step solution assembly.

The stability of the electronic performance of the pristine and blend films during mechanical deformation was further compared by measuring the conductivity ($\sigma$) as a function of applied strain ($\varepsilon$) (Figure 5). Pristine RR-97 P3HT and 10/90 wt % RR-97/RR-66 blend solutions were spin-coated to produce approximately 100-nm-thick films on PSS-coated glass substrates, which were then transferred to polydimethylsiloxane (PDMS) elastomers by floating them on water. Doping of the films on the PDMS elastomers was conducted by spin-coating 3 mM FeCl$_3$ in nitromethane on the films as described previously. $^61$ The initial ($\varepsilon = 0\%$) conductivity ($\sigma_0$) values of the pristine RR-97 and 10/90 wt % RR-97/RR-66 films were measured to be 12.08 ± 2.08 and 2.77 ± 0.22 S cm$^{-1}$, respectively, and they showed very different responses to mechanical deformation. For example, as $\varepsilon$ increased, the $\sigma$ of the pristine RR-97 film decreased rapidly. Total mechanical failure of the film was observed with the complete loss of $\sigma$ before the $\varepsilon$ reached 30%. To visually demonstrate the mechanical failure under applied strain, a small light-emitting diode (LED) lamp was connected to the films and 5 V was applied. As the $\varepsilon$ increased, the light intensity decreased gradually, and the lamp turned off before $\varepsilon$ reached 30%. On the contrary, superior mechanical stability was observed for the 10/90 wt % RR-97/RR-66 film with a $\sigma$ of 0.18 S cm$^{-1}$ and stable operation of the LED lamp, even at the extremely high $\varepsilon$ value of 70%. We note that the strain at current failure was observed to be much larger than the value of the elongation at break of the pristine polymer film measured from the direct tensile test because the $\varepsilon$ value at mechanical failure is strongly dependent on the adhesion of the film to the elastomeric substrate. Therefore, we produced highly stretchable P3HT films composed of high RR NWs and a low RR matrix that provided stable electronic operation under extremely high mechanical deformation.

3. CONCLUSIONS

In this work, we successfully demonstrated the coexistence of high electronic performance and mechanical stability in P3HT blend films, which consisted of chemically identical P3HTs with different RR contents. While the conflicting correlation between electronic performance and mechanical compliance in conjugated polymer films is well-known, we took advantage of this conflicting relationship to produce films with both high electronic performance and mechanical reliability by solution-assembled blending of two different P3HTs: RR-97 exhibited high electronic properties and poor mechanical stability resilience, while RR-66 had high elasticity and poor electronic performance. Solution assembly of both polymers in o-xylene allowed the one-step construction of percolated networks of RR-97 NWs embedded in a RR-66 matrix. The 10/90 wt % RR-97/RR-66 film exhibited superior mechanical stability, with 20- and 50-fold higher elongation at break and toughness, respectively, than the pristine RR-97, while maintaining mobilities comparable to pristine RR-97. Our study provides important guidelines for the design of electroactive polymer films suitable for portable and stretchable electronic applications, in particular for the optimization of electrical and mechanical performance.

4. EXPERIMENTAL SECTION

Solution Assembly of RR-97 and RR-66 Polymers. RR-97 and RR-66 polymers were first dissolved in o-xylene ($4$ mg mL$^{-1}$) with heating and sonication. The solutions were passed through a PTFE syringe filter (0.45 μm) and moved to a 60 °C water bath. Then, the temperature of the water bath was slowly cooled to room temperature with an average cooling rate of 5 °C min$^{-1}$. The resulting solutions were aged for 48 h with gentle stirring to enable homogeneous nucleation of the NWs.

OTFT Device Fabrication. OTFT devices were fabricated on heavily doped n-type (100) silicon wafers ($\approx0.004\ \mu m$) with a 300-nm-thick thermally grown SiO$_2$ layer ($C = ca. 10\ nF\ cm^{-2}$) as the substrate and dielectric, and 4 mg mL$^{-1}$ of RR-97, RR-66, and blended solutions with a variety of weight fractions of RR-97 in o-xylene was heated to above 60 °C and then cooled down to 20 °C, followed by aging for 48 h. The blended solutions in either CB or o-xylene were spin-coated at 2000 rpm for 60 s. The gold source and drain electrodes (thickness $\approx 40\ nm$) were patterned through a shadow mask by thermal evaporation below S.0 $\times 10^{-6}$ Torr. The channel length and width of the OTFTs were 50 and 1000 μm, respectively. The electrical characterization was performed in a N$_2$-filled glovebox using a Keithley 4200 SCS and probe station with a micro-manipulator (MST-400A, MS-TECH).

GI-WAXS Measurements. For preparing GI-WAXS samples, RR-97, RR-66, and a series of blended solutions were spin-coated on a Si wafer. The GI-WAXS measurements of the polymer samples were
carried out at beamlines 3C and 9A in the Pohang Accelerator Laboratory (Pohang, South Korea), and a wavelength of 1.101 Å was used. The incidence angle of the beam was set between the critical angles of the polymer film and the silicon substrate (in the range of 0.12°–0.15°). The X-ray beams scattered by the films were collected by a two-dimensional CCD detector at a sample-to-detector distance of 0.2 m.

**Free-Standing Tensile Test.** To prepare the tensile testing specimens, RR-97 solution in CB (10 mg mL⁻¹) and a series of RR-97/RR-66 blended solutions (10 mg mL⁻¹) in xylene were spin-coated onto a PSS-coated glass substrate. The film thicknesses were 80–100 nm as measured by Detak-8 surface profiler. The P3HT/PPS glass specimen was cut into bar type specimens with dimensions of 5 mm × 25 mm using a diamond cutter. The floated P3HT specimen on water was prepared by dissolving the PSS sacrificial layer on the water-air surface. Specimen gripping was achieved by attaching PDMS-coated Al grips on the specimen gripping areas using van der Waals adhesion. The tensile test was performed by applying tensile force using a linear stage with a strain rate of 0.06 × 10⁻³ s⁻¹. Detailed experimental procedures are described in our previous works.⁸,¹⁰

During the tensile test, stress and strain data were obtained through a load cell (LTS-10GA, KYOWA) and a digital image correlation (DIC) device, respectively.

**Conductivity Measurements.** Stretchable elastic PDMS substrates were prepared from a commercially available silicon elastomer base and curing agent (Sylgard 184, Dow Corning). A mixture of the elastomer base and curing agent (91/9 w/w) was vigorously stirred for 40 min. Any bubbles generated during mixing were removed by repeatedly evacuating and purging the mixtures in a vacuum oven. The PDMS substrates with thicknesses of 0.5 mm were obtained by thermal curing of the mixture on a template for 12 h at 80 °C and then peeled off from the template. RR-97 and 10/90 wt % RR-97/RR-66 films (thickness ∼ 100 nm) were floated on water and then transferred to the PDMS substrates. The prepared samples were attached to glass substrates and then doping was conducted by spin-coating 3 mM KETEP and the MOTIE of the Republic of Korea (No. 20163003016320). We acknowledge support by the Research Projects of the KAIST-KUSTAR.

**REFERENCES**


**ASSOCIATED CONTENT**

▲ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b16703.

Detailed experimental procedures and additional characterization data (Figures S1–S7 and Tables S1 and S2) (PDF)

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**Notes**

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