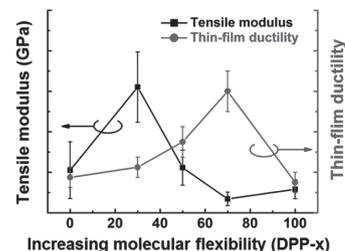
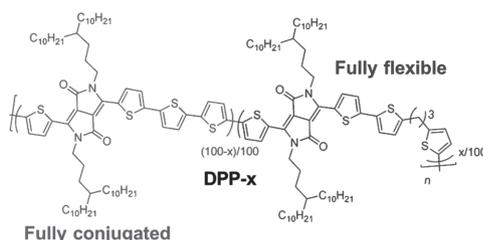


Effect of Broken Conjugation on the Stretchability of Semiconducting Polymers

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Increasing the flexibility of polymer chains is a common method of increasing the deformability of solid polymeric materials. Here, the effects of “conjugation-break spacers” (CBSs)—aliphatic units that interrupt the sp^2 -hybridized backbone of semiconducting polymers—on the mechanical and photovoltaic properties of a diketopyrrolopyrrole-based polymer are described. Unexpectedly, the tensile moduli and cracking behavior of a series of polymers with repeat units bearing 0%, 30%, 50%, 70%, and 100% of the CBS are not directly related to the percent incorporation of the flexible unit. Rather, the mechanical properties are a strong function of the order present in the film as determined by grazing-incidence x-ray diffraction. The effect of the CBSs on the photovoltaic performance of these materials, on the other hand, is more intuitive: it decreases with increasing fraction of the flexible units. These studies highlight the importance of solid-state packing structure—as opposed to only the flexibility of the individual molecules—in determining the mechanical properties of a conjugated polymer film for stretchable, ultraflexible, and mechanically robust electronics.



1. Introduction

A recurring challenge in materials engineering is overcoming apparent mutual incompatibilities of useful physical properties. For example, conductivity and transparency,^[1] elasticity and impermeability,^[2] and

mechanical deformability and charge transport^[3] are pairs of physical properties that derive their mutual exclusivity either from fundamental physics or practical difficulty. In the field of organic electronics, solubility of π -conjugated polymers necessitates alkyl side chains that in some cases reduce the efficiency of charge transport, and in all cases limit the mechanical strength.^[4,5] For flexible, stretchable, and durable applications of these materials, they should have a high elasticity (low modulus), elastic limit (yield point), strain at fracture, and toughness.^[6,7] The ability to accommodate mechanical deformation without fracture is a prerequisite for using organic electronic devices in flexible, stretchable, and portable applications, as in the outdoor environment (where they are subjected to a range of thermomechanical stresses) and for fabrication by roll-to-roll processing.^[8]

Despite the interest in using these materials for applications demanding mechanical deformability, the

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mechanical properties of low-bandgap polymers are generally unreported,^[7] and the molecular characteristics that determine these properties are not straightforward to predict.^[7,9] For poly(3-alkylthiophene)s (P3ATs) with similar molecular weight, the compliance, yield point, and crack-onset strain all increase with increasing length of the alkyl side chain, with A = heptyl (P3HpT) seeming to embody the best of both worlds in mechanical deformability and electronic performance (for solar cells, but probably not for thin-film transistors).^[10–12] The microstructure also plays an important role; increased order correlates with increased stiffness and brittleness.^[13,14] The effect of the rigidity of the main chain has been reported to increase the stiffness of the films, with fused rings in the main chain being stiffer than isolated rings, at least in preliminary observations.^[9,15–17] However, the effect of conjugation break spacers (CBSs)—aliphatic groups in the main chain—has not been investigated.

Flexible linkers represent a promising unit for tuning the physical properties, namely the solubility and melting point, of semiconducting polymers.^[18–21] The Mei group has recently introduced low-bandgap conjugated polymers bearing CBSs (Figure 1, aliphatic units in the main chain with three or more methylene units), which offer increased solubility and the opportunity to process the materials from the melt.^[18–20] While the charge-carrier mobility decreased with increasing fraction of the CBSs,^[18] similar CBSs have been shown in a system reported by Bao and co-workers to improve processability without compromising device performance.^[21] Given the interest of the Lipomi group in molecularly stretchable electronics,^[22] we sought to test the hypothesis that the flexibility of CBSs might provide a route to materials that maximized both charge-transport and mechanical deformability for stable and stretchable electronics. In particular, this communication describes the mechanical and photovoltaic properties of these materials, and correlates these results to previous measurements of the mobility and solid-state microstructure.

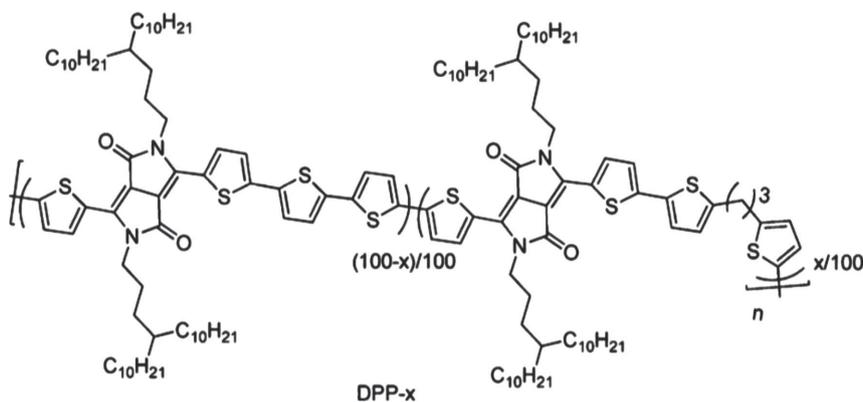


Figure 1. Chemical structure of the polymers bearing conjugation-break spacers (CBSs). In particular, this paper examines a series of five materials, where $x = 100$ (fully flexible), 70, 50, 30, and 0 (fully conjugated).

2. Results and Discussion

In this study, we measured two mechanical properties, the tensile modulus and crack-onset strain, using film-on-elastomer methods, of the diketopyrrolopyrrole (DPP)- x polymers, where $x = 100$ (fully flexible), 70, 50, 30, and 0 (fully conjugated). The low-bandgap polymers comprised diketopyrrolopyrrole flanked by two thiophene rings as the electron-deficient monomer alternating with bithiophene as the electron-rich subunit^[18] (the polymer was originally called DPPT-2T).^[23] The CBSs were introduced by substituting the bithiophene unit with an aliphatic propyl group with a thiophene ring at either end.^[18] Introduction of either the bithiophene unit or the unit with broken conjugation into the polymerization at various ratios produced materials with differing overall flexibility in the main chain: from DPP-100 to DPP-0. The physical properties of the polymers used in this study have been previously reported by Zhao et al.^[18] and are reproduced in the Supporting Information.

The tensile modulus represents the force needed to deform a material elastically per unit area normal to the load. For deformable applications, it is thought that lower moduli would produce more stable devices because a highly elastically deformable film would minimize interfacial stresses between the active material and the substrate or the electrodes.^[7] In some systems, such as P3ATs with increasing length of the side chain but of similar molecular weight, low tensile modulus correlates with high ductility.^[13,24] The tensile modulus was measured by the buckling technique.^[24,25] The ductility was measured by the crack-onset strain; that is, the strain at which cracks first appear when the film is stretched while supported by an elastomeric substrate. In typical devices, cracking of the organic semiconductor is a principal cause of failure.^[26] Given the increased flexibility in the polymer backbone of an isolated chain bearing CBSs compared to that of an all-conjugated chain, our hypothesis was that

a film comprising the more flexible polymer would have the greatest compliance and ductility. The mechanical properties of a film, however, are not dependent only on molecular structure, but also on how the molecules pack in the solid state.^[7,13,27,28] Interdigitation of side chains along the lamellar axis in particular is known to produce a stiff morphology in films of PBTTT.^[13] The predicted mechanical behavior could be consistent with one of two competing hypotheses, or a combination thereof. (1) The flexibility of the main chain determines the compliance and ductility of the

Table 1. Summary of mechanical properties, the lamellar spacing, the lamellar FWHM, and the semiconducting properties of the DPP-*x* polymers. The values of the lamellar spacing and lamellar FWHM were reproduced from ref. [18]. The photovoltaic properties were taken from the composite of 1:2 polymers:[6o]PCBM with $N \geq 12$. The values of the mobility of the spin-coated films were reproduced from ref. [18].

	Polymer				
	DPP-0	DPP-30	DPP-50	DPP-70	DPP-100
Mechanical properties					
Tensile modulus [GPa]	0.315 ± 0.21	0.931 ± 0.26	0.334 ± 0.13	0.103 ± 0.05	0.174 ± 0.07
Crack-onset strain [%]	3.5 ± 1.0 (pinholes)	4.5 ± 1.0 (pinholes)	7.0 ± 1.5 (pinholes)	12 ± 2.0 (pinholes)	3.0 ± 1.0 (brittle)
Lamellar spacing [Å]	22.28	22.07	21.96	21.75	21.64
Lamellar FWHM [Å ⁻¹]	0.044	0.038	0.039	0.041	0.035
Semiconducting properties					
V_{oc} [mV]	610 ± 5.1	664 ± 4.6	675 ± 4.4	666 ± 4.0	690 ± 3.7
J_{sc} [mA cm ⁻²]	8.46 ± 0.35	4.98 ± 0.31	4.68 ± 0.56	3.07 ± 0.21	1.95 ± 0.08
FF [%]	42 ± 2.7	66 ± 1.2	59 ± 2.2	55 ± 1.5	48 ± 1.1
PCE [%]	2.18 ± 0.18	2.17 ± 0.14	1.87 ± 0.20	1.13 ± 0.11	0.65 ± 0.04
Mobility [cm ² V ⁻¹ s ⁻¹]	3.52	0.91	0.27	0.065	0.014

film. (2) The order in the film determines these mechanical properties, with greater order producing greater stiffness and brittleness.

We summarized the results of our mechanical measurements in Table 1. The tensile moduli of the five polymers occupied a range of nearly an order of magnitude, between 0.103 ± 0.05 GPa (DPP-70) and 0.931 ± 0.26 GPa (DPP-30). The modulus of the stiffest material (DPP-30) was typical of the ≈1 GPa measured by our laboratory for P3HT and low-bandgap polymers.^[9,24] We observed that the crack-onset strains for the DPP-0 and DPP-100 were similar and lower than those of the DPP-30, 50, and 70. The lower values in the apparent ductility of the monomerically pure samples DPP-0 and DPP-100 could be a manifestation of the lack of randomness along the backbones of these materials (i.e., good order and efficient packing).^[29] In addition, the lack of statistical randomness in the molecular structures could potentially explain the reduction in the π - π stacking distance of DPP-0 and DPP-100 (3.62 Å for both) when compared to DPP-30, 50, and 70 (3.64, 3.65, and 3.65 Å, respectively).^[18] Full crystallographic parameters are summarized in Table S2 in the Supporting Information.

Zhao et al. found that the lamellar stacking distance decreased monotonically with increasing fraction of CBSs, possibly because of closer packing of the alkyl chains due to increased molecular ordering.^[18] The full-width-at-half-maximum (FWHM) of the lamellar stacking signal—a measure of crystalline order determined by grazing-incidence x-ray diffraction (smaller FWHM correlates with greater order)—exhibited a nonlinear trend in which the DPP-0 had the greatest FWHM (least order),

DPP-100 had the smallest FWHM (greatest order), and the FWHM increased in the series from DPP-30, DPP-50, and DPP-70 (decreasing order). The rationale for this finding is that DPP-0 has the least order because it permits the least interdigitation, while the opposite is true for DPP-100. In the series of polymers with increasing main-chain flexibility ($x = 30, 50, 70$), the order is intermediate but decreases somewhat within this series (the reason for this decrease is not yet clear). We found that the mechanical behavior does not correlate with number-average molecular weight, as estimated by size exclusion chromatography. The values of 30.7, 23.0, 19.5, 16.9, and 12.5 kDa for DPP-0, DPP-30, DPP-50, DPP-70, and DPP-100 may be distorted because of the larger hydrodynamic volume (and thus larger apparent molecular weight) of stiff polymer chains (e.g., DPP-0).^[18] In addition, no noticeable thermal transitions, beside the melting temperatures of DPP-70 and DPP-100, were observed via differential scanning calorimetry.

Despite our initial hypothesis that the DPP-100, with fully flexible backbone, would be the most ductile, we observed that this material had the greatest brittleness. Characteristics of DPP-100 in support of this finding are that it exhibits the smallest attachment density of side chains (and thus smallest lamellar spacing) and also the greatest lamellar order (smallest FWHM). Moreover, the brittleness of DPP-100 could be consistent with the highly crystalline 2D lamellar aggregates observed by atomic force microscopy.^[18] In contrast, DPP-0 exhibited fibril-like microstructures, and the thin-film morphologies gradually transitioned from fibril-like textures to lamellar aggregates with the addition of CBSs.^[18] The most striking

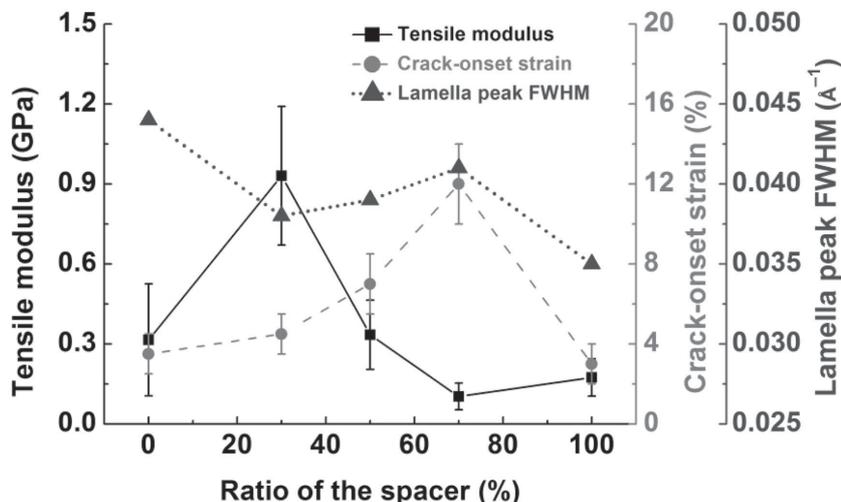


Figure 2. Comparison of mechanical properties and microstructural data of the DPP-*x* polymers.

characteristic of the data is thus that the stiffness of the films is not correlated with the stiffness of the polymer chains. As another example, the modulus increases from DPP-0 to DPP-30, indicating that not only were the mechanical properties of the film determined by the molecular structure, but also strongly dependent on the solid-state packing structure. Figure 2 plots the mechanical properties and the FWHM as reported by Zhao et al.^[18] The trends are partial inverses, with the stiffness and ductility highly correlated with the order (low FWHM). DPP-100 was observed to be the exception to the trend, where the low stiffness did not correlate with high ductility.

Photovoltaic properties were measured by mixing the DPP-*x* series of polymers with [6,6]-phenyl C₆₁butyric acid methyl ester ([60]PCBM) in a 1:2 ratio. Given our ultimate interest in deformable electronics, we used only stretchable electrodes: PEDOT:PSS as the transparent anode and eutectic gallium–indium (EGaIn) as the reflective cathode.^[15] While the use of these electrode materials generally produces devices that are less efficient than those made using typical electrodes—i.e., indium–tin oxide as the anode and evaporated aluminum as the cathode—the performance of the devices is reproducible.^[15] Moreover, for our purposes, uncovering trends in the figures of merit was more important than producing the greatest absolute values. We note that while the red shift in maximum absorption was observed from DPP-100 to DPP-0, due to the extension of the conjugation along the polymer backbone, the differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) among the polymers are only 0.16 and 0.08 eV, respectively (Table S1, Supporting Information).^[18] The overall trend of

the photovoltaic properties is decreasing performance with increasing fraction of the CBSs (Figure 3a and Table 1). Despite vastly different values between DPP-0 and DPP-30 of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF), the two polymers actually have the same overall power conversion efficiency (PCE) when combined with [60]PCBM.

The PCE for these solar cells is compared to the field-effect mobilities for films cast spin-coating in Figure 3b. While both mobility and PCE decrease with increasing ratio of the CBSs, addition of 30 wt% of the monomer bearing the CBSs has a large deleterious impact on the mobility of the polymer, but

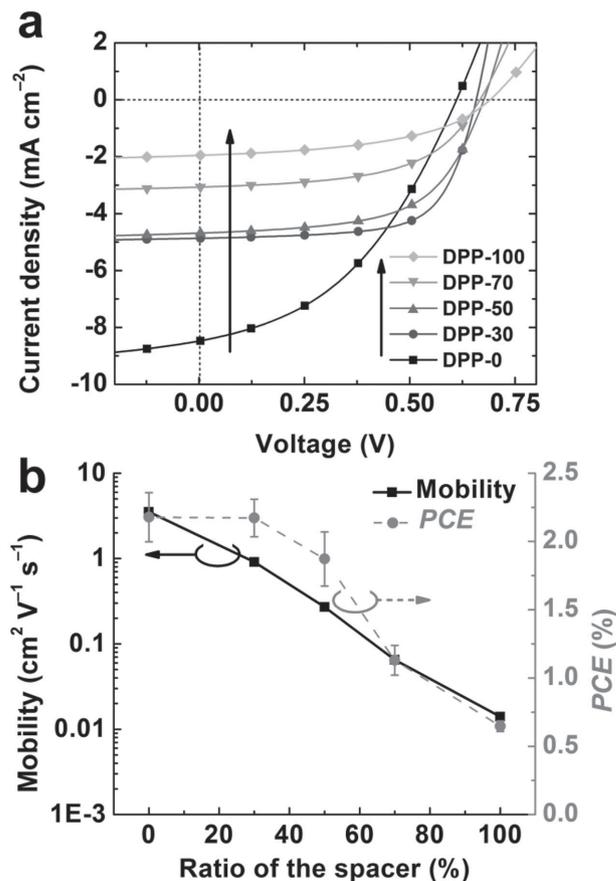


Figure 3. Photovoltaic properties and mobility of the DPP-*x* polymers. a) Current density versus voltage curves for DPP-*x* polymers when fabricated into photovoltaic cells with the architecture PEDOT:PSS/active layer/EGaIn. The active layers were spin-coated from a mixture 1:2 polymer:[60]PCBM at the concentration of 10 mg mL⁻¹ in 1:4 ODCB:CHCl₃. b) Comparison between mobility and power conversion efficiency of the DPP-*x* polymers. The mobility values were reproduced from ref. ^[18].

almost no effect on PCE. This effect is a combination of the reduction of J_{sc} and the increases in V_{oc} and FF. This observation is consistent with those observed in poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and also poly(3-heptylthiophene), where acceptable photovoltaic performance is not predicted by low field-effect mobility.^[11] We did not investigate the performance of the devices under strain because in our experience the crack-onset strains of the films are the primary predictors of failure in the devices. Moreover, we have observed for systems of bulk heterojunctions comprising polymeric electron donors and [60]PCBM that the photovoltaic properties of the strained films were similar to the unstrained films when the applied strains were below the crack-onset strains for the materials.^[24]

Finally, we explored Zhao et al.'s interesting observation that the blend of 1 wt% of DPP-0 in DPP-100 had a greater mobility than pure DPP-100 by a factor of nearly 100 (nearly as high as that of pure DPP-0).^[20] The rationale was that the presence of rigid, high-mobility tie chains of DPP-100 bridged the crystalline domains of DPP-100. We thus tested the hypothesis that the large weight fraction of the flexible DPP-100 in a 99:1 blend of DPP-100:DPP-0 would produce solar cells when combined with [60]PCBM with both high efficiency and mechanical compliance. Unfortunately, this experiment produced the "worst of both worlds." That is, the PCE was as low as the value obtained for pure DPP-100 and the polymer blend films were stiffer (0.50 GPa) than DPP-100 alone (0.17 GPa). It appears thus that the effect of the tie chains of DPP-0 is negated by the presence of the [60]PCBM in the bulk heterojunction film; in the blend containing polymers only, one possible explanation is that the tie chains of rigid DPP-0 not only bridge the crystallites of DPP-100 electronically, but mechanically as well (i.e., the tie chains have a substantial stiffening effect). These results support the notion that charge-carrier mobility of polymer films in thin-film transistors is not directly predictive of efficiency in polymer:fullerene solar cells. Moreover, the results highlight the intricacies of the ways in which microstructure and the presence of impurities even in small weight fractions affect mechanical properties of organic semiconductors.

3. Conclusion

This paper shows that the mechanical properties of conjugated polymers containing large fractions of subunits bearing flexible aliphatic groups are not easily predicted based only on the flexibility of the isolated molecules. Rather, the molecular structure must be combined with knowledge of its packing arrangement in the solid state. This work is also the first to show the effect of adding

flexible groups along the conjugated backbone on the mechanical properties. In comparing mechanical measurements of polymers whose structural differences are along the backbones with other work focused on the effect of the length of side chains, we suggest that engineering the main chain may be a less promising strategy than engineering the side-chain in producing conjugated polymers with increased flexibility, stretchability, and robustness.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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