Improving Miscibility of a Naphthalene Diimide-Bithiophene Copolymer with n-Type Dopants through the Incorporation of “Kinked” Monomers

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N-type doping of polymer semiconductors is necessary to enable printable and efficient organic thermoelectric generators. A recently reported method relies on blending air-stable benzimidazole derivative dopant molecules with good electron transporting materials, such as the well-known poly[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-[2,2′-bithiophene}], also known as PNDIT2. One of the main limitations to doping efficiency is miscibility of the dopant with the polymer. In order to overcome such limitation, controlled amounts of the covalently incorporated, meta-substituted monomer 1,3-bis(2-thienyl)benzene (TPT) ("kinked monomer") are introduced into the otherwise straight backbone of PNDIT2. Differential scanning calorimetry shows that crystallinity of P(NDI-alt-[T2-co-TPT]) first decreases with increasing TPT content up to 5 mol%, but then increases again for higher TPT contents. Miscibility of P(NDI-alt-[T2-co-TPT]) with the dopant 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)-N,N-diphenylaniline increases with increasing TPT content up to 30 mol%. The electrical conductivity of doped P(NDI-alt-[T2-co-TPT]) films is reduced with respect to PNDIT2, owing to a lower charge mobility caused by TPT units which break conjugation. Nevertheless, the doping efficiency at high doping concentration is substantially improved, with an estimated ≈20-fold increase with respect to PNDIT2, as a result of the improved miscibility of dopant and copolymer.

1. Introduction

There is a growing interest in the application of solution-processable organic semiconductors for thermoelectrics with the aim of developing economically viable, flexible, and lightweight waste heat energy harvesting applications,[1−7] as well as active coolers.[8] Any efficient thermoelectric generator requires both p-doped and n-doped materials,[9,10] with high electrical conductivity, high Seebeck coefficient, and low thermal conductivity. While p-type doped poly(3,4-ethylenedioxythiophene-based semimetals reaching a dimensionless figure of merit \(zT\) in excess of 0.1 have been demonstrated, solution-processable n-type doped materials are still very scarce, both because of the limited availability of good electron-transporting semiconductors,[11,12] and also because of the intrinsic difficulty in devising environmentally stable electron-donating, doping moieties.[13,14] In this respect, the replacement of a direct charge transfer scheme by hydride transfer followed by subsequent electron transfer was proposed. To this end, environmentally stable benzimidazole derivatives such as 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyldiphenylamine (N-DPBI) (Scheme 1) or 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyldimethylamine (N-DMBI) were used in combination with electron accepting semiconductors. These dopants produced a strong increase in the electrical conductivity of films of [6,6]-phenyl-C61-butyric acid methyl ester,[15,16] and poly[(N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-[2,2′-bithiophene}] (PNDIT2)[17−20] (Scheme 1). The latter case is particularly notable.
because doped conjugated polymers are particularly useful for the realization of flexible organic thermoelectric generators owing to their mechanical properties and facile tuning of rheology of formulations to enable scalable printing technologies.

In recent studies, PNDIT2 was n-doped in solution by adding N-DMBI, achieving a maximum electrical conductivity $\sigma$ in the range of $10^{-3}$–$10^{-4}$ S cm$^{-1}$ for a dopant concentration of 9 mol%.[17] Several explanations were proposed to explain limitations in the maximum electrical conductivity. One cause was ascribed to strong charge intrachain localization,[21] which can be overcome using ladder-type copolymers featuring a planarized backbone.[22] However, in the latter approach vapor phase doping was performed, which is not compatible with large-scale printing. Another strong limitation was that only ~1% of the added dopant molecules were active, and ~0.1% of the repeat units of PNDIT2 were doped, likely as a result of phase separation between the copolymer and dopant molecules. This limitation in miscibility between dopant and the semicrystalline polymeric host is likely caused by the strong tendency of PNDIT2 to aggregate in solution,[21–25] and also by its semicrystalline nature, which prevent an homogeneous distribution of the dopant molecules within the polymer phase.

In this contribution, we address the limited miscibility of PNDIT2 (Scheme 1a) with N-DMBI (Scheme 1b). In order to control polymer aggregation in solution and bulk crystallinity, and finally to enable a stronger interaction of the polymer backbone with the dopant, we use an additional meta-monomer to introduce 120° angles into the otherwise straight backbone of PNDIT2. This is realized by the statistical direct arylation polycondensation of the monomers 2,6-naphthalene diimide dibromide (NDIBr2), bithiophene (T2) and 1,3-dithienylbenzene (TPT) as a “kinked” monomer (Scheme 1c). The miscibility of the resulting terpolymers P[Ndi-alt-[T2x-co-TPTy]] with N-DMBI is investigated using differential scanning calorimetry (DSC) and atom force microscopy (AFM), which show that films of terpolymers with increasing TPT content can accommodate an increasing dopant fraction before dopant segregation sets in. By investigating charge carrier mobility and electrical conductivity, we show that the reduced degree of crystallinity of P[Ndi-alt-[T2x-co-TPTy]] enables an increase in charge carrier density of more than one order of magnitude. The overall electrical resistivity, however, is higher with respect to PNDIT2, mainly owing to a reduced electron mobility caused by TPT comonomers which act as conjugation breaks.

### 2. Results and Discussion

To introduce statistical kinks into the linear structure of PNDIT2, the direct arylation polycondensation[26] of NDIBr2, T2 and TPT was performed with varying ratios TPT/(TPT + T2) ranging from 0 to 1 (Scheme 1c, Table 1). Characterization of the resulting polymers of type P[Ndi-alt-[T2x-co-TPTy]] by size exclusion chromatography (SEC), $^1$H NMR spectroscopy, UV–vis spectroscopy, and DSC was done to investigate the effect of the statistical incorporation of TPT onto the optical and thermal properties. $^1$H NMR analysis confirms that the monomer feed ratio corresponds to incorporated TPT (Figures S1–S3, Supporting Information). To study the effect of the TPT monomer content on conjugation length in solution, UV–vis spectroscopy in 1-chloronaphthalene solution was done to investigate charge carrier mobility and electrical conductivity, which show that films of terpolymers with increasing TPT content can accommodate an increasing dopant fraction before dopant segregation sets in. By investigating charge carrier mobility and electrical conductivity, we show that the reduced degree of crystallinity of P[Ndi-alt-[T2x-co-TPTy]] enables an increase in charge carrier density of more than one order of magnitude. The overall electrical resistivity, however, is higher with respect to PNDIT2, mainly owing to a reduced electron mobility caused by TPT comonomers which act as conjugation breaks.

### Table 1. Molecular weight and thermal properties of P[Ndi-alt-[T2x-co-TPTy]].

| Sample | $M_w$/$M_m$ | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J g$^{-1}$) | $\Delta H_f$ (J g$^{-1}$) |
|--------|-------------|------------|------------|--------------------------|--------------------------|
| P(NDI2) | 32/78       | 313.1      | 290.3      | 16.4                     | 15.4                     |
| P[Ndi-alt-[T2x-co-TPTy]] | 52/204 | 307.4      | 288.7      | 8.1                      | 7.1                      |
| P[Ndi-alt-[T2x-co-TPTy]] | 56/246 | 307.0      | 290.7      | 6.4                      | 6.2                      |
| P[Ndi-alt-[T2x-co-TPTy]] | 49/186 | 301.7      | 280.0      | 6.8                      | 6.5                      |
| P[Ndi-alt-[T2x-co-TPTy]] | 53/227 | 299.5      | 280.6      | 7.8                      | 7.3                      |
| P[Ndi-alt-[T2x-co-TPTy]] | 45/111 | 252.3      | 226.5      | 8.3                      | 6.8                      |
| P(NDIPT) | 56/83       | 217.2      | 189.4      | 10.8                     | 9.8                      |

*By size exclusion chromatography in chloroform.*
performed. Figure 1 shows that the wavelength of the charge transfer band of P(NDI-alt-[T2-co-TPT]) only very slightly moves to lower λ\textsubscript{max} values for ≤10 mol% TPT. This effect becomes more pronounced starting from 30 mol% TPT, indicating that the conjugation length in solution is limited for TPT contents >10 mol%. DSC measurements on this series revealed the melting enthalpies \(\Delta H\textsubscript{m}\) first to decrease with increasing TPT content up to 5–10 mol% TPT and afterward to increase again (Figure 2, Table 1; for DSC curves see Figure S4 in the Supporting Information). This is somewhat unexpected as the introduction of meta-monomers has been associated with a major loss of crystallinity.\[2\] The melting and crystallization temperatures \(T\textsubscript{m}\) and \(T\textsubscript{c}\) decreased continuously with increasing TPT content (Figure S5, Supporting Information). The lowest unoccupied molecular orbital (LUMO) level energies of P(NDI-alt-[T2-co-TPT]) are all between ~3.7 and ~3.8 eV, hence not drastically altered by the statistical incorporation of TPT. This is rationalized by the LUMO level being mainly determined by the acceptor naphthalene diimide (NDI) and only weakly by the donor comonomer (Figure S6, Supporting Information).

To investigate miscibility of P(NDI-alt-[T2-co-TPT]) with N-DPBI, DSC measurements were employed. To this end, solution blends were prepared from P(NDI-alt-[T2-co-TPT]) of varying TPT content and different amounts of N-DPBI in chlorobenzene. The melting enthalpies \(\Delta H\textsubscript{m}\) of the dopant N-DPBI in the blends were evaluated, normalized to their weight fraction, and compared to \(\Delta H\textsubscript{m}\) of the pure dopant (Figure 3a–c). All copolymers P(NDI-alt-[T2-co-TPT]) including the parent PNDIT2 did not show melting of N-DPBI up to a dopant concentration of ~23 wt%. This is interesting as 23 wt% corresponds to ~43 mol% dopant per repeat unit of PNDIT2. Note that here we use wt% to simplify thermal analysis. A table with mol% dopant per repeat unit is given in the Supporting Information (see Table S1 in the Supporting Information). However, for dopant concentrations larger than ~23 wt%, \(\Delta H\textsubscript{m}\) of N-DPBI increased with increasing dopant concentration for a given TPT content, but decreased with increasing TPT comonomer content for a given dopant concentration. For a TPT content of 30 mol%, \(\Delta H\textsubscript{m}\) of N-DPBI was similar compared to the fully kinked control PNDI TPT. All these data are reported in Figure 3d. Along with the decreased \(\Delta H\textsubscript{m}\) values of N-DPBI in the blends, both \(\Delta H\textsubscript{m}\) as well as \(T\textsubscript{m}\) of the copolymers decreased as well, indicating a lower degree of crystallinity and smaller crystals, respectively. This is a direct consequence of the presence of N-DPBI in the blend (Figure 3a–c).

The results from DSC analysis regarding reduced dopant segregation were confirmed by AFM images taken on films spun from the same solution as used for DSC sample preparation. Figure 4 shows examples of PNDIT2 and P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]}). In case of pristine copolymers (Figure 4a,c), fibril formation of P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]}) was found to be reduced compared to PNDIT2. Upon doping, round topographical objects were detected on the surface which can be ascribed to segregated dopant (Figure 4b,d).\[17\] However, the number of dopant aggregates on the film surface was markedly reduced for P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]]) compared to PNDIT2.

This latter observation suggests a possible pathway to improving doping efficiency of the copolymer as a consequence of better miscibility. In order to verify this assumption, we resorted to electrical measurements, for which PNDIT2, P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]]) and P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{30}]]) were selected. P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]}) features 2 mol% TPT, has the same conjugation length in solution as PNDIT2 (Figure 1), a decreased degree of crystallinity by about a factor of two (Figure 2) and better miscibility with N-DPBI for high doping concentrations. P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{30}]}) has 30 mol% TPT, exhibits a shorter conjugation length in solution, a similar degree of crystallinity than P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]]) and the highest miscibility with N-DPBI among all copolymers investigated. Thus, these two copolymers are examples which are expected to allow investigating the effects of balanced electronic properties of the copolymers and enhanced miscibility with N-DPBI.

Figure 5a shows the electrical conductivities for PNDIT2, P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]]) and P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{30}]]) as a function of dopant concentration. For the parent PNDIT2, the conductivity reached a maximum of \(1.9 \times 10^{-3}\) S cm\(^{-1}\) for a doping concentration of 15 wt% and then decreased afterward. The lightly kinked P(NDI-alt-[T2\textsubscript{29:0-co-TPT\textsubscript{10}]}) system displayed...
an overall decrease of $\sigma$ with respect to PNDIT2 with a peak of $\approx 6 \times 10^{-4}$ S cm$^{-1}$ for a similar doping concentration, and a reduced variation of $\sigma$ with doping concentration. The strongly kinked P(NDI-alt-[T270-co-TPT30]) showed generally lower conductivities compared to PNDIT2 at any doping concentration, with a maximum conductivity of $\approx 4 \times 10^{-4}$ S cm$^{-1}$ at 15 wt% doping as well. The decrease in conductivity for doping concentrations larger than 15–20 wt% can be viewed together with Figure 3d, which shows at which doping concentration a melting point for the dopant appears. Apparently, while for doping concentrations up to 15–20 wt% the dopant mixes with the amorphous part of the semicrystalline morphology, larger amounts lead to dopant phase segregation which may break up conduction pathways of doped polymer chains. The larger amounts of dopant, miscible with copolymers of high TPT content, lies, however, at a high doping range, for which conductivity has decreased again.

For what concerns the comparison between doped PNDIT2 and the two terpolymers, the introduction of TPT does not lead to an improvement in conductivity. However, upon analyzing the trend of $\sigma$ with doping concentration for P(NDI-alt-[T298-co-TPT2]), we find that for higher doping levels the decrease in conductivity is lower compared to the PNDIT2 case. This effect may be related to lower phase separation between the polymer and dopant (Figure 5b) with increasing doping concentration, leading to a higher number of free charges. This would also suggest that the overall decrease in conductivity is instead due to a lower charge carrier mobility.

Figure 3. a–c) Examples of DSC measurements of pristine materials and solutions blends: first heating curves of N-DPBI (blue), pristine P(NDI-alt-[T2-co-TPT]) (black), and P(NDI-alt-[T2-co-TPT]) doped with 28 wt% N-DPBI (red). TPT content increases from 0 mol% (a) to 2 mol% (b) and to 30 mol% (c). d) $\Delta H_m$ of N-DPBI for different dopant concentration and TPT content.

Figure 4. AFM height images of a) pristine PNDIT2, b) doped PNDIT2, c) pristine P(NDI-alt-[T270-co-TPT30]), and d) doped P(NDI-alt-[T270-co-TPT30]). Doping concentration was 23 wt% in both cases.

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These findings require further investigations of the charge carrier mobility $\mu$. To this extent, we resorted to field-effect devices in order to evaluate the electron mobility as a function of TPT content. We fabricated bottom-contact-top-gate field-effect transistors (FET) (Figure 6a) and extracted the electron mobility from the saturation regime (Figure 6b) for an accumulated areal charge density of $\approx 1.2 \text{ cm}^{-2}$, corresponding to a volumetric density of about $10^{19}$ cm$^{-3}$ (for FET transfer curves see Figure S7 in the Supporting Information). Measurements done on the parent PNDIT2 showed a saturation mobility of $\approx 8 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. For P(NDI-alt-[T270-co-TPT30]), the electron mobility decreased by a factor 2.3 to $\approx 3 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. P(NDI-alt-[T298-co-TPT30]) showed a lower saturation mobility of $2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, which corresponds to a decrease by a factor of 40 compared to PNDIT2. This strong decrease can be rationalized by the comonomer TPT posing conjugation breaks, which are ultimately expected to decrease the intrachain electron mobility and to reduce the degree of crystallinity.

From these electrical measurements, we suggest that the introduction of kinked monomers negatively affects conductivity as electron mobility is reduced. However, as the reduction in $\sigma$ is much lower than the reduction in electron mobility with increasing kink density at any given doping concentration, an enhanced interaction with the dopant up to 33 wt% doping concentration, and thus a higher charge density, may be at play.

To gain a first estimation of the charge carrier density introduced upon doping, we used the FET data to disentangle the contributions of charge mobility and charge density to conductivity. Since the values of the field-effect mobility correspond to a situation of high doping level of the order of the one reached in PNDIT2 at 15 wt% doping, we assumed that the observed ratio of field-effect mobilities PNDIT2/P(NDI-alt-[T2co-TPT]) is substantially the same at all doping levels. It is important to note that in a FET we probe carrier mobility present only in a nanometer-thin accumulation channel at the polymer/dielectric interface, and not in the bulk of the film.

Also, dopant ions, which are known to affect microstructure and transport, are not present in the FET. Our assumption is therefore very strong, however, still quite reasonable in order to obtain a first assessment of doping efficiency given the limited span in doping concentration.

Therefore, as $\sigma = e \times n \times \mu$ (with $n$ being charge carrier density and $e$ the elementary charge), we can extrapolate a ratio between the charge carriers of P(NDI-alt-[T298-co-TPT30]) and P(NDI-alt-[T298-co-TPT30]) with respect to PNDIT2.

As shown in Figure 7, for P(NDI-alt-[T298-co-TPT30]), no net change in charge carrier concentration is estimated compared to PNDIT2, for each doping level studied. This can be tentatively ascribed to the low concentration of kinked monomers in the copolymer used in the blend, leading to a similar miscibility with the dopant and therefore similar doping efficiency as in the case of PNDIT2.

For P(NDI-alt-[T298-co-TPT30]), a net increase in doping efficacy is estimated until 33 wt% doping concentration, with a peak of 22 for the ratio between the number of charge carriers of the kinked polymer and that of the standard PNDIT2, reached at 25 wt% of doping concentration.
To further corroborate this result, we have performed electron paramagnetic resonance (EPR) spectroscopy at the doping level of 25 wt%. Figure 8 shows that at this doping level, the signal intensity increases from doped PNDIT2 to P(NDI-alt-[T298-co-TPT2]) and further for P(NDI-alt-[T270-co-TPT30]) by factors of 1.3 and 5.5, respectively. Thus, the number of charge carriers is higher in the polymers having TPT monomers compared to PNDIT2, and the trend corresponds to the estimated increase in carrier concentration obtained from the FET measurements.

Also, we note that P(NDI-alt-[T270-co-TPT30]) does not yet show dopant melting in 25 wt% dopant blends. Therefore, up to this doping level, an increased amount of charge carriers is available because of a better copolymer–dopant miscibility in comparison with PNDIT2. However, already at 33 wt% doping the ratio drops quickly until 50 wt% doping, at which a net gain is no longer observed (the ratio is ≈1 at this doping concentration). This is also in line with the DSC data of the P(NDI-alt-[T298-co-TPT2]) blend, which indicates a strong increase of $\Delta H_m$ of N-DPBI for doping concentrations higher than 50 wt%. Therefore, we conclude that the presence of kinked TPT monomer covalently incorporated into PNDIT2 is an effective mean to increase the number of available free charge carriers in blends with N-DPBI due to an enhanced miscibility of the two components at large doping concentration. However, as electron mobility decreases at the same time and as the maximum conductivity is seen for lower doping concentrations compared to those where the increased miscibility is an advantage, the absolute conductivities are lower for the kinked copolymers.

3. Conclusion

In summary, we have synthesized a series of ternary copolymers of type P(NDI-alt-[T2-co-TPT]) with meta-monomer (TPT) concentrations ranging from 0 to 100 mol%. Crystallinity of P(NDI-alt-[T2-co-TPT]) first decreases and then again increases with increasing TPT content. Miscibility of P(NDI-alt-[T2-co-TPT]) with the n-dopant N-DPBI is enhanced with increasing TPT concentration as deduced from calorimetry data. Conductivity and mobility measurements of lightly kinked P(NDI-alt-[T298-co-TPT2]) reveal a decreased conductivity and a slightly reduced electron mobility. Thus, the low number of TPT monomers appears to be insufficient for improving the polymer/dopant miscibility and only causes a slight decrease in the electrical conductivity due to the reduction of the film crystallinity as shown also by DSC data. On the other hand, the stronger kinked P(NDI-alt-[T270-co-TPT30]) displays better miscibility that allows for a more effective doping as demonstrated by the higher number of available charge carriers (with a maximum increase by a factor of 22 at 25 wt% doping). Unfortunately, the introduction of TPT, which breaks conjugation, negatively influences electron mobility, which is reduced by a factor of 40 compared to the parent PNDIT2. Therefore, while the presence of kinked monomers improves polymer/dopant miscibility, the overall effect is a reduction of the electrical conductivity of the blend. However, the strategy of introducing meta-kinks into the polymer chain to improve miscibility enhances doping efficiency by more than an order of magnitude and, with a proper balance between the increase of available carriers and the loss of mobility, higher conductivities could be reached in the future.

4. Experimental Section

TPT Synthesis: 1,3-dibromobenzene (4.126 mmol, 973.35 mg), thiophene (15 equiv., 61.89 mmol, 5 mL), and PivOK (10.32 mmol, 1.45 mg) were added into a two-neck flask and flushed with N2 for 10 min. Degassed dimethylacetamide (50 mL) was added into the flask under an inert atmosphere, and then Pd(OAc)2 (0.206 mmol, 46.32 mg) was added. After 48 h of stirring at 70 °C, the solvent was evaporated, the crude mixture was dissolved in 50 mL isohexanes, washed with water and concentrated. The residue was subjected to column chromatography with isohexanes as eluent, and the product was isolated as white crystals in 65% yield.
The electrical characteristics of transistors were measured in a nitrogen-filled glovebox on a Wentworth Laboratories probe station with a semiconductor device analyzer (Agilent B1500A). The saturation mobility values were calculated using the gradual-channel approximation.

EPR Spectroscopy: EPR spectra were recorded at room temperature on an Elexys E580 (Bruker Biospin) spectrometer equipped with a 4119HS-W1 (Bruker) cavity. Microwave frequency: 9.788 GHz; microwave power: 474.3 μW (25 dB attenuation, 150 mW source power); modulation frequency: 100 kHz; modulation amplitude: 0.005 mT. Each spectrum is a single recording. Samples were produced under inert atmosphere by drop-casting 20 μl solution (concentration of 5 mg mL⁻¹) on synthetic quartz glass substrates of dimension 25 × 3 mm (Ilmasil PS, QSIL GmbH), followed by annealing at 120 °C for 30 min after films were dried completely. The annealed films were placed in EPR tubes made of synthetic quartz glass (Ilmasil PS, QSIL GmbH) with 3.8 mm outer and 3.0 mm inner diameter and the tubes sealed afterwards.

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

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Conflict of Interest
The authors declare no conflict of interest.

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