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Solution processable polydiacetylenes (PDAs) through acyclic enediyne metathesis polymerization†

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Novel polydiacetylenes (PDAs) bearing alkyl and phenyl substituents have been synthesized, for the first time, by solution polymerization using acyclic enediyne metathesis. The resulting polymers are soluble in common organic solvents and show distinct physical and photophysical properties both in solution and as thin films, caused by different steric and electronic effects from the side-groups. Bulk heterojunction solar cells employing these PDAs have been fabricated and evaluated.

Introduction

Since the first report on the solid-state preparation of polydiacetylene (PDA) in 1969,[1] extensive research efforts have been devoted to this classic type of conjugated polymers.[2] PDAs are considered quasi one-dimensional semiconductors having macroscopic long-range coherence and anisotropy.[3] These materials undergo intriguing optical changes among blue, red and yellow phases upon exposure to external stimuli including temperature,[4] solvents,[5] pressure,[6] light exposure[7] and specific biological analytes.[8] PDAs have found widespread applications in non-linear optics,[9] organic conductors[10] and sensory materials.[11] Despite a large number of examples, PDAs reported to date have been synthesized exclusively from a single type of reaction, *i.e.* irradiation induced topochemical polymerization of diacetylene (DA) monomers in crystals, films, gels and micellar structures.[2a] Such reactions occur efficiently only if the DA monomers are able to pack into periodic structures within very strict geometrical boundaries.[12] Flexibility around diacetylene moieties is required to accommodate spatial rearrangement when two sp hybridized carbon atoms in every DA monomer change to sp^2 hybridization in resulting PDA chains.[13] As a result, few types of DA monomers, typically having alkyl spacers between DA cores and functional side-groups, can be successfully polymerized.[2] Electronic properties of resulting PDAs are thus difficult to modify by substituent variation.[14] Moreover, the obtained PDAs usually have limited solubility, making integration of these materials into solution-fabricated electronic devices challenging.

Notably, there have been efforts in building short-chain PDA analogs having a few eneyne repeating units through iterative condensation reactions and the resulting oligomers serve as discrete models for studying corresponding long-chain polymer properties.[15] Although these synthetic methods have led to well-defined oligomers with precise structural control, high molecular weight polymers are difficult to achieve using these step-by-step approaches.

We report here the synthesis of solution processable PDAs through acyclic enediyne metathesis polymerization[16] of methyl terminated *trans*-enediyne[17] monomers bearing different substituents. Physical and electronic properties of the resulting PDAs are shown both experimentally and theoretically to depend on the nature of the side-groups. To the best of our knowledge, our method represents the first example of PDA synthesis by solution polymerization and of alkyne metathesis on enediyne substrates.

Results and discussion

The synthesis of enediyne monomers bearing *n*-undecyl and 4-*tert*-butylphenyl substituents, and their metathesis polymerization are summarized in Scheme 1; detailed experimental procedures and characterization data are included in the ESI.† Notably, compounds **3a** and **3b**, obtained, respectively, from McMurry coupling reactions of **2a** and **2b**, have *trans* configurations in the central double bonds due to the bulky triisopropylsilyl moieties.[18] Solution polymerization of **M-a** and **M-b** was initially attempted using $Mo(CO)_6$ and various phenolic ligands,[19] as well as the well-defined Schrock alkylidyne complex $(^tBuO)_3WCCMe_3$,[20] as catalysts under conditions that have been successfully applied in alkyne metathesis and preparation of poly(aryleneethynylene)s. No polymerization was detected, however, as no color change was observed and only starting materials were recovered after prolonged reaction times. This lack of reactivity may be attributed to enhanced conjugation and thus higher stability of triple bonds in these *trans*-enediyne molecules relative to those in isolated and aromatic alkynes.

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† Electronic supplementary information (ESI) available: Synthetic details, SEC profiles, thermochromism studies, DFT calculations, DSC curves, XRD profiles, device data and NMR spectra. See DOI: 10.1039/c3sc51264a

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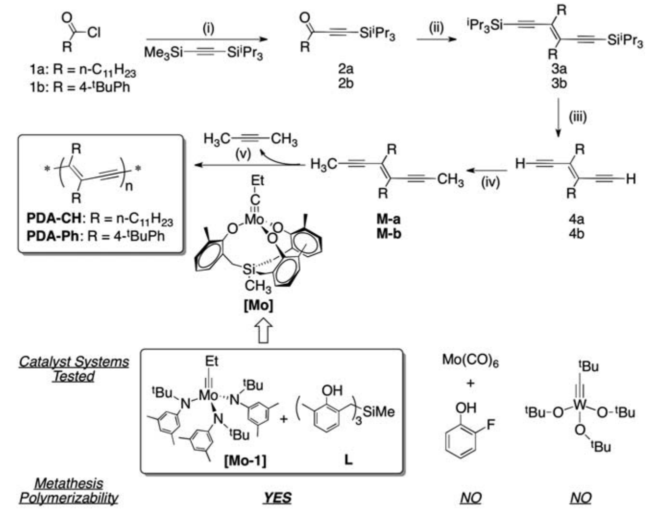

(i) $AlCl_3$, CH_2Cl_2, 0 °C; (ii) $TiCl_4$/Zn, THF, reflux; (iii) tetrabutylammonium fluoride, r.t.; (iv) $^nBuLi/CH_3I$, THF, −78 °C; (v) 5Å molecular sieves, CCl_4, 60 °C, 3d.

Scheme 1 Synthesis of monomers and polymers.

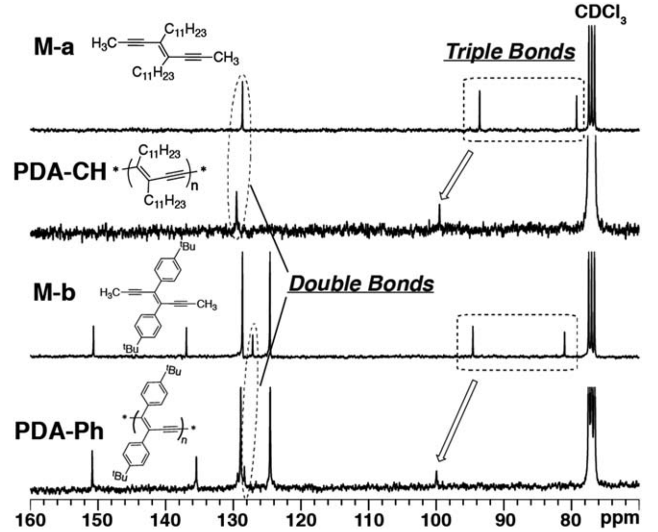

Fig. 1 ^{13}C NMR spectra (aromatic region) of **M-a**, **M-b**, **PDA-CH** and **PDA-Ph**.

We have recently developed a well-defined and highly active alkyne metathesis catalyst [**Mo**] obtained by treating the pre-catalyst [**Mo-1**] with triphenolsilane ligand **L** *in situ*, as shown in Scheme 1.[21] By using such podand ligand design,[22] one of the two open substrate-binding sites is blocked and small alkyne polymerization side reactions are completely suppressed. Both **M-a** and **M-b** were successfully polymerized in CCl_4 using *ca.* 7–8 mol% *in situ* generated [**Mo**] in the presence of 5 Å molecular sieve powders (scavenger for the 2-butyne by-product)[23] to give respective **PDA-CH** and **PDA-Ph** in high yields as red solids. Molecular weights of these polymers were estimated against polystyrene standards from size exclusion chromatography (SEC, Fig. S1†) to be $M_n = 15\,600$, PDI = 1.9 and DP (degree of polymerization) = 47 for **PDA-CH**; and $M_n = 10\,200$, PDI = 1.4 and DP = 32 for **PDA-Ph**. Chemical structures of both polymers were confirmed by ^1H and ^{13}C NMR spectroscopy[24] as shown in Fig. 1 and ESI.† As shown in Fig. 1, two acetylenic ^{13}C signals are observed at 79.2 and 93.6 ppm for **M-a** and 81.0 and 94.5 ppm for **M-b**. Upon polymerization, each set of signals downfield shifts and merges into a single signal at 99.3 ppm for **PDA-CH** and 99.9 ppm for **PDA-Ph**, respectively. Such observation confirms the successful polymerization leading to symmetrically substituted triple bonds along polymer backbones. The fact that the acetylenic chemical shift values for both polymers are close to 100 ppm, a value previously predicted by extrapolating oligomer data toward infinite chain length,[15d] confirms high molecular weights for both polymers. ^{13}C signals of double bonds in both polymers are also slightly downfield shifted from those in corresponding monomers due to enhanced conjugation. Additionally, in the ^1H NMR spectra of both polymers (ESI†), signals corresponding to terminal methyl groups as observed in the spectra of respective monomers disappear, suggesting relatively high molecular weights for the polymers. We have also performed matrix-assisted laser desorption–ionization time-of-flight (MALDI-TOF) mass spectrometry analysis in order to probe the possibilities of ring-formation during the polymer synthesis. However, no polymeric ions could be observed presumably due to the non-polar nature of these polymers.

UV-Vis absorption and fluorescence measurements are performed on dilute chloroform solutions of the polymers (2.5×10^{-4} M r.p. units) with gradual additions of methanol up to 58% by volume, beyond which both polymers start to precipitate. As shown in Fig. 2, **PDA-CH** has a λ_{max} of 430 nm in chloroform, blue-shifted by *ca.* 30 nm from typical values for solutions of yellow-chain PDAs bearing side-chains capable of non-covalent interactions, which have been shown to adopt "Porod–Kratky" worm-like conformations in solution.[25] The blue-shifted absorption of **PDA-CH** thus suggests a more flexible backbone and shorter persistence and effective conjugation lengths, presumably due to the absence of intramolecular non-covalent

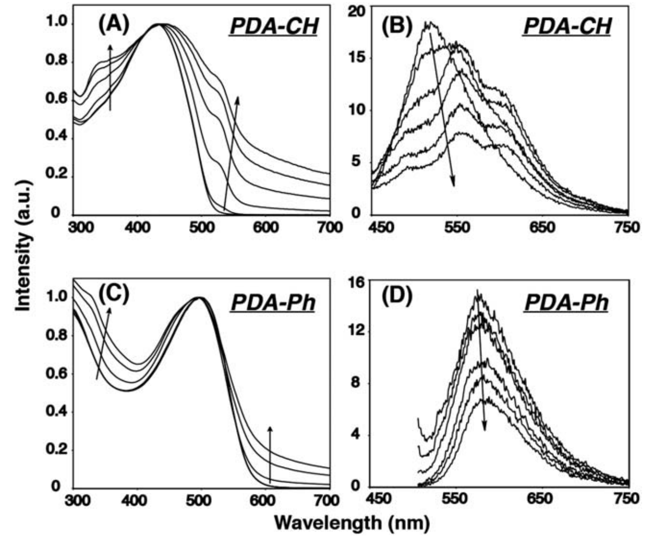

Fig. 2 UV-Vis absorption (normalized, A and C) and fluorescence (B and D) spectra of **PDA-CH** (A and B) and **PDA-Ph** (C and D), respectively, in chloroform solutions (2.5×10^{-4} M r.p. units) with gradual additions of methanol. Black arrows indicate increasing methanol volume fractions at 0, 17, 29, 40, 49 and 58%.

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interactions.[26] On the other hand, **PDA-Ph** shows a λ_{max} at 500 nm, a value close to those of red-chain PDAs. Upon gradual additions of methanol, λ_{max}'s of **PDA-CH** slightly red shift and a shoulder at *ca.* 525 nm becomes apparent, indicating the formation of red-chain species.[4b] Fluorescence signals (λ_{exc} = 430 nm, λ_{em} = 515 nm, chloroform) also red shift and become more structured (λ_{em} = 495, 555 and 605 nm, 58% methanol). This yellow to red transition in **PDA-CH** is attributed to aggregation and planarization of the polymer main-chain, leading to enhanced delocalization and longer conjugation lengths.

On the other hand, only a slight blue shift of λ_{max} up to 10 nm and no apparent change in fluorescence (λ_{em} = 580 nm, λ_{exc} = 500 nm) are observed for **PDA-Ph** (Fig. 2C and D). This is presumably caused by the presence of bulky *tert*-butylphenyl substituents that prevent close packing and planarization of PDA chains. Aggregation may even force the main-chain to be more twisted, leading to the observed blue shift in absorption. Such aggregation behavior is also observed in thermochromism studies as shown in Fig. S3.† While the THF solution of **PDA-CH** shows red-shifted λ_{max}'s and pronounced absorption shoulders at *ca.* 530 nm at low temperatures, blue-shifted and completely featureless absorption profile is observed at 70 °C. On the contrary, only a slight red-shift in λ_{max} (*ca.* 10 nm) is observed for **PDA-Ph** in THF by going from 70 to 0 °C, and no shoulder peaks can be observed. Thus, the red appearance of **PDA-Ph** is most likely due to modification of the main-chain electronic states through direct conjugation of the aromatic substituents, even though the main-chain conformation may still be in a "yellow form". Fluorescence quantum yields in dilute chloroform solutions are estimated to be 0.1% for **PDA-CH** and 0.09% for **PDA-Ph** using quinine bisulfate (in 0.1 M H_2SO_4) as a standard.[15k] Such low quantum efficiencies are consistent with literature reported values for yellow-chain PDAs.[27]

The observed side-group effects are elucidated by density functional theory (DFT) calculations (B3LYP, 6-31G(d)) performed on trimeric model compounds bearing methyl (TriDA-Me) and phenyl (TriDA-Ph) groups (Fig. S4†). TriDA-Ph has a bandgap of 2.6 eV, 0.5 eV smaller than that of TriDA-Me, consistent with the longer wavelength absorptions by **PDA-Ph**. TriDA-Me shows a completely planar optimized geometry while TriDA-Ph has a slightly bent backbone with twisted phenyl substituents, indicating difficulties in close packing of polymer chains in the case of **PDA-Ph**. Indeed, differential scanning calorimetry (DSC) measurements on both polymers show distinct thermal behaviors (Fig. S5†). Multiple melting transitions are observed for **PDA-CH**, indicating high crystallinity in the solid state. The transitions at *ca.* 15 °C and 40 °C are assigned to side group melting and that at *ca.* 140 °C to main-chain melting. On the contrary, **PDA-Ph** shows no melting behavior up to 250 °C with only a glass transition observed at *ca.* 155 °C (onset), indicating its amorphous nature. The crystalline nature of **PDA-CH** is further confirmed by powder X-ray diffraction (XRD) as multiple sharp scattering peaks are observed (Fig. S6†). The lamellar distance is calculated to be 30.6 Å ($2\theta = 2.84°$), corresponding to stacking of fully stretched $C_{11}H_{23}$ side-chains without interdigitation. On the other hand, only two broad peaks are observed in the XRD profile of **PDA-Ph** (Fig. S7†), giving a lamellar packing distance of *ca.* 16 Å.

Similar trends are observed in thin films of **PDA-CH** and **PDA-Ph** as shown in Fig. 3.[28] Compared with solution data, λ_{max} of as-cast **PDA-CH** thin film red shifts to *ca.* 475 nm and the shoulder peak at 525 nm becomes more pronounced. Three emission peaks (λ_{exc} = 460 nm) are observed at 482, 568 and 610 nm. The 482 nm peak blue shifts and decreases in relative intensity, when compared with solution emission profiles, and the other two both red shift and increase in intensities. After annealing the same film at 155 °C for 10 min, the 525 nm absorption shoulder peak becomes more resolved, accompanied by a decrease in relative intensity of the 482 nm peak as well as slight red shift and increase in relative intensities of the peaks at 570 and 615 nm. Raman scattering measurements show identical signals at 1525 and 2121 cm^{-1} for as-cast and annealed films. These frequencies are due to respective double and triple bond stretches and correspond to red–yellow-chain PDA species.[29] Thus, the red-shift in emission spectra of annealed film is likely due to conformational change and ordering of the side-groups without perturbing significantly the main-chain structures and bond orders.[30] Exact nature of the yellow- and red-chain species requires further investigation.

As expected, thin films of **PDA-Ph** show almost identical photophysical properties as in solutions (Fig. 3B). λ_{max} blue shifts slightly to 485 nm in as-cast film and further to 480 nm in thermal annealed film. Fluorescence profiles in both as-cast and annealed films show no difference with those in solutions and identical Raman scattering is observed for both films. The observed blue

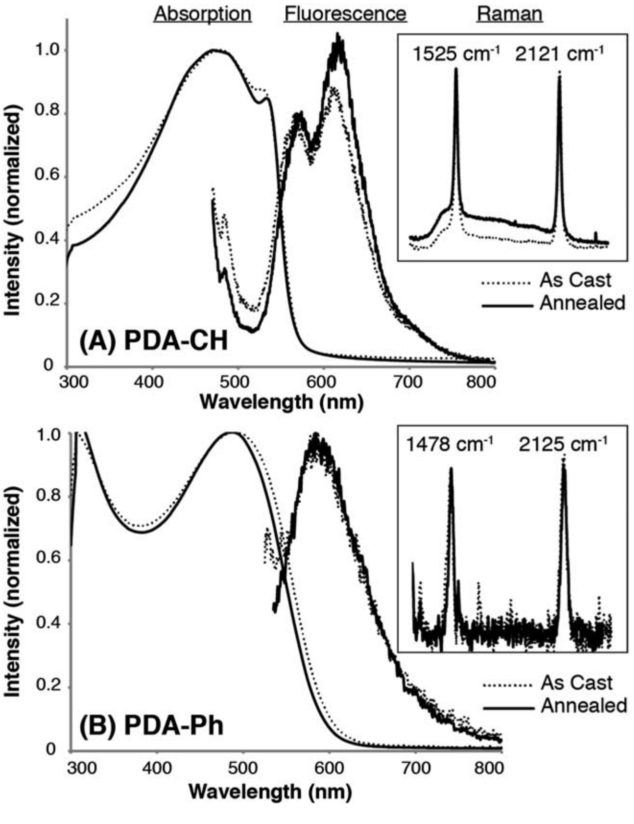

Fig. 3 UV-Vis absorption, fluorescence and Raman spectra of thin films of **PDA-CH** (A) and **PDA-Ph** (B) drop-cast from chloroform solutions. Data for both as-cast films and the same films annealed at 155 °C for 10 min are presented.

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shift in absorption is likely due to ordering of the bulky side-groups that leads to conformations favoring slightly more twisted main-chain geometries. The double bond stretch of **PDA-Ph** at 1478 cm^{-1} is surprisingly in the range of typical "blue-chain" PDAs.[29] This is likely due to electron delocalization from double bonds to the phenyl side-groups, thus reducing electron density and bond strengths, causing reduction in vibrational frequencies.

There have been increasing interests in using conjugated polymers for organic electronic devices through low-cost high-throughput solution processes.[31] Existing PDAs have rarely been applied in electronic devices due to limited solubility and tunability in electronic properties. Our methodology provides a facile way to produce soluble PDAs having different side-groups directly attached to the main-chains. For a proof of concept, we have fabricated bulk heterojunction (BHJ) organic solar cells using **PDA-CH** and **PDA-Ph**, respectively, blended with equal weight of phenyl-C_{61}-butyric acid methyl ester (PCBM) as active layers. A conventional device structure of ITO/MoO_3/active layer/Al is applied and device performances are summarized in Fig. S9.† The best devices are made from **PDA-CH**, giving on average a short circuit current (J_{SC}) of 0.44 mA cm^{-2}, an open circuit voltage (V_{OC}) of 0.6 V, a fill factor (FF) of 35% and a power conversion efficiency (PCE) of 0.09%. Devices made from **PDA-Ph** showed reduced J_{SC}, thus lower PCEs, likely caused by the polymer's amorphous nature. Both polymers out-performed, by more than 100-fold, the only previous example of solar cells employing PDAs from solid-state polymerization.[32] We are currently optimizing cell performance and studying charge generation mechanisms in these PDA devices in more detail.

Conclusion

In summary, we have developed a versatile methodology for the synthesis of soluble and functional PDAs. Physical and electronic properties of the resulting polymers can be tuned by careful selection of different side-groups. We are currently optimizing the reaction conditions in order to achieve higher molecular weight polymers and to gain deeper insights in their structure–property relationship. Our findings open up doors for PDAs towards previously less explored areas in solution-processed electronic device applications.

Acknowledgements

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