



Full paper

Cyclic alkyl chains promote the polymer self-assembly and packing orders for solar cells

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ABSTRACT

The micro-structure ordering of the π -conjugated polymer film self-assembling from solution governs its electrical characteristics and performances for organic electronics. The side chains appended on the conjugated backbone could impact the self-assembling characteristics of the polymer, which show us how to design novel substituents to optimize the polymer arrangement and packing in its solid state. Here, cyclic alkyl chains are proven to be excellent ones for designing of narrow bandgap polymers, the design feature of which with preferential conformations can promote the polymer self-assembly and result in higher degree of lamellar order as well as tighter lamellar packing in the active layer, comparing with linear alkyl chains. The linear ones have poorer ordering in the polymer:fullerene blends as well as in the single crystals of the monomers. The well-organized polymer micro-structures facilitate polymer:fullerene phase separation together with balanced hole/electron transporting, and ultimately, improve the power conversion efficiency impressively compared to linear chains.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have already aroused great concern in the recent twenty years, because of their bright future in realization of a printable, flexible and renewable energy source [1–3]. The π -conjugated polymer and fullerene derivative mixed into a specific solvent, and then spin coated to fabricate a film with thickness of 100 nm to 1 μ m, which could absorb sunlight, create and transport charge carriers, finally, form an external circuit [4]. Any of these physical processes will significantly influence the open-circuit voltage (V_{OC}), the short-circuit current density (J_{SC}) and the fill factor (FF) of a PSC device. The π -conjugated polymer self-assembling as the solvent evaporating determines the film-forming property, micro-structure and phase separation in the polymer:fullerene blends, which governs the performances of the solution processed PSCs [5–9]. By optimizing the motifs of the π -conjugated backbones and patterns of the alkyl side chains, as well as hand-picking the film processing conditions that could direct the polymer arrangement and stacking, the power conversion efficiencies (PCEs) of the state-of-the-art PSCs have

exceeded 10% and always been ongoing [10–13].

Over the years, a number of studies have emphasized that the alkyl side chains could impact the organization of the π -conjugated polymers, and in turn, influence their electrical conductivity [14], carrier mobility [15,16] and PCE [17–20]. The uniform alkyl side chain arrangement could promote side chain inter-chain interdigitation, degree of lamellar order and packing of backbones, ultimately, facilitate high performances of the polymer based organic electronics [21–23]. However, these insulated and unconjugated *n*- or *iso*-alkyl chains are flexible and always adopt variable twisted conformations beyond their ideal linear “zigzag” conformation appending on the organic semiconductors [24–27], showing high degree of disorder, which, in actuality, may destroy the pristine π -conjugated skeleton arrangement and decrease their ordered self-assembly. Thus, improving the order of alkyl chains may be interesting, and possibly, could weaken the resistance and lead to higher degree of ordered self-assembly. Cyclic alkyl chains are the analogs of *n*- and *iso*-alkyl chains, but, they adopt preferential conformations, exhibiting better symmetry and stronger rigidity. However, π -conjugated polymers appended with these cyclic

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alkyl chains are less concerned for organic electronics [28], particularly for PSCs. The factor that limits their talents is the larger steric hindrance effect (SHE), which could distort the π -conjugated backbone and result in wider bandgap (E_g) [29–31]. Very recently, we have reported that the cyclohexyl could distort the polymer backbone and help to improve the device V_{OC} in both the 4,7-bis(thiophen-2-yl) benzo[c] [1,2,5] thiadiazole (DTBT) and diketopyrrolopyrrole (DPP) based polymers [32,33]. However, the structure–property relationships of the ordered cyclic alkyl chains improving the device performances are still unknown, and the functions of cyclic alkyl chains that may impact the molecular arrangement and stacking are desired to be further deeply explored.

In this report, six benzo [1,2-*b*:4,5-*b'*]dithiophene (BDT) and DTBT alternated polymers (P-*R*) were synthesized with linear (pentyl, hexyl and heptyl) and cyclic (cyclopentyl, cyclohexyl and cycloheptyl) alkyl chains, the corresponding polymers were named as P-*n*5, P-*n*6, P-*n*7, P-*c*5, P-*c*6 and P-*c*7, respectively. The DTBT monomers show variable packing patterns depending on the types of alkyl chains, and meanwhile, the cyclic chains could also influence the physical and electrical properties of the polymers. Finally, for PSCs studies, employing 1,8-diiodooctane (DIO) as processing additive, the cyclic alkyl chains substituted polymers were found to give PCEs approaching 8% in PSCs blending with [6,6]-phenyl C₇₁ butyric acid methyl-ester (PC₇₁BM), a significant improvement over their linear alkyl chains substituted counterparts, for which PCEs are lower than 6%. Our experiments indicated the cyclic alkyl chains promote the polymers rearranging into ordered micro-structures and forming interpenetrating networks with PC₇₁BM, which accelerate charge carrier transport. The substantial improvements of V_{OC} , J_{SC} and FF make cyclic alkyl chains promising candidates for designing high efficiency D–A type π -conjugated polymers.

2. Experimental section

2.1. General Information

Nuclear magnetic resonance (NMR) spectra were measured in CDCl₃ on a Bruker AVANCE 600 MHz Fourier transform NMR spectrometer; chemical shifts were quoted relative to the internal standard tetramethylsilane (TMS). High resolution mass spectra (HRMS) were obtained using a Bruker Maxis UHR–TOF, Ion Source: APCI system. The melting points of the monomers were measured using WRS–1B digital melting point apparatus, and confirmed by differential scanning calorimeter (PerkinElmer Diamond DSC, instrument DSC Q20 V24.11 Build 124) carried out under inert atmosphere with a scan speed of 10 °C/min. Absorption spectra were recorded with a Hitachi U–4100 UV–vis–NIR scanning spectrophotometer. The molecular weights of the polymers were measured by the gel permeation chromatography (GPC) performed using an ELEOS system, and polystyrene was used as the standard (room temperature, tetrahydrofuran (THF) as the eluent). The highest occupied molecular orbit (HOMO) energy levels, were determined by calculating the empirical formula of $E_{HOMO} = -e(E_{ox} + 4.8 - E_{1/2}^{(Fc/Fc+)})$ where E_{ox} was the onset oxidation potential. Bright field transmission electron microscopy (TEM) images were acquired using a HITACHI H–7650 electron microscope operating at an acceleration voltage of 100 kV. The film structures of the polymers and polymer/PC₇₁BM blends were analyzed using X-ray diffraction (XRD, Bruker D8 ADVANCE). The grazing incidence X-ray diffraction (GIXD) data of the pure polymers and polymer/PC₇₁BM blend films were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2398 Å and incident angle of 0.1 degree. BL14B1 is a beamline based on bending magnet and a Si (111) double crystal monochromator is employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection.

GIXD patterns were recorded with a two-dimensional image detector. The single-crystals were obtained through slow evaporation of dichloromethane/hexane solution for DTBT-*c*6 (CCDC deposition no. 1497792), dichloromethane/methanol mixed solutions for DTBT-*c*5 (CCDC deposition no. 1497791) and DTBT-*c*7 (CCDC deposition no. 1497793). The X-ray crystal structures were performed on a Bruker Smart Apex II diffractometer (Mo *K* α radiation, graphite monochromator, $l = 0.71073$ Å, $T = 296$ K). The structure was solved using SHELXS-97. CCDC deposition nos. 1497791, 1497792, 1497793 contains the supplementary crystallographic data for this paper.

2.2. PSC device fabrication and characterization

PSCs were fabricated as a standard device architecture, ITO/PEDOT:PSS/Polymer: PC₇₁BM/Ca/Al [34,35]. ITO coated glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone and iso-propanol, followed by treating in an oxygen plasma (Plasma Preen II-862 Cleaner) for 6 min. The cleaned substrates were covered by a 40-nm-thick layer of PEDOT: PSS (Heraeus Clevios TM P AI 4083) by spin coating. After annealing in an oven at 150 °C for 20 min, the substrates were transferred to a glove box filled with N₂. Polymers and PC₇₁BM (American Dye Source) were dissolved in *o*-DCB with or without DIO solvent. The solution was stirred overnight at room temperature, and then spin-coated on PEDOT:PSS modified ITO coated glass to form the active layer (~100 nm). The devices were completed after the deposition of Ca (10 nm)/Al (100 nm) as cathode through a shadow mask under high vacuum (~10⁻⁴ Pa). The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and estimated using Veeco Dektak150 surface profiler. The effective area of the device was measured to be 0.1 cm². Current density–voltage (J – V) characteristics of the PSCs were recorded using Keithley 2420 source measurement unit under the illumination of AM 1.5 G (100 mW cm⁻², Newport solar simulator). Light intensity was calibrated with a standard silicon solar cell. The incident photon-to-electron conversion efficiency (IPCE) of solar cells were analyzed using a certified Newport IPCE measurement system.

Hole and electron mobility were measured using the space-charge-limited-current (SCLC) model [36], using device configuration of ITO/PEDOT:PSS/polymer: PC₇₁BM (1:1.5)/Au or ITO/ZnO/polymer: PC₇₁BM (1:1.5)/Ca/Al by taking current-voltage in the range of 0–5 V and fitting the results to a space charge limited form for hole-only or electron-only device. In the presence of carrier traps in the active layer, a trap-filled-limit (TFL) region exists between the ohmic and trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized by using the Mott-Gurney square law, where ϵ is the static dielectric constant of the medium and μ is the carrier mobility, V is the voltage drop across the device, and L is the thickness of active layer.

$$J = \frac{9\epsilon\mu V^2}{8L^3}$$

3. Results and discussion

3.1. Physical properties

P-*R* were synthesized through Stille coupling polymerization of BDT and DTBT monomers according to the literature method [37], the polymer structures are shown in Fig. 1a, and the detailed synthetic routes of the monomers and polymers are shown in Scheme S1. The cyclic alkyl chains on the DTBT acceptors have little effect on the solubility of the polymers relative to linear alkyl chains, all the P-*R* are readily soluble in common organic solvents such as chloroform and 1,2-dichlorobenzene (*o*-DCB) at room temperature, enabling facile solution processing of PSC devices. P-*n*5, P-*n*7, P-*c*5 and P-*c*7 have relatively high number-average molecular weight ($M_n > 20$ kg mol⁻¹),

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