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Short-time synthesis of poly[4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole-*alt*-9,9-dioctylfluorene], its photophysical, electrochemical and photovoltaic properties

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ABSTRACT

Short-time synthesis of new low-bandgap copolymer, CEHTF8, consisting of 4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole and 9,9-dioctylfluorene by Suzuki coupling reaction in high-boiling solvents, such as chlorobenzene, dichlorobenzene and xylene is reported. Such synthesis yields high molecular copolymers in short reaction times of about 30 min; compared with these, several days are required using tetrahydrofuran (THF). It is proved that chlorinated solvents do not interfere with the reaction procedure and the final copolymers have the same structure and quality as those prepared in xylene or THF. High-molecular CEHTF8 copolymers of various molecular weights (MW) up to weight-average of MW 220 000 with low polydispersity index *PDI* 1.4–1.5 are synthesized. Their photophysical and electrochemical properties are reported. Photovoltaic devices with bulk heterojunction made of blends of copolymers possessing various MW and fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) are prepared and characterized.

1. Introduction

Low-bandgap donor–acceptor copolymers belonging to the third generation of semiconducting polymers are of interest due to the potential application in optoelectronics, namely in photovoltaics [1–10]. They are prepared by copolymerization of electron-donor (D) and electron-acceptor (A) monomers the choice of which enables fine tuning of the bandgap due to the intrachain charge transfer (ICT) from the donor to the acceptor. Various electron-acceptor building blocks were used to prepare such D–A copolymers [6–14]. In addition to thiadiazole nucleus widely used in benzothiadiazole or benzothiadiazole-based forms, the thienothiadiazole unit is also interesting for electron-acceptor blocks for D–A copolymer syntheses [15–21].

Recently, we used 4,6-di(thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole (T) and its derivatives with linear alkyl chains (hexyls or dodecyls) or branched 2-ehylhexyls attached to the thiophene rings as an interesting acceptor building blocks for the synthesis of low-bandgap D–A copolymers. At first we synthesized a soluble low-bandgap D–A copolymer, CTF, consisting of T and 9,9-bis(2-ethylhexyl)fluorene with a lower molecular weight (MW); weight-average M_w of ~5000 [16]. Further we synthesized and used new comonomers based on T unit with various alkyl chains attached to the thiophene rings for D–A copolymer syntheses to obtain copolymers with higher MW possessing better solubility. The copolymers CDTF and CEHTF consisting of 9,9-bis(2-ethylhexyl)fluorene and 3′,3′-dialkyl T derivatives, 4,6-bis(3′-dodecylthien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole (DT) and 4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole (EHT), respectively, were prepared with $M_w = 73\,700$ with a polydispersity index $PDI = 2.54$ for CDTF, and $M_w = 95\,000$ with $PDI = 2.99$ for CEHTF [18,19]. All these copolymers were synthesized by Suzuki coupling reaction of corresponding comonomers in tetrahydrofuran (THF). In some syntheses performed in THF, the copolymer started to precipitate during reaction procedure (typically 12–48 h). Such precipitation may lead to undesirable effects, such as broadening of molar mass distribution. Also long polymerization time in THF represents a problem, since the Pd catalyst deactivates in the course of time, forming metallic palladium [22]. The high-boiling solvent chlorobenzene (CB) or dichlorobenzene (DCB) as the best solvents for many non-polar conjugated polymers are widely used for the fabrication of optoelectronic devices such as photovoltaic cells or organic light emitting diodes. Therefore we decided to investigate if

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CB and DCB can be used as solvents in the Suzuki cross-coupling copolymerization. According to our best knowledge we did not find any information about Suzuki cross-coupling polymerization in CB or DCB in the literature. There was reported that chlorinated aromatics (e.g. 1-alkoxy-3,5-dichlorobenzene) can be even employed as substrate for Suzuki coupling reactions [23,24]. Using Pd catalysts with special ligands was necessary in this case.

In this paper we report on short-time syntheses of a new low-bandgap copolymer, CEHTF8, consisting of 4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole (EHT) and 9,9-dioctylfluorene by Suzuki coupling reaction using various high-boiling solvents including chlorinated ones. New CEHTF8 copolymers of various MW were synthesized. Their photophysical and electrochemical properties were studied to find if there is an influence of MW on the properties. The copolymers were also tested in photovoltaic devices with active layer made of polymer blend with fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester ([60]PCBM).

2. Experimental

2.1. Materials

The 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (OFE), catalyst tetrakis(triphenylphosphine)palladium(0) [99.99%, $Pd(PPh_3)_4$], chlorobenzene (CB, 99%, ReagentPlus), trioctylmethylammonium chloride (Aliquat 336) and other common chemicals were purchased from Sigma–Aldrich. The 1,2-dichlorobenzene (DCB, 99%, extra purity grade) was purchased from Acros and xylene (mixture of isomers, multisolvent grade XI0059) was supplied by Scharlau. The EHT and its brominated derivative 4,6-bis(5′-bromo-3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole (EHTBr) were prepared via a multistep synthesis starting from 2,5-dibromo-3,4-dinitrothiophene and 3-(2-ethylhexyl)-2-(tributylstannyl)thiophene as described in our previous paper [19].

2.2. Methods

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured ($CDCl_3$) with an upgraded Bruker Avance DPX-300 spectrometer at 300.13 MHz and 75.45 MHz, respectively. The hexamethyldisiloxane was used as an internal standard. Fourier transform infrared (FTIR) spectra were measured on a Perkin-Elmer Paragon 1000 PC FTIR spectrometer by means of diamond attenuated total reflection (ATR). The size-exclusion chromatography (SEC) measurements were performed using Pump Deltachrom (Watrex Comp.), autosampler Midas (Spark; with two columns PL gel MIXED-C LS, particle size 5 μm), evaporative light scattering detector PL-ELS-1000 (Polymer Laboratories), and the DCB as a mobile phase. Polystyrene standards were used for calibration. Thermogravimetric analysis (TGA) was performed in air or nitrogen flow (50 ml min^{-1}) at a heating rate of 10 K min^{-1}, using Perkin-Elmer TGA 7 Thermogravimetric Analyzer, operated with Pyris 1 software.

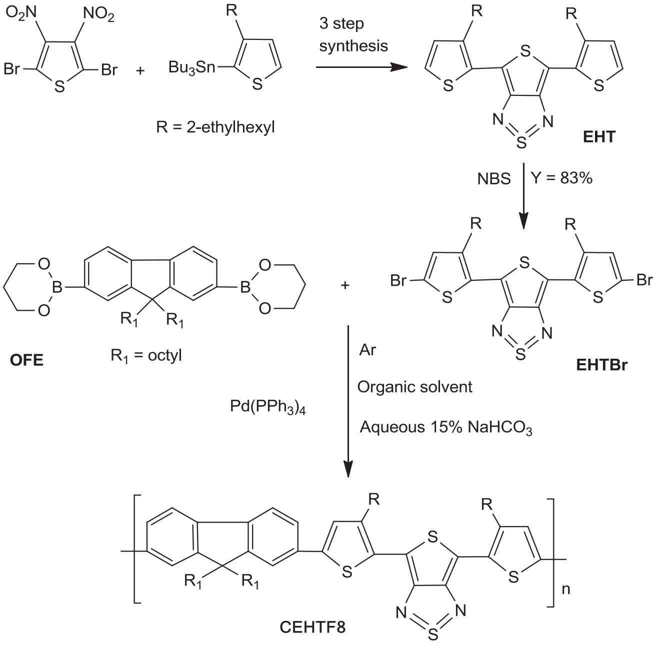
2.3. General procedure of copolymer syntheses

Comonomers EHTBr (0.3719 g, 0.54 mmol) and OFE (0.3015 g, 0.54 mmol) were dissolved in 7.0 mL of appropriate solvent (Table 1) in a three-necked reaction vessel equipped with magnetic stirrer, condenser and argon inlet. Aqueous 15 wt.-% $NaHCO_3$ (10 mL) was added and the mixture was flushed with argon for 15 min. The catalyst $Pd(PPh_3)_4$ (12.5 mg, 1 mol-% per both monomers) and Aliquat 336 (40 mg) were added. Reaction apparatus was degassed repeating vacuum/argon cycles (5×), and the reaction mixture was heated at 131 °C under argon. After cooling, the reaction mixture was poured into an excess of methanol. The precipitated polymer was filtered off, washed with water and methanol, and dried. The raw material was extracted (Soxhlet apparatus) with hexane for 15 min, and the soluble fraction was obtained by extraction with chloroform (8 h). The $CHCl_3$ solution was reduced and precipitated into methanol. Finally, the copolymer was re-precipitated from chloroform into methanol, and dried *in vacuo* to a constant weight. The copolymer poly[4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole-*alt*-9,9-dioctylfluorene] (CEHTF8, Scheme 1, Table 1) was received as a dark green powder with the yields of 75, 96, 72, 80, 75, 42, 54, and 72% for copolymers CEHTF8-c, CEHTF8-d, CEHTF8-d_1, CEHTF8-d_2, CEHTF8-x, CEHTF8-t_1, CEHTF8-t_2, CEHTF8-t_3, respectively. The abbreviation -c, -d, -x and -t denotes the solvent CB, DCB, xylene and THF, respectively. All copolymers had the same ^1H, ^{13}C NMR, and FTIR spectra. δ_H (300.13 MHz, $CDCl_3$, 330 K, Me_6Si_2O): 7.68 (4H, br s, arom. H), 7.61 (2H, br s, arom. H), 7.27 (2H, br s, arom. H), 2.98 (4H, br s, 2 × thiophene-CH_2), 2.07 (4H, br s, 2 × fluorene-CH_2), 1.85

Table 1
Characteristic data of copolymers prepared by Suzuki coupling in various solvents (M_w weight-average of molecular weight, *PDI* polydispersity index, P_n polymerization degree).

Exp	Copolymer	Solvent/time(h)	M_w[b]	*PDI*	P_n	Yield (%)
1	CEHTF8-c	CB/0.5	222 330	1.44	242	75
2	CEHTF8-d	DCB/0.5	142 710	1.47	155	96
3[a]	CEHTF8-d_1	DCB/0.5	63 980	1.45	70	72
4[a]	CEHTF8-d_2	DCB/0.5	64 480	1.45	70	80
5	CEHTF8-x	Xylene/0.5	97 790	1.45	106	75
6–1	CEHTF8-t_1	THF/24	46 780	1.55	51	42
6–2	CEHTF8-t_2	THF/48	51 840	1.57	56	54
6–3	CEHTF8-t_3	THF/72	60 270	1.61	66	72

[a] The syntheses performed with the comonomer stock solutions.
[b] Measured by SEC in DCB as the mobile phase at 60 °C.



Scheme 1. Synthesis of poly[4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole-*alt*-9,9-dioctylfluorene] (CEHTF8) and 4-step synthesis [19] of EHTBr [1. $(Ph_3P)_2PdCl_2$, CuI, Y = 74%; 2. Zn, HCOOH, Y = 90%; 3. Ph–N=SO, Y = 48%; 4. NBS, Y = 83%].

(2H, br s, 2 × CH), 1.44 (8H, br s, 4 × CH_2), 1.30 (8H, br s, 4 × CH_2), 1.10 (24H, br s, 12 × CH_2), 0.93 (12H, m, 4 × CH_3), 0.87 (6H, m, 2 × CH_3). δ_C (75.45 MHz, $CDCl_3$, 330 K, Me_6Si_2O): 157.23 (2C), 152.22 (2C), 145.21 (2C), 140.94 (2C), 140.84 (2C), 133.28 (2C), 129.26 (2C), 126.97 (2C), 124.97 (2C), 120.31 (2C), 120.22 (2C), 113.19 (2C), all aromatic, 55.76 (1C, fluorene central ring), 40.56 (2C), 40.22 (2C), 35.24 (2C), 33.05 (2C), 31.92 (2C), 30.17 (2C), 29.30 (4C), 29.06 (2C), 26.35 (2C), 24.09 (2C), 23.23 (2C), 22.69 (2C), 14.14 (2C), 14.05 (2C), 11.00 (2C), all aliphatic. FTIR (ATR): ν = 2954, 2922, 2852, 1606, 1540, 1486, 1464, 1420, 1376, 1264, 1146, 1134, 876, 834, 814, 722, 592 cm^{-1}.

Elemental analysis. Found: C, 73.70; H, 8.30; N, 2.9 (CEHTF8-d_1). C, 74.43; H, 8.64; N, 3.00 (CEHTF8-d_2). C, 74.47; H, 8.61; N, 3.03 (CEHTF8-x). Calc. for $C_{57}H_{76}N_2S_4$ structural unit: C, 74.62; H, 8.35; N, 3.05%.

2.4. Device preparation and measurements

Thin films of copolymers and their blends with [60]PCBM were prepared by spin coating from DCB solutions. Thin films for optical studies were spin-coated onto fused silica substrates or coated on Pt wire electrode by dipping for electrochemical measurements. For polymer photovoltaic (PV) devices, polymer layers were prepared on indium–tin oxide (ITO) substrates covered with a thin layer of poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDOT:PSS). All polymer films were dried in vacuum (10^{-3} Pa) at 353 K for 2 h. The ITO glass substrates were purchased from Merck (Germany) and PEDOT:PSS (Baytron PH500) from HC Starck AG (Germany). The 50-nm thick PEDOT:PSS layers were prepared by spin coating and dried in air at 396 K for 15 min. The calcium (20 nm), and subsequently aluminium electrodes (60–80 nm) were vacuum-evaporated on the top of polymer films to form PV devices. Typical active areas of the PV devices were about 12 mm^2. Layer thickness (d) was measured using a KLA-Tencor P-10 profilometer.

Ultraviolet–visible (UV–VIS) spectra were measured on a Perkin-Elmer Lambda 35 UV–VIS spectrometer. Cyclic voltammetry (CV) was performed with a PA4 polarographic analyser (Laboratory Instruments, Prague, CZ) with a three-electrode cell. Platinum (Pt) wire electrodes were used as both working and counter electrodes, and a non-aqueous Ag/Ag^+ electrode (Ag in 0.1 M $AgNO_3$ solution) was used as the reference electrode. CV measurements were made in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) in anhydrous acetonitrile in nitrogen atmosphere. Typical scan rates were 20, 50 and 100 mV s^{-1}. Current–voltage characteristics of PV devices were measured using the Keithley 237 source measure unit. A 300 W xenon lamp (Oriel) with a 1.5 AM filter Daylight-Q X-7460 (Labimex CZ) was used for illumination. The light intensity was set using a calibrated solar reference cell SRC-1000-TC-QZ (VLSI Standards, Inc.) and checked by radiometer Rs 3960 (Laser Precision Corp.). All thin film preparations and the device fabrication were conducted in a glove box under a nitrogen atmosphere.

3. Results and discussion

3.1. Synthesis

The synthesis of comonomer EHTBr was performed according to the procedure described in our previous paper [19], and both the EHTBr and copolymer CEHTF8 syntheses are shown in Scheme 1. The results of the copolymerization by Suzuki coupling reaction in chlorinated and non-chlorinated solvents are shown in Table 1. Copolymers CEHTF8-c, CEHTF8-d and CEHTF8-x were prepared by Suzuki copolymerization (at 131 °C for 30 min) in CB, DCB and xylene, respectively. The amount of Pd catalyst (1 mol-% per both comonomers), phase transfer agent (Aliquat 336), the ratio between reactants, solvent, and base solution was kept constant. The copolymers CEHTF8-t_1, CEHTF8-t_2 and CEHTF8-t_3 were prepared by Suzuki coupling in: THF at 66 °C with reaction times of 24, 48 and 72 h, respectively; 1 mol-% of Pd catalyst per monomers; and with the same ratio between reactants, solvent and base solution as for the experiments using the high temperature boiling solvents mentioned above. All CEHTF8 copolymers were soluble in common organic solvents such as THF, toluene, xylene, chloroform, CB and DCB.

Rapid polycondensation with formation of copolymer proceeded in all high-boiling solvents (CB, DCB and xylene). It could be easily followed because of colour change from blue (colour of terthiophene comonomer) to green (colour of longer conjugated structures). After 30 min, the reaction was stopped by pouring resulting mixture into MeOH and the dark green precipitated material was subjected to usual workup. The copolymers were characterized by SEC, NMR, IR and elemental analysis data.

Using high-boiling solvents CB, DCB and xylene, copolymers with high molar weights M_w = 60 000–222 000, monomodal and narrow distributions of molar masses PDI = 1.4–1.5 were prepared in very short time with yields in the range 75–96 %. SEC curves are displayed in Fig. 1 and the molar masses are given in Table 1. The molar weights M_w = 222 000 of CEHTF8-c and M_w = 143 000 of CEHTF8-d are the highest values we succeeded using CB and DCB, respectively. The longest copolymers, CEHTF8-c and CEHTF8-d consist of 242 and 155 repeating units, respectively. It must be noted that molar weights of polymers prepared by Suzuki polycondensation are strongly dependent on a molar ratio between comonomers. An exact mole ratio of 1:1 is needed in order to achieve high molar masses. It was reported that a mere 0.5 mol-% excess of one monomer leads to more than ten-fold decrease of an average degree of polymerization [25]. At the same time, a perfect equimolar ratio of comonomers is difficult to ensure. Therefore, Exps. 3 and 4 were performed with stock comonomer solutions to check the reproducibility of the short time synthesis. Exps. 3 and 4 showed good reproducibility of the copolymer synthesis in DCB as an example. The same molar weights were obtained as can be documented by the comparison of SEC curves of the copolymers CEHTF8-d_1 and CEHTF8-d_2 (identical curves in Fig. 1).

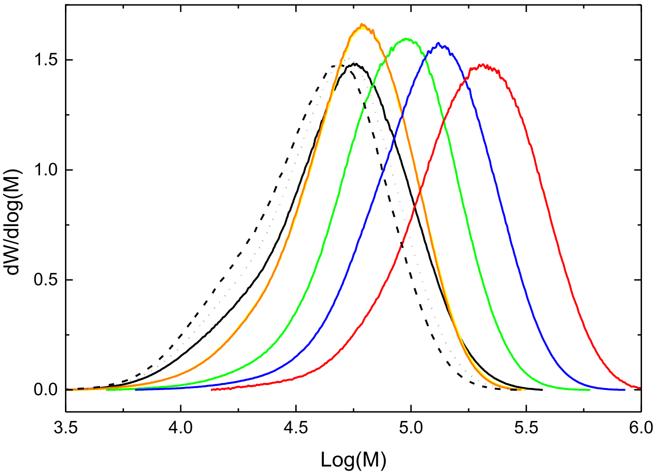


Fig. 1. SEC curves of the copolymer CEHTF8 samples prepared in various solvents: in CB CEHTF8-c (red), in DCB CEHTF8-d (blue) CEHTF8-d_1 (orange), CEHTF8-d_2 (yellow-identical with orange), CEHTF8-x (green), in THF CEHTF8-t (black), for various reaction times: 24 h (dashed), 48 h (dotted) and 72 h (solid), measured with DCB as the mobile phase at 60 °C. Polystyrene standards were used for calibration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Exps. 3–6, a comparison of the synthesis in DCB with the non-chlorinated solvents, xylene and THF, is shown. Using a mixture of xylenes as a solvent, copolymer CEHTF8-x with a slightly higher molar mass was obtained. In all these cases, similar monomodal polymers were formed (Fig. 1), although xylene is a chlorine-free solvent and DCB has two chlorine atoms on the benzene ring.

As can be seen in Figs. 2 and 3, ^{1}H and ^{13}C NMR spectra of polymers CEHTF8-d$_1$ and CEHTF8-x are identical and consistent with an expected chemical structure of a high purity. This can be taken as proof that chlorine atoms of DCB (or CB) do not interfere in Suzuki coupling copolymerization at high temperature (131 °C), at least at short reaction time (30 min). In other words, we did not find any differences in NMR spectra of copolymers prepared using chlorinated and non-chlorinated solvents.

Copolymer CEHTF8 was also prepared in THF for comparison; see Exp. 6 (CEHTF8-t$_1$, CEHTF8-t$_2$ and CEHTF8-t$_3$) in Table 1. In this solvent, polymeric material started to precipitate after ca. 8 h and it formed a swollen lump after ca. 10 h. With an increasing reaction time a broadening of molar mass distribution was observed (Fig. 1).

3.2. Thermal properties

New CEHTF8 copolymer exhibited good thermal stability even in the air as was proved by TGA. An example of typical TGA curves measured in nitrogen and in air at a heating rate of 10 K min^{-1} is shown in Fig. 4. Weight loss of about 1% was observed at high temperatures, at 352 and 312 °C in nitrogen and air, respectively. The 3% weight loss temperatures were 419 and 358 °C, the 10% weight loss temperatures detected at 455 and 425 °C in nitrogen and air, respectively. It indicates a very good thermal and/or oxidation stability of the new copolymer, better than CEHTF with all ethyl hexyls. The decrease is a result of an additional decomposition of alkyl chains on thiophene rings and fluorene. The residual weight percentage in nitrogen at 780 °C was 43%, which corresponds to the high aromatic content.

3.3. Photophysical properties

Photophysical properties of copolymers were studied in solutions and thin films. An example of absorption spectra of the copolymer CEHTF8-c measured in THF and DCB solutions ($c = 10^{-5}$ M) is shown in Fig. 5. Three maxima are present in the absorption spectra. The shortest-wavelength maximum is located at 316 nm at the same position as in the spectrum of the EHT comonomer unit [19]. The absorption band with a maximum at 454 nm in DCB solution corresponds to the lowest π–π* transition of the conjugated backbone, whereas the lowest-energy absorption

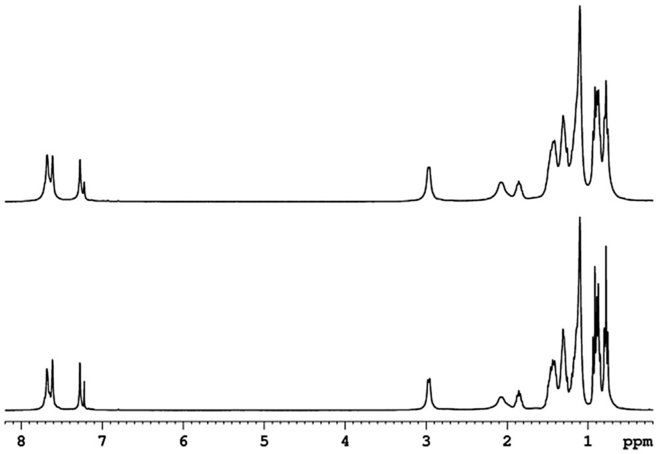


Fig. 2. ^{1}H NMR spectra of copolymer CEHTF8-d$_1$ prepared in DCB (top) and CEHTF8-x prepared in xylenes (bottom), measured in CDCl$_3$.

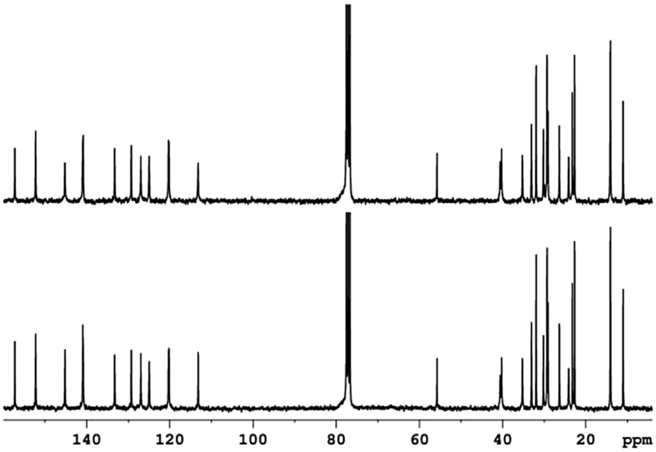


Fig. 3. ^{13}C NMR spectra of copolymer CEHTF8-d$_1$ prepared in DCB (top) and CEHTF8-x prepared in xylenes (bottom), measured in CDCl$_3$.

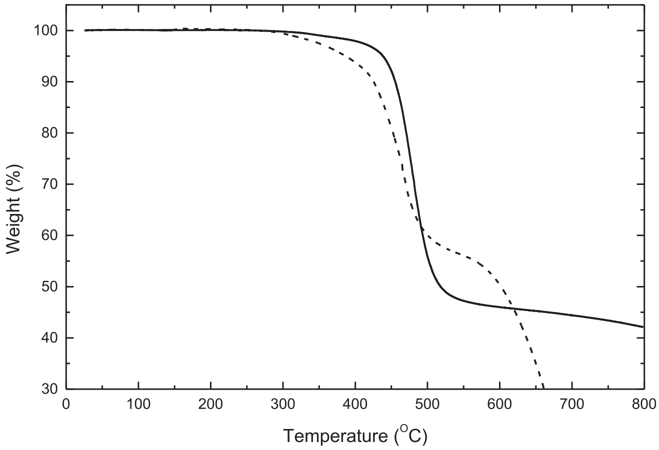


Fig. 4. TGA curves of CEHTF8-c measured at scan rate of 10 K min^{-1} in nitrogen (solid) and in air (dashed).

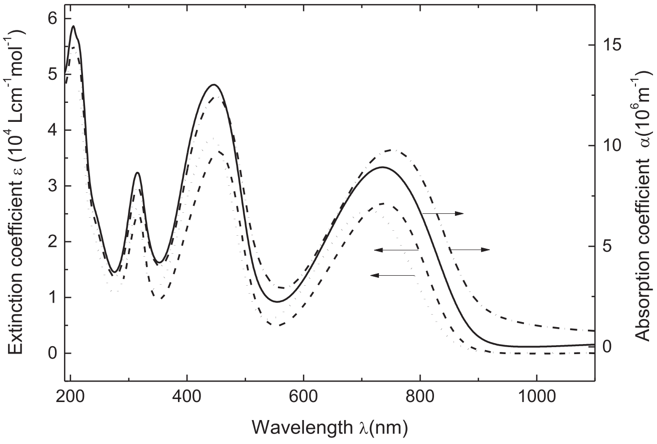


Fig. 5. UV–VIS absorption spectra of CEHTF8-c measured in DCB (dashed) and THF (dotted) solution and thin films with various thicknesses: 60 nm (dash and dot) and 224 nm (solid).

band with a maximum 736–738 nm to the ICT transition between the thiophene donor and thienothiadiazole acceptor moiety [18,19,26].

The copolymer exhibits solvatochromic and thermochromic behaviour. Blue-shifts of both long-wavelength maxima were observed in absorption measured in THF or toluene solution compared with absorption in DCB, which can be explained by different conformational modifications in various solvents and also with temperature. In THF solution spectra the maxima were at 444 and 712 nm and at 446 and 716 nm for toluene solution. In solutions, optical properties of the copolymers under study, i.e. in the range of $M_w = 46\,000–222\,330$, are without any differences. Thin film spectra differ for different thicknesses (see Fig. 5). Thin film spectra were similar to those measured in DCB solution: slight red-shifts of long wavelength maxima were observed. In spectra of thin films with thicknesses 40–60 nm 10–15 nm red-shifts in position of the longest wavelength maximum (ICT) were observed, which could be also influenced by reflection losses [27]. The characteristic data are summarized in Table 2, where the data for the copolymers CDTF and CEHTF with branched 2-ethylhexyls on C-9 of fluorene unit are also given for comparison.

The absorption maxima of CEHTF8 are slightly red-shifted compared with absorption spectra of CEHTF (i.e. copolymer with the branched 2-ethylhexyl chains attached on both comonomer units) contrary to the copolymer CDTF with dodecyl linear side chains on thiophenes, where significant red-shifts of both long-wavelength maxima in thin film absorption spectra were observed. This supports that the strong intermolecular interactions in solid state are due to the close S–N intermolecular contacts which are more pronounced in copolymers with linear side chains on thiophenes, whereas the nature of side chains on fluorene units has only slight influence on thin film absorption changes.

3.4. Electrochemical properties

CV was used to obtain the information on electronic structure of the copolymers. New copolymer exhibited reversibility in both oxidation and reduction. Typical CV curves are shown in Fig. 6. They show two clear p- and n-doping peaks followed by corresponding undoping peaks. The ionization potential (HOMO level), E_{IP}, and electron affinity (LUMO level), E_A, were estimated from onset potentials, E_{onset}, of the first oxidation and reduction peaks on the basis of the reference energy level of ferrocene (4.8 eV below the vacuum level) using the equation $E_{IP}\ (E_A) = |-(E_{onset} - E_{ferr}) - 4.8|$ eV, where E_{ferr} is the value for ferrocene vs. the Ag/Ag$^+$ electrode. Their values are evaluated from CV curves measured at the scan rate of 50 mV s^{-1}. All copolymers, despite various molecular weights, possess similar ionization potentials at about 5.04 eV and electron affinities at about 3.53 eV. The electrochemical bandgap values $E_g^{elc} = 1.5$ eV were evaluated. The E_g^{elc} values are in good agreement with the optical bandgap values, E_g^{opt}, evaluated from the absorption edge of thin film spectra as 1.42–1.45 eV. These values are similar to those evaluated for the other copolymers with 2-ethylhexyls on fluorene unit [18,19]. The electrochromic behaviour was also observed.

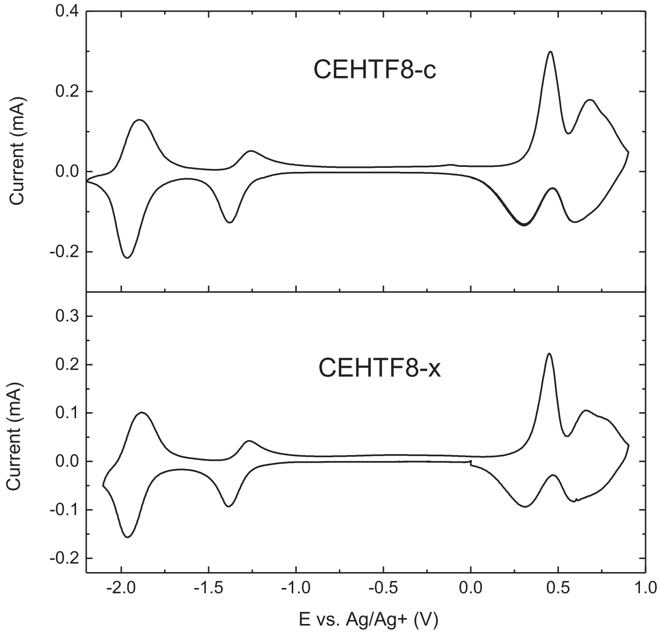


Fig. 6. Representative cyclic voltammograms of CEHTF8-c and CEHTF8-x thin films coated on Pt wire recorded at the scan rate of 50 mV s^{-1}.

3.5. Photovoltaic properties

New low bandgap copolymer CEHTF8 was tested in photovoltaic devices with bulk heterojunction. Active layers were made of blends of copolymers with various MW and fullerene derivative [60]PCBM in weight ratio 1:2; ITO/PEDOT:PSS and Ca/Al were used as hole- and electron-collecting electrodes. Absorption spectra of the active blend layers shown in Fig. 7 exhibited an increase in UV absorption in the blend layers, observed due to the [60]PCBM content and a decrease in absorption in visible region compared with the absorption of thin films made of neat polymer. The long-wavelength absorption maxima of blend layer located at 435–436 nm and 750–755 nm are located similarly compared with maxima of the neat CEHTF8 thin film absorption.

The photoconversion efficiency (*PCE*) of the devices with the active layer made of CEHTF8+[60]PCBM (1:2 wt.) blends with various molecular weights of CEHTF8 was similar, in the range 1.3–1.9%. The characteristic data for several samples are shown in Table 3. Typical open circuit voltages, V_{oc}, were about 0.6–0.7 V, short-circuit currents, I_{sc}, were 7–10 mA cm^{-2}, and fill factor, *FF*, was 31–35%. No significant dependence on the CEHTF8 molecular weight was found. It should be noted that only slightly higher V_{oc} values were observed in the blends made of the longest molecular weight copolymer CEHTF8-c. On the other hand slightly higher I_{sc} values were observed in PV devices with active blend layer made of

Table 2
Photophysical properties of copolymers measured in diluted DCB solutions and thin films (λ_{max} absorption maximum, *d* thin film thickness).

Copolymer	DCB solution	Thin film	
	λ_{max} (nm)	λ_{max} (nm)	*d* (nm)
CEHTF8-c	316, 454, 738	316, 451, 753	50
		316, 451, 751	66
		315, 446, 736	224
CEHTF8-d	316, 454, 737	315, 447, 747	86
CEHTF8-d$_1$	316, 454, 737	316, 455, 754	50
CEHTF8-d$_2$	316, 454, 737	316, 453, 754	40
CEHTF8-x	316, 453, 737	316, 449, 751	60
CEHTF8-t$_1$	316, 454, 736		
CEHTF8-t$_2$	316, 454, 736		
CEHTF8-t$_3$	316, 454, 738	316, 451, 750	57
CEHTF[a]	316, 450, 734	315, 441, 734	104
		315, 442, 727	168
CDTF[b]	316, 456, 747	315, 473, 785	44
		314, 465, 771	97
		314, 463, 759	173

[a] $M_w = 95\,000$ and *PDI* = 2.99.
[b] $M_w = 73\,700$ and *PDI* = 2.54.

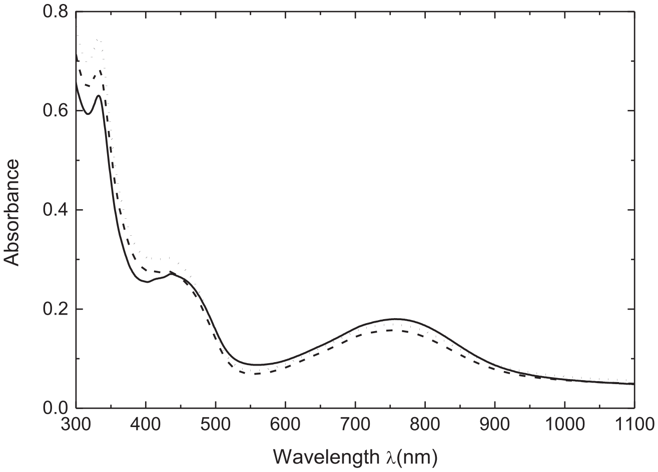


Fig. 7. UV–VIS absorption spectra of active blend layers: CEHTF8-c+[60]PCBM (1:2 wt.) (solid), CEHTF8-d_1+[60]PCBM (1:2 wt.) (dashed) and CEHTF8-x+[60]PCBM (1:2 wt.) (dotted).

Table 3
Characteristic data of PV devices with polymer active layer made of CEHTF8 and [60] PCBM in weight ratio 1:2, with ITO/PEDOT:PSS and Ca/Al electrodes (U_{oc} open circuit voltage, J_{sc} short-circuit current, *FF* fill factor, *PCE* photoconversion efficiency).

Polymer active layer Polymer+[60]PCBM (1:2 wt.)	U_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE*
CEHTF8-c	0.65	8.15	32	1.70
M_w = 222 330	0.68	7.32	34	1.71
	0.66	7.28	33	1.58
CEHTF8-d_1	0.59	8.3	34	1.69
M_w = 63 980	0.57	10.06	34	1.96
	0.56	8.63	35	1.71
CEHTF8-x	0.60	7.52	31	1.40
M_w = 97 790	0.59	8.59	32	1.60
	0.60	7.08	31	1.34

CEHTF8-d with a shorter molecular weight. Examples of dark and photovoltaic current–voltage characteristics for some selected PV devices with active layers made of CEHTF8 with various molecular weights (CEHTF8-c, CEHTF8-d_1, CEHTF8-x) are shown in Fig. 8.

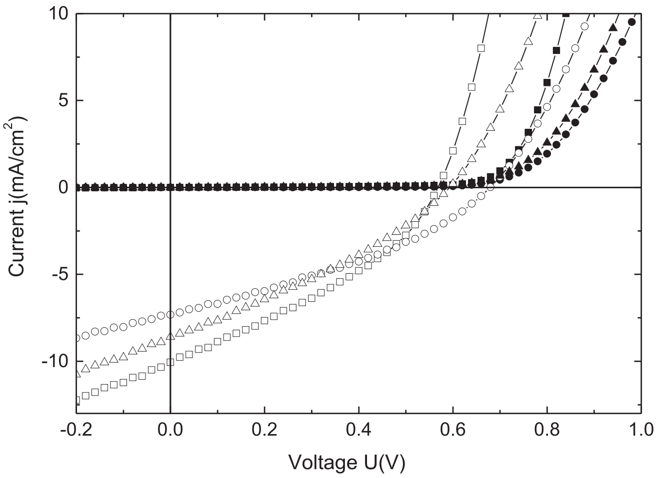


Fig. 8. Current–voltage characteristics of PV ITO/PEDOT:PSS/blend layer/Ca/Al devices measured in dark (solid symbols) and under illumination 100 mW/cm^2 (open symbols). Active layer: CEHTF8-c+[60]PCBM (1:2 wt., d = 145 nm) (circles), CEHTF8-d_1+[60]PCBM (1:2 wt., d = 105 nm) (squares) and CEHTF8-x+[60]PCBM (1:2 wt., d = 110 nm) (triangles).

The *PCE* of CEHTF8+[60]PCBM PV devices is higher than *PCE* of CEHTF+[60]PCBM PV devices with active layer made of copolymer with 2-ethylhexyls branched side chains on both comonomer units, where both V_{oc} and I_{sc} were lower. On the other hand, the *PCE* is lower than *PCE* measured on PV devices made of blend CDTF+[60] PCBM (the same weight ratio 1:2), i.e. using copolymer with linear side chains on thiophenes, which exhibited the *PCE* value 3–5% depending on the quality of blend active layer. The lower *PCE* is given mainly by lower fill factors and lower short-circuit currents, whereas V_{oc} values were slightly higher for CEHTF8+[60]PCBM PV devices. It should be noted that the materials were tested in PV devices without any optimization. As we recently showed, fullerene aggregation in blend layer occurs which can negatively influence the device performance [28]. Further PV device improvement can be reached by more appropriate device architecture or mutual component ratio variation [29].

4. Conclusions

New D–A alternating copolymer, poly[4,6-bis(3′-(2-ethylhexyl) thien-2′-yl)thieno[3,4-*c*][1,2,5]thiadiazole-*alt*-9,9-dioctylfluorene], consisting of 4,6-bis(3′-(2-ethylhexyl)thien-2′-yl)thieno[3,4-*c*] [1,2,5]thiadiazole and 9,9-dioctylfluorene was synthesized by Suzuki copolymerization reaction in various high-boiling solvents. It was shown that the polymer synthesis is accomplished in a very short time (about 30 min) compared with the synthesis in THF with a reaction time of several days (typically 72 h). CEHTF8 copolymers with M_w = 60 000–220 000 (*PDI* 1.4–1.5) were prepared. It was proved that chlorinated solvents did not interfere with the reaction procedure and the final copolymers had the same structure and quality as those prepared in xylene or THF. All copolymers, despite various molecular weights, possess similar ionization potentials at about 5.04 eV and electron affinities at about 3.53 eV. The electrochemical bandgap values, E_g^{elc} = 1.5 eV, are in good agreement with the optical bandgap values, E_g^{opt}, evaluated from the absorption edge of thin film spectra as 1.42–1.45 eV.

Photovoltaic devices with bulk heterojunction made of blends of copolymers possessing various MW and fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) were prepared and characterized. The *PCE* of the devices with the active layer made of CEHTF8+[60]PCBM (1:2 wt.) blends with various molecular weights of CEHTF8 were similar, in the range 1.3–1.9%.

New CEHTF8 copolymer study served as an example for the short-time synthesis which could be also useful for the syntheses of other conjugated copolymers. Recently, we also used various donor units in copolymerization with the 3′,3′-dialkyl T derivatives to extend the series of D-A copolymers with T unit. Preliminary results are reported in our papers [30,31].

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