Poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene vinylene): Synthesis, Optical and Photovoltaic Properties

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ABSTRACT: A new benzodithiophene (BDT)-based polymer, poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene vinylene) (PBDTV), was synthesized by Pd-catalyzed Stille-coupling method. The polymer is soluble in common organic solvents and possesses high thermal stability. PBDTV film shows a broad absorption band covering from 350 nm to 618 nm, strong photoluminescence peaked at 545 nm and high hole mobility of 4.84×10^{-3} cm²/Vs. Photovoltaic properties of PBDTV were studied by fabricating the polymer solar cells based on PBDTV as donor and PC₇₀BM as acceptor. With the

weight ratio of PBDTV: PC₇₀BM of 1:4 and the active layer thickness of 65 nm, the power conversion efficiency of the device reached 2.63% with $V_{\rm oc} = 0.71$ V, $I_{\rm sc} = 6.46$ mA/cm², and FF = 0.57 under the illumination of AM1.5, 100 mW/cm². © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1822–1829, 2010

KEYWORDS: conjugated polymers; PC₇₀BM; poly(benzodithiophene vinylene); polymer solar cells; synthesis; UV-Vis spectroscopy

INTRODUCTION Conjugated polymer photovoltaic materials and polymer solar cells (PSCs) have attracted great attention in recent years because of the promising application of PSCs in solar energy conversion.¹⁻⁴ PSCs are composed of a blend film of conjugated polymer donor and soluble fullerene derivative (typically PCBM) acceptor sandwiched between an ITO positive electrode and a low workfunction metal negative electrode. At present, the power conversion efficiency (PCE) of the PSCs is still low in comparison with the Sibased solar cells. To improve the efficiency, most of the efforts have been devoted to the design and synthesis of new conjugated polymers with broad and strong absorption band in visible region, higher hole mobility and suitable LUMO and HOMO energy levels.⁵⁻¹⁹ For example, polythiophene derivatives with conjugated side chains were synthesized for broadening their absorption band and improving the hole mobility of the polymers.⁵ Crosslinked polythiophene derivatives with conjugated bridges were prepared for enhancing their hole mobility.6 Various low bandgap D-A copolymers were designed and synthesized for red-shifting their absorption and dropping their HOMO energy levels.⁷⁻¹⁵ Poly(thienylenevinylene) derivatives also draw attention for their simple molecular structure, low bandgap characteristic and high hole mobility.¹⁶ Recently, Hou et al. synthesized a new series of conjugated polymers containing benzodithiophene (BDT) unit, and the polymers show broad absorption, low energy bandgap, tunable electronic energy levels and promising photovoltaic properties.¹⁷ By now, the copolymers composed of BDT unit and thieno[3,4-b]thiophene unit show high photovoltaic efficiency of 5–7%.^{18,19} The results indicate that BDT could be a useful unit in constructing new conjugated polymer donors for high performance PSCs.

To combine the advantage of the BDT unit and the simple vinylene unit in the polymer main chain, in this paper, we synthesized a new BDT-containing polymer, poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene vinylene) (PBDTV), as shown in Scheme 1. We used two 2-ethylhexyloxy groups as the substituents on the BDT unit for improving the solubility of the polymer. PBDTV shows good solubility in common organic solvents, high thermal stability with 5% weight loss at the temperature higher than 300 °C, and high hole mobility of about 5×10^{-3} cm²/Vs. The power conversion efficiency (PCE) of the PSC based on PBDTV as donor and PC₇₀BM as acceptor reached 2.63% with $V_{oc} = 0.71$ V, $I_{sc} = 6.46$ mA/cm² and FF = 0.57 under the illumination of AM1.5, 100 mW/cm².

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PBDTV

SCHEME 1 Molecular structure of PBDTV.

EXPERIMENTAL

Materials

Bromine, *n*-Butyllithium (2.5 mol/L in hexane, heptanoyl chloride), NaOH and tetrabutylammonium bromide were obtained from Acros organics. (*E*)-1,2-bis(tributylstannyl) ethane was purchased from Alfa Company. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled before use. Compound **1** was synthesized with the method reported in the literature.¹⁷ The other materials were common commercial level and used as received.

Measurement and Characterization General Methods

All new compounds were characterized by ¹H NMR. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DMX-400 spectrometer. Chemical shifts of ¹H NMR were reported in ppm relative to the singlet of $CDCl_3$ at 7.26 ppm. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. Molecular weight of the polymers was measured by GPC using THF as solvent and polystyrene as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. Polymer thin films were formed by drop-casting 1.0 mm³ of polymer solutions in THF (analytical reagent, 1 mg /mL) onto the working electrode, and then dried in the air. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode.

Fabrication of Photovoltaic Devices

Polymer solar cells were fabricated with ITO glass as a positive electrode, LiF/Al as a negative electrode and the blend film of the polymer/PC₇₀BM between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT: PSS (Baytron AI 4083 from H. C. Starck) which was spin-cast from a PEDOT: PSS aqueous solution on the ITO substrate, and the thickness of the PEDOT: PSS layer is about 45 nm. The photosensitive layer was prepared by spin-coating a blend solution of the polymer and PC70BM with a weight ratio of 1:2, 1:3, or 1:4 in o-dichlorobenzene at different spin speed on the ITO/PEDOT: PSS electrode. Then the LiF/Al cathode was deposited on the polymer layer by vacuum evaporation under 6 imes 10⁻⁶ Pa. The thickness of the photosensitive layer is 45-125 nm (depending on the weight ratio and spin speed), determined by a Dektak 6Msurface profilometer. The effective area of one cell is between 4 mm² and 6 mm² which is calculated from the measured width and length of the crossover area of the ITO and metal electrodes of the device. The current-voltage (I-V) measurement of the devices was recorded using a Keithley 2400 Source Meter under illumination of AM 1.5 with intensity of 100 mW cm⁻² from a solar simulator (Model SS-50A, photo Emission Tech).

Synthesis of the Monomers

4,8-Di(2-ethylhexyloxy)benzo[1,2-b;3,4-b]dithiophene, 2

Compound 1 (8.8 g, 40 mmol), zinc powder (5.46 g, 84 mmol), and 100 mL of water were put into a 250 mL flask; then 24 g of NaOH was added into the mixture. The mixture was well stirred and heated to reflux for 2 h. Then, 3-(bromomethyl)heptane (23 g, 120 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed for 6 h, the reactant was poured into cold water and extracted by diethyl ether for several times. The ether layer was dried over anhydrous MgSO₄. After removing solvent, the crude product was re-adsorbed in silica gel and purified by silica gel chromatography using hexane as eluent. 12.5 g of compound 2 (28 mmol, yield 70%) was obtained as light yellow oil. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.65 (d, 2H), 7.45 (d, 2H), 4.18 (t, 4H), 1.78 (m, 2H), 1.53-1.17 (m, 16H), 0.88 (t, 12H). Elemental analysis: Calculated for C₂₆H₃₈O₂S₂: C, 69.96; H, 8.52. Found: C, 69.56; H, 8.47.

2,6-Dibromo-4,8-di(2-ethylhexyloxy)benzo[1,2-b;3,4b]dithiophene, 3

Compound **2** (8.92 g, 20 mmol) was dissolved into 300 mL of methylene chloride in a 500 mL flask. Bromine (6.4 g, 40 mmol) was dissolved into 60 mL of methylene chloride in a funnel and slowly dropped into the flask under an ice-water bath, and then the reactant was stirred for 12 h at ambient temperature. After removing solvent, the crude product was re-adsorbed in silica gel and purified by silica gel chromatog-raphy using hexane as eluent. 10.87 g of compound **3** (18 mmol, yield 90%) was obtained as a light yellow oil. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.43 (s, 2H), 4.17 (t, 4H), 1.76(m, 2H), 1.54–1.20 (m, 16H), 0.89 (t, 12H). Elemental



SCHEME 2 Synthetic route of the monomer. (i) Zinc powder, NaOH, H₂O, reflux 1 h; then, 2-ethy-1-bromo-hexane, tetrabuty-lammonium bromide, reflux 2 h; (ii) Bromine, methylene, room temperature, 24 h.

analysis: Calculated for $C_{26}H_{36}Br_2O_2S_2$: C, 51.66; H, 5.96. Found: C, 51.55; H, 5.89.

Synthesis of the Polymer PBDTV

The synthesis of PBDTV was carried out using palladium-catalyzed Stille-coupling between monomer **3** and (E)-1,2-bis (tributylstannyl)ethane, as shown in Scheme 3. All starting materials, reagents, and solvents were carefully purified, and all procedures were performed under an air-free environment.

Under the protection of Argon atmosphere, monomer 3 (1 mmol) was dissolved in 10 mL dried toluene, (E)-1, 2-bis (tributylstannyl) ethane (1 mmol) was added to the mixture. The solution was flushed with argon for 10 min, and then 10 mg of Pd $(PPh_3)_4$ were added. After another flushing with argon for 20 min, the reactant was heated to reflux for 10 h. The reaction solution was cooled to room temperature, the reaction mixture was added dropwise to 200 mL methanol, and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The polymer was purified with bio-beads S-1 column chromatography eluted with THF, the solvent was removed in vacuum, and the solid was dried under vacuum for 1 day to get PBDTV. The yield of the polymerization reaction was about 30–50%. GPC: $M_{\rm w}$ = 9.4 kg/mol, $M_{\rm n}$ = 5.1 kg/mol, $M_{\rm w}/M_{\rm n}$ = 1.84. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.60–6.80 (br, 4H), 4.19 (m, 4H), 1.83–1.30 (m, 22H), 1.00 (t, 12H). Elemental analysis for $(C_{28}H_{38}S_2O_2)_n$ Calculated: C, 71.49; H, 8.09; S, 13.62. Found: C, 70.58; H, 7.72; S, 12.76.

RESULTS AND DISCUSSION

Synthesis of the Monomer and Polymer

The synthetic routes of monomer and polymer PBDTV are outlined in Scheme 2 and 3, respectively. PBDTV was prepared by Stille-coupling reaction.^{18–20} Molecular structures of the monomer and the polymer PBDTV were confirmed by ¹H NMR spectra (see Figs. 1 and 2) and elemental analysis. The molecular weight (M_w) of PBDTV is 9.4 kg/mol.

Figure 2 shows the ¹H NMR spectrum of PBDTV. The hydrogen atoms in the benzo[1,2-b:4,5-b']dithiophene ring and carbon-carbon double bond peak at 7.60–6.80 ppm, the hydrogen close to oxygen atoms in alkyl chain of PBDTV peaks at 4.17 ppm. The peak at about 0.1 ppm could be ascribed to the hydrogen atoms in TMS in the solvent used in the NMR measurement. The positions of other hydrogen atoms are shown in Figure 2. PBDTV with the lower M_w is soluble in common organic solvents, such as chloroform, toluene, and THF at room temperature. But the solubility will become poorer when the molecular weight higher than 10 kg/mol.

Thermal Property

Thermal stability of PBDTV was investigated with thermogravimetric analysis (TGA), as shown in Figure 3. PBDTV shows onset decomposition temperature with 5% weight loss at 307 °C. The thermal stability is enough for the application of PBDTV in polymer optoelectronic devices.

Optical Property

Figure 4(a) shows the absorption spectra of PBDTV solution in chloroform and film on quartz plate. There are two absorption peaks, located at 515 nm and 553 nm, respectively, in the visible absorption band of PBDTV solution. The two absorption peaks agree with that reported in the literature for the similar polymer,¹⁷ which should be ascribed to π - π * transition absorption of the polymer main chains. The visible absorption band of PBDTV film is broadened but the two peak positions are almost the same in comparison with that of the PBDTV solution, which indicates that the intermolecular interaction of PBDTV film is weak probably due to



SCHEME 3 Synthetic route of PBDTV. (i) Pd (PPh₃)₄, toluene, Argon, reflux, 10 h.

ARTICLE





the two big alkoxy side chains of the polymer. The absorption edge of the PBDTV film is at about 617 nm, which is corresponding to a bandgap of 2.01 eV. The bandgap of PBDTV is smaller than that (2.13 eV) of the homopolymer PBDT,^{17,21} which implies that the vinylene unit in PBDTV can reduce the bandgap of the polymer for some extent. But it is larger than that (ca. $1.5 \sim 1.6$ eV) of the copolymers of BDT unit and thieno[3,4-b]thiophene unit,^{19b} indicating that the thieno[3,4-b]thiophene unit is very important for reducing the bandgap of the copolymers. In addition, PBDTV solution shows strong photoluminescence in the wavelength range from 550 to 900 nm peaked at about 664 nm, as shown in Figure 4(b).

Electrochemical Property

The electrochemical property is one of the most important properties of conjugated polymers and the electronic energy levels can be estimated from the onset oxidation and onset reduction potentials from the electrochemical measurements.²² Therefore, we studied the electrochemical properties of PBDTV by cyclic voltammetry.

Figure 5 shows the cyclic voltammogram of the polymer film on Pt electrode. It can be seen that there are *p*-doping/ dedoping (oxidation/re-reduction) processes in positive potential range and n-doping/dedoping (reduction/re-oxidation) processes in negative potential range. The HOMO and LUMO energy levels of the polymer were calculated from its onset oxidation potential (φ_{ox}) and its onset reduction potential (φ_{red}) according to the following equations:²³

$$E_{\text{HOMO}} = -e(\varphi_{\text{ox}} + 4.71)(\text{eV});$$

$$E_{\text{LUMO}} = -e(\varphi_{\text{red}} + 4.71)(\text{eV});$$

Where the units of φ_{ox} and φ_{red} are V vs Ag/Ag⁺. The value of $\varphi_{\rm ox}$ and $\varphi_{\rm red}$ are 0.45 V and -1.89 V vs. Ag/Ag⁺,



PBDTV.



FIGURE 3 TGA plot of the polymer with a heating rate of 10 °C/min under inert atmosphere.



FIGURE 4 (a) Normalized absorption spectra of PBDTV in chloroform solution and film spin-coated on quartz plate; (b) Photoluminescence spectrum of PBDTV in chloroform solution (concentration 10^{-5} *M*) excited at 480 nm.



FIGURE 5 Cyclic voltammogram of PBDTV film on Pt electrode in 0.1 mol/L Bu_4NPF_6 , CH_3CN solution at a scan rate of 100 mV/s.

respectively. Accordingly, the HOMO and LUMO energy levels of PBDTV were calculated to be -5.16 eV and -2.82 eV, respectively. In comparison with the high efficiency copolymers of benzo[1,2-b:4,5-b']dithiophene and thieno[3,4-b]thiophene, PBDTTT-E, PBDTTT-C and PBDTTT-CF,19b the HOMO energy level of PBDTV (-5.16 eV) is a little lower than that of PBDTTT-E (-5.01 eV) and PBDTTT-C (-5.12 eV), and a little higher than that of PBDTTT-CF (-5.22 eV).^{19b} The relative lower HOMO energy level of PBDTV is desirable for getting higher open-circuit voltage when it is used as donor blended with PCBM in PSCs. The electrochemical bandgap of PBDTV calculated from the difference of the LUMO and HOMO energy levels is 2.34 eV, which is a little higher than that (2.01 eV) of the optical bandgap aforementioned. The higher electrochemical bandgap than optical bandgap is a common phenomenon for the conjugated polymers,^{5,24}



FIGURE 6 Current-voltage data from the device of ITO/ PEDOT:PSS/PBDTV/Au, plotted in the format $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$, where J is the current density and d is the thickness of the polymer layer. The line is the fit to the experimental data points.

| PBDTV: PC ₇₀ BM (w/w) | Spin Speed (rpm) | Thickness (nm) | J _{sc} (mA/cm²) | $V_{\rm oc}$ (V) | FF | PCE (%) |
|----------------------------------|------------------|----------------|--------------------------|------------------|------|---------|
| 1:2 | 2,000 | 60 | 5.47 | 0.71 | 0.62 | 2.43 |
| | 2,500 | 50 | 4.71 | 0.70 | 0.63 | 2.07 |
| | 3,000 | 40 | 4.27 | 0.70 | 0.63 | 1.86 |
| 1:3 | 1,000 | 125 | 4.49 | 0.64 | 0.39 | 1.11 |
| | 2,000 | 70 | 6.30 | 0.70 | 0.57 | 2.50 |
| | 2,500 | 55 | 6.00 | 0.70 | 0.58 | 2.45 |
| | 3,000 | 40 | 4.73 | 0.71 | 0.61 | 2.04 |
| 1:4 | 2,000 | 80 | 6.97 | 0.68 | 0.48 | 2.30 |
| | 2,500 | 75 | 6.81 | 0.69 | 0.53 | 2.51 |
| | 3,000 | 65 | 6.46 | 0.71 | 0.57 | 2.63 |
| | 4,000 | 60 | 6.26 | 0.70 | 0.58 | 2.54 |

TABLE 1 Photovoltaic Performance of the PSC Devices Based on PBDTV: PC₇₀BM Under the Illumination of AM1.5, 100 mW/cm²

because of the energy barrier of the charge transfer at electrodes during the electrochemical measurement.

Hole Mobility of PBDTV

Hole mobility is an important parameter of the conjugated polymers for the photovoltaic application. Here, we investigated the hole mobility of PBDTV with the space-charge-limited current (SCLC) model²⁵ with a device structure of ITO/PEDOT: PSS/PBDTV (135 nm)/Au (70 nm). The results are plotted as ln (Jd^3/V^2) vs $(V/d)^{0.5}$, as shown in Figure 6. Herein, *J* stands for current density, *d* the thickness of the device, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential. Hole mobility of PBDTV is 4.84×10^{-3} cm²/Vs calculated from the intercept of the corresponding lines on the axis of ln $(Jd^3/V^2)^{25(e)}$ according to the following equations.

$$j_{\rm SCLC} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{\left(V - V_{\rm bi}\right)^2}{d^3} \exp\left[0.89\gamma \sqrt{\frac{V - V_{\rm bi}}{d}}\right]$$

The hole mobility of about 5 \times 10⁻³ cm²/Vs is a high value for the solution processed conjugated polymer films.

Photovoltaic Property

The motivation of design and synthesis of the polymer PBDTV is to look for novel conjugated polymer photovoltaic materials. We fabricated the PSCs with the structure of ITO/PEDOT-PSS/PBDTV: $PC_{70}BM/LiF(6Å)/Al(80 \text{ nm})$, and optimized photovoltaic performance of the devices by changing the PBDTV: $PC_{70}BM$ weight ratio, spin speed, and thickness of the active layer.

Table 1 shows the photovoltaic performance of the devices based on the blend of PBDTV and $PC_{70}BM$ at different device fabrication conditions under the illumination of AM1.5, 100 mW/cm². Herein, the thickness of the active layer is an important parameter for the photovoltaic performance. It can be seen from Table 1 that, within the same weight ratio of PBDTV: $PC_{70}BM$, the PSCs with the active layer thickness in the range of 60–75 nm exhibit higher PCEs than others. Too thick active layer (thicker than 80 nm) results in lower fill

factor, because of limited charge transport property. Too thin active layer (thinner than 60 nm) leads to lower short circuit current (J_{sc}) due to the limited absorption of the thin active layer. Furthermore, when comparing the device performance among different weight ratio of PBDTV: PC70BM, the decrease of FF as a function of PC70BM loading can be observed, which may be caused by the decrease of hole mobility. Moreover, the increase of J_{sc} as a function of PC₇₀BM loading can be ascribed to the increasing absorption contribution from PC₇₀BM part. By balancing the absorption and carrier transport properties of the photosensitive layer, the optimized device with the PBDTV: PC70BM weight ratio of 1:4 and an active layer thickness of 65 nm shows a PCE of 2.63% with $V_{\rm oc} = 0.71$ V, $I_{\rm sc} = 6.46$ mA/cm² and FF = 0.57 under the illumination of AM1.5, 100 mW/cm². Actually, the LUMO level (-2.82 eV) of PBDTV is too high when it is used as donor blended with PCBM as acceptor, which results in big energy loss during the charge separation of excitons. The PCE could be further improved by decreasing the LUMO and HOMO energy levels of the polymer according to the design rule for the polymer donor in high performance PSCs.²⁶



FIGURE 7 External quantum efficiency of the device with the PBDTV: $PC_{70}BM$ weight ratio of 1:4 and an active layer thickness of 65 nm.



FIGURE 8 AFM images of the devices based on PBDTV and PC70BM with different weight ratio.

Figure 7 shows the external quantum efficiency (EQE) of the optimized PSC device with the PBDTV: $PC_{70}BM$ weight ratio of 1:4 and an active layer thickness of 65 nm. Comparing the EQE of device and the absorption of PBDTV, pronounced contribution from $PC_{70}BM$ to the photo current make the EQE much more broadened, and the EQE of device covers most of the visible wavelength range from 350 nm to 700 nm. The highest EQE value reached about 55% at around 500 nm corresponding to the absorption peak of PBDTV.

Morphology of the Active Layer

AFM images of the blend films of PBDTV and $PC_{70}BM$ with different weight ratios of 1:2, 1:3, and 1:4 are shown in Figure 8. There is not much difference among the height images of the three films. The surfaces of the three films are quite smooth, their root mean square (RMS) roughness values are 1.25 nm, 1.14 nm, and 1.24 nm for the 1:2, 1:3 and 1:4 films, respectively. The results indicate that PBDTV possesses good film-forming properties when blended with $PC_{70}BM$ in dichlorobenzene solvent. The uniform morphology of the blend films is coincident with the good photovoltaic performance of the PSC devices.

CONCLUSIONS

Poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b4,5-b']dithiophene vinylene) (PBDTV) was synthesized by the Pd-catalyzed Stille-coupling method. PBDTV shows good solubility in common organic solvents, high thermal stability, broader absorption band covering from 350 nm to 618 nm, higher hole mobility of about 5 \times 10⁻³ cm²/Vs and deeper HOMO energy level of -5.16 eV. The higher hole mobility and deeper HOMO level are beneficial to the photovoltaic application. The PSCs were fabricated with PBDTV as donor and $PC_{70}BM$ as acceptor, and the device fabrication conditions such as weight ratio of PBDTV:PC₇₀BM and the active layer thickness were optimized. Power conversion efficiency of the PSC with the PBDTV:PC₇₀BM weight ratio of 1:4 and the active layer thickness of 65 nm reached 2.63% with $V_{\rm oc} = 0.71$ V, $I_{\rm sc} = 6.46$ mA/cm² and FF = 0.57 under the illumination of AM1.5, 100 mW/cm². The results indicate that PBDTV with the simple structure is a promising photovoltaic material.

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