

Short communication

Synthesis and electrochemical characterization of a new polymer constituted of alternating carbazole and oxadiazole moieties

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Abstract

We report herein the synthesis and electrochemical characterization of a novel copolymer containing an electron rich carbazole moiety and an electron deficient oxadiazole unit—poly[*N*-(2'-ethylhexyl)-carbazole-3,6-diyl-1'',3'',4''-oxadiazole-2'',5''-diyl] (PCO). PCO can be dissolved in THF, CHCl₃, xylene, and DMSO. The structure of the polymer is confirmed by FT-IR, NMR and elemental analysis. The optical and electronic properties of the polymer are investigated by UV-Vis absorption spectroscopy and photoluminescence spectroscopy as well as cyclic voltammetry. The results show that the polymer films emit greenish-blue light (λ_{\max} 485 nm) upon UV excitation. Both p-doping and n-doping processes are observed in cyclic voltammetric investigation. A comparison between the properties of polycarbazole and polycarbazole-oxadiazole has been presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbazole; Oxadiazole; Fluorescence; Cyclic voltammetry

1. Introduction

The electronic and optical properties of conjugated polymers have been paid great attention in the field of molecular electronics [1,2]. Typically, conjugated polymers such as PPV, PT and their derivatives tend to be p-type, that is, they favor hole-transport [3,4]. There are few known polymers with good electron-injection capability. Studies have proven that the modification of the chemical structure of the polymer backbone or substitution of the conjugated polymers can endow the polymers with unique physical properties and thus can successfully lead to the new functionalities of the polymers [5].

Our previous work towards the study of p-n diblock copolymers constituted of the electron-rich thiophene unit and electron-deficient oxadiazole moiety in the polymer backbone have been demonstrated to be meaningful and successful [6–9]. Oxadiazole-based polymers have been widely investigated in the field of polymer light-emitting diodes (PLEDs) as well as other fields of polymer electronics [10,11]. It was reported that 3,6-di-acceptor substi-

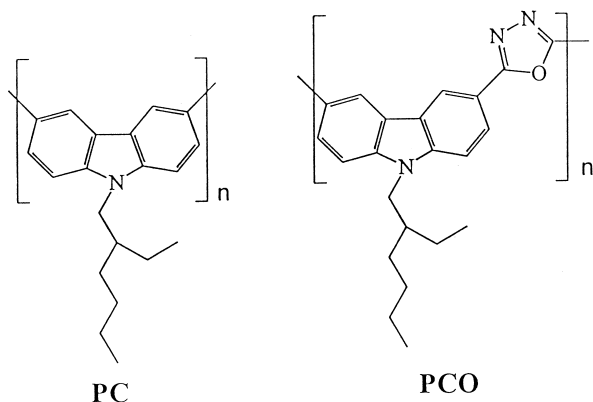
tuted carbazole chromophores have some unique optical properties as NLO materials [12]. Carbazole-based polymers have been paid increasing interest because of their unique optical properties and strong hole-transporting ability in opto-electronic devices [13,14].

In order to develop novel functional polymers and exploit their properties, herein we report our recent efforts in using carbazole to act as the electron-rich unit in the polymer backbone to form a new family of oxadiazole-based polymers. The combination of carbazole and oxadiazole properties makes this type of polymer poly[*N*-(2'-ethylhexyl)-carbazole-3,6-diyl-1'',3'',4''-oxadiazole-2'',5''-diyl] (PCO) of interest for the development of a novel series of polymeric materials for opto-electronics in the light of the p-n diblock copolymer concept [6–9] (Scheme 1).

2. Materials**2.1. Monomer and polymer synthesis**

Diethyl ether was distilled over sodium/benzophenone and hexane was distilled over calcium hydride. Triethylamine (purchased from Aldrich, A.R. grade) was re-dis-

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Scheme 1. The chemical structure of PCO and PC.

tilled prior to use. Carbazole, 2-ethylhexyl bromide, aluminum chloride, dimethylcarbamoyl chloride, ethylene chloride, thionyl chloride were used as received (Fluka or Aldrich chemicals). The detailed synthetic route to the target monomer and polymer is depicted in Scheme 2.

2.2. Experimental

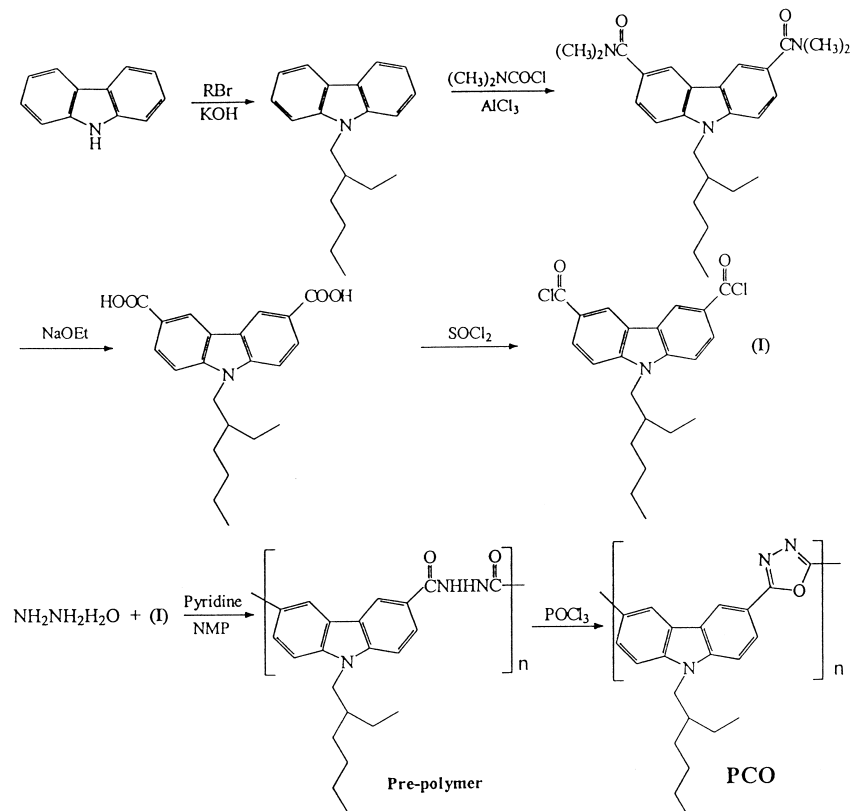
2.2.1. Measurements

NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* as solvent and tetramethylsilane as internal standard. FT-IR spectra were recorded

on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr disks. UV–visible and fluorescence spectra were obtained on a Shimadzu UV 3101PC UV–Vis-NIR spectrophotometer and Perkin Elmer LS 50B luminescence spectrometer with a xenon lamp as light source, respectively. Thermogravimetric analysis (TGA) was conducted with a DuPont thermal analyst 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 20°C/min and nitrogen flow rate of 75 ml/min. Differential scanning calorimetry (DSC) was run on a DuPont DSC 2910 module in conjunction with the DuPont thermal analyst system. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer for C, H, N, and S determinations. Cyclic voltammetry was performed using an EG&G Model 273A potentiostat/galvanostat under argon atmosphere. All potentials were measured against a Ag/Ag⁺ (0.1 M in acetonitrile) electrode (0.34 V vs. SCE) and all experimental values in this report were corrected with respect to SCE. Gel permeation chromatography (GPC) analysis was conducted with a Perkin elmer Model 200 HPLC system equipped with Phenogel™ MXL and MXM columns using polystyrene as standard and THF as eluent.

2.2.2. *N*-(2'-ethylhexyl)carbazole [15,16]

To the mixture of 16.7 g (0.10 mol) of carbazole dissolved in 120 ml of ethanol was added 11.2 g (0.20 mol)



Scheme 2. The synthetic routes of the monomer and polymer.

of potassium hydroxide. The mixture was refluxed for 0.5 h, and then 38.6 g (0.20 mol) of 2-ethylhexyl bromide was added dropwise over a period of 1 h. The mixture was further refluxed for 6 h. After cooling down to room temperature, the mixture was poured into water (250 ml) and extracted with ether three times (60 ml each). The organic layer was dried with anhydrous magnesium sulfate. The solvents were removed by rotary evaporation and the residue was distilled to remove the excess 2-ethylhexyl bromide. The residue was further purified by silica-gel column chromatography using hexane: ethyl acetate (10:1) as the eluent. The yield is 81%. MS: m/z 279. ^1H NMR (CDCl_3) δ 8.21–8.18 (m, 2H), 7.57–7.34 (m, 4H), 7.31–7.29 (m, 2H), 4.23–4.20 (d, $J = 7.2$, 2H), 2.18–2.14 (m, 1H), 1.51–1.33 (m, 8H), 1.02–0.94 (m, 6H) ppm. ^{13}C NMR (CDCl_3) δ 141.07, 125.65, 122.97, 120.39, 118.82, 109.08, 47.42, 39.49, 31.15, 28.95, 24.55, 23.20, 14.18, 11.03 ppm. Anal. Calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$: C, 86.02; H, 8.96; N, 5.02. Found: C, 85.79; H, 9.09; N, 5.27.

2.2.3. 3,6-bis(*N,N*-dimethylcarbamoyl)-9-(2'-ethylhexyl)carbazole

To a stirred mixture of 9.6 g (0.070 mol) of aluminum chloride and 30 ml of ethylene chloride under nitrogen was added a solution of 9.8 g (0.035 mol) of *N*-(2'-ethylhexyl)carbazole dissolved in 30 ml of ethylene chloride. A solution of 7.5 g (0.070 mol) of *N,N*-dimethylcarbamoyl chloride in 30 ml of ethylene chloride was added dropwise over 20 min. The mixture was refluxed for 24 h under nitrogen. Then, cooled and poured into 50 ml water and extracted with chloroform three times (20 ml each). The combined organic layer was washed with water until the washings were neutral to litmus paper, and dried over magnesium sulfate.

The solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using ethyl acetate as the eluent. Yield 73%. MS: m/z 421. ^1H NMR (CDCl_3) δ 8.18–8.17 (m, 2H), 7.60–7.56 (m, 2H), 7.40–7.38 (m, 2H), 4.17–4.16 (d, $J = 7.2$, 2H), 3.12 (s, 12H), 1.85–1.80 (m, 1H), 1.37–1.20 (m, 8H), 0.93–0.81 (m, 6H) ppm. ^{13}C NMR (CDCl_3) δ 172.32, 141.80, 127.01, 125.63, 122.10, 120.00, 108.86, 47.57, 39.24, 30.86, 28.66, 24.26, 22.86, 13.89, 13.85, 10.76 ppm. Anal. Calcd. for $\text{C}_{26}\text{H}_{35}\text{N}_3\text{O}_2$: C, 74.07; H, 8.37; N, 9.97. Found: C, 74.05; H, 8.35; N, 9.33.

2.2.4. *N*-(2'-ethylhexyl)carbazole-3,6-dicarboxylic acid

A mixture of 6.0 g (0.014 mol) of 3,6-bis(*N,N*-dimethylcarbamoyl)-9-(2'-ethylhexyl)carbazole and 40 ml of 20% ethanolic potassium hydroxide was heated under reflux for 6 h. The solvent was evaporated and the residue was poured into water, then the solution was acidified with concentrated hydrochloric acid. The precipitate was collected by filtration and washed with water. Recrystalliza-

tion from ethanol gave a white powder product. Yield 70%. MS: m/z 367. ^1H NMR ($\text{DMSO}-d_6$) δ 12.66 (s, br, 2H), 8.87 (s, 2H), 8.11–8.09 (d, $J = 8.9$, 2H), 7.70–7.67 (d, $J = 8.7$, 2H), 4.35–4.32 (d, $J = 7.4$, 2H), 2.01–1.97 (m, 1H), 1.35–1.14 (m, 8H), 0.86–0.72 (m, 6H) ppm. ^{13}C NMR ($\text{DMSO}-d_6$) δ 167.68, 143.54, 127.54, 122.62, 122.12, 121.80, 109.69, 40.28, 38.46, 29.99, 27.83, 23.50, 22.33, 13.64, 10.53 ppm. Anal. Calcd. for $\text{C}_{22}\text{H}_{25}\text{NO}_4$: C, 71.91; H, 6.86; N, 3.81. Found: C, 72.27; H, 7.00; N, 4.22.

2.2.5. *N*-(2'-ethylhexyl)carbazole-3,6-dicarbonyl chloride (**I**)

A mixture of 1.0 g (2.72 mmol) of *N*-(2'-ethylhexyl)carbazole-3,6-dicarboxylic acid and 15 ml of thionyl chloride under nitrogen was refluxed for 8 h. The excess thionyl chloride was removed by distillation. The residue solid was purified by recrystallization from hexane and dichloromethane to afford a light yellow powder. Yield 79%. MS: m/z 404. ^1H NMR (CDCl_3) δ 8.91 (s, 2H), 8.28–8.26 (d, $J = 8.2$, 2H), 7.50–7.47 (d, $J = 8.7$, 2H), 4.26–4.23 (d, $J = 7.4$, 2H), 2.10–1.99 (m, 1H), 1.44–1.22 (m, 8H), 0.96–0.83 (m, 6H) ppm. ^{13}C NMR (CDCl_3) δ 167.72, 143.53, 129.98, 125.71, 125.28, 122.80, 109.83, 48.13, 39.35, 30.83, 28.60, 24.27, 22.82, 13.83, 10.73 ppm. Anal. Calcd. for $\text{C}_{22}\text{H}_{23}\text{Cl}_2\text{NO}_2$: C, 65.35; H, 5.69; N, 3.47, Cl, 17.57. Found: C, 65.00; H, 5.79; N, 3.95; Cl, 17.38.

2.2.6. Preparation of the precursor polymer polyhydrazide

To a stirred solution of hydrazine monohydrate (0.50 mmol) in *N*-methylpyrrolidinone (NMP) (20 ml) containing 0.10 g of LiCl and 1–2 drops of triethylamine (TEA) was added monomer **I** (0.50 mmol) at room temperature. The reaction mixture was then heated to 80°C and was stirred at this temperature for 3 h. After cooling down to room temperature, the pre-polymer was precipitated in methanol and washed with water and ethanol. Further purification of the pre-polymer was carried out by dissolving the polymer in NMP and precipitating in methanol again. Drying in vacuum at 60°C for 24 h afforded a high yield (90%) of a polyhydrazide. ^1H NMR ($\text{DMSO}-d_6$) δ 10.78 (s, 2H), 10.17 (s, 1H), 8.87 (s, br, 1H), 8.09 (s, br, 2H), 7.65 (br, 2H), 4.41 (br, 2H), 2.05 (br, 1H), 1.86–0.77 (m, 14H) ppm. Anal. Calcd. for $(\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_2)_n$: C, 72.73; H, 6.89; N, 11.57. Found: C, 71.39; H, 7.37; N, 10.88.

2.2.7. Preparation of polymer PCO

0.70 g of polyhydrazide was dispersed in 20 ml of POCl_3 at room temperature. The mixture was refluxed for 8 h. After cooling down to room temperature, the reaction mixture was poured into water. The precipitate was collected by filtration and washed with water, ethanol and then ether and finally dried under vacuum at room temperature to afford a greenish-yellow solid. The yield is 76%.

^1H NMR (CDCl_3 ; TFA- $d = 20:1$): δ 8.82 (br, 2H), 7.91 (br, 2H), 7.50 (br, 2H), 3.97 (br, 2H), 1.83–0.56 (br, 15H) ppm. Anal. Calcd. for $(\text{C}_{22}\text{H}_{23}\text{N}_3\text{O})_n$: C, 76.52; H, 6.67; N, 12.17. Found: C, 75.87; H, 7.13; N, 11.09.

3. Results and discussion

3.1. Polymer characterization

The polymer is synthesized by the polycondensation method as reported in our previously published papers [6–9]. The hydrazine reacts with the bischlorocarbonyl of *N*-(2'-ethylhexyl)-carbazole and TEA as a base acts as an acid absorbent reagent to promote the polymerization. *N*-(2'-ethylhexyl)-carbazole was synthesized using a modified method reported by Lee et al. [15,16]. Polymer PCO is greenish-yellow color and dissolved in DMSO, NMP, and CHCl_3 . Because the polymer is partially soluble in THF, only the molecular weight of the THF-soluble parts of the polymer was measured by means of GPC with THF as eluent and polystyrene as standard. The results indicated that $M_w = 6640$ with the polydispersity of 1.54. The molecular weight of the polymer should be determined by the process of the polycondensation. The actual molecular weight of the polymer should be higher than the measured value because of the insoluble part with a higher molecular weight.

The FT-IR spectra of the polymer and its pre-polymer are depicted in Fig. 1 for the sake of comparison. Fig. 1 shows the result of such a conversion by observing the changes of functional groups. It is found that the main broad peak observed at 1620 cm^{-1} , attributable to the carbonyl of the polyhydrazide, diminishes and two new peaks at 1540 cm^{-1} and 1018 cm^{-1} , attributable to the oxadiazole ring, emerge and become pronounced. In addition, the absence of absorption peaks in the range 3200 cm^{-1} – 3300 cm^{-1} due to the N–H stretching indicates the completion of the cyclodehydration reaction.

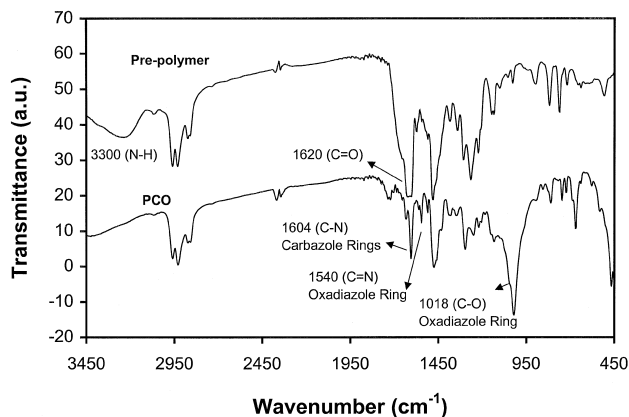


Fig. 1. The FT-IR spectra of PCO and its pre-polymer.

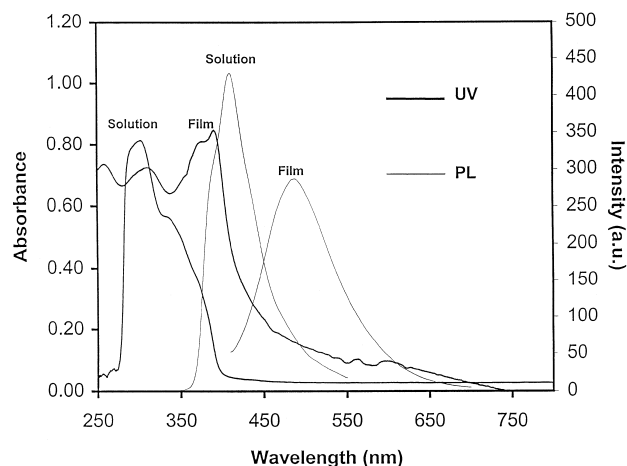


Fig. 2. The UV-Vis spectra and fluorescence spectra of the polymer in solution and as films.

3.2. Electronic (UV-Vis) and fluorescence spectra

Fig. 2 shows the UV-Vis spectra and fluorescence spectra of the polymer. The absorption and photoluminescence spectra of the polymer, both in the solution of chloroform containing a small amount of TFA and as thin

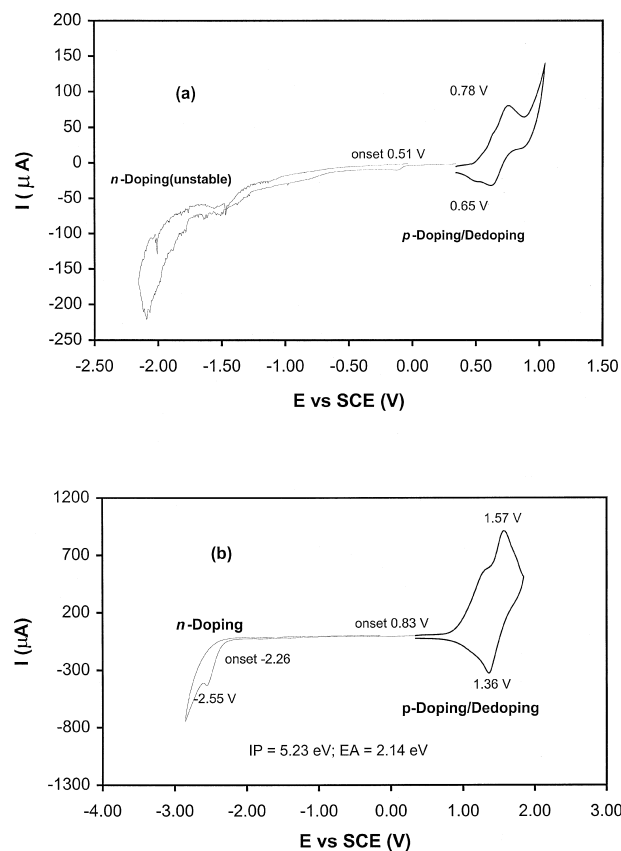


Fig. 3. The cyclic voltammograms of PC (a) and PCO (b) coated on Pt electrodes in acetonitrile containing $0.1\text{ M } n\text{-Bu}_4\text{NClO}_4$ at a scan rate of 50 mV/s .

films which were prepared by spin-coating the solution on a quartz plate, were measured at room temperature. In solution, the polymer gives a main absorption peak at 310 nm and a shoulder at 340 nm, respectively, while the main absorption peak of the solid films of the polymer appears at 400 nm with a shoulder at 328 nm. In comparison with its solution emission peak at 430 nm, the main emission peak in the solid films shifts to 485 nm. This may be due to the intrachain and/or interchain mobility of the excitons and excimers generated in the polymer in the solid state.

The peaks of fluorescence appear at the onset positions of their absorption bands. The excitation spectra of the polymer films show peaks at the positions of their absorption peaks. These results indicate that the fluorescence takes place by migration of electron in a conduction band (π^* level) to a valence band (π level) [17,18]. The high quantum efficiency of fluorescence of PCO (58%) compared with the polycarbazole (PC) (9%) measured under identical conditions could be attributed to the fact that the oxadiazole moiety connected to the carbazole ring resulting in a more rigid configuration. The fluorescence quantum yield of the polymers were determined in a dilute chloroform solution (ca. 1×10^{-5} M) and was carried out using quinine sulfate dye dissolved in 0.1 M H_2SO_4 employed as standard in obtaining relative quantum yields [19]. The efficiency of the fluorescence of these polymers is stable in air.

3.3. Electrochemical properties of polymers

The polymer films on a Pt electrode was scanned anodically and cathodically separately in an acetonitrile solution of $n-Bu_4NClO_4$. Fig. 3 depicts the C–V spectra of both the p-doping and n-doping processes of the polymer. Electrochemically polymerized polycarbazole CV spectra has also been studied and compared with PCO.

During cathodical scan, PCO exhibits irreversible n-doping process. The cathodical peaks occur at -2.55 V (vs. SCE) with the onset potential of the reduction at -2.26 V (vs. SCE). However, the reduction process has rarely been observed in polycarbazole PC itself which indicates that PCO is a good electron transport material if used in PLEDs [20,21]. When we scanned the polymer films anodically, PCO showed a reversible anodic peak at 1.57 V with a cathodic peak at 1.36 V (vs. SCE). The onset potential was determined to be 0.83 V. PC also showed reversible p-doping process but with the anodic peak at 0.78 V (v.s. SCE) and a cathodic peak at 0.65 V (vs. SCE). This means that PCO has a higher oxidation potential compared to PC.

4. Conclusion

In conclusion, we have successfully designed a route to synthesize a new totally conjugated polymer constituted of alternating *N*-(2'-ethyl hexyl)carbazole and 1,3,4-oxadiazole by incorporating the oxadiazole moiety into the carbazole ring. A combined study of the electronic, optical and electrochemical properties of the polymer indicates that PCO possesses promising electron-transporting/hole-blocking properties and relatively high fluorescence owing to the introduction of oxadiazole segment which leads to the highly rigid structure of the polymer. Further evaluation of the polymer for the application in the fields of NLO and PLEDs are in progress.

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