Synthesis, Characterization, and Electroluminescent Properties of a Novel Perylene-Containing Copolyimide

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ABSTRACT: A novel diphenylfluorene-based Cardo copolyimide containing perylene (PFB5) was designed and synthesized by polycondensation of a diamine 4,4′-(9H-fluoren-9-ylidene)bisphenylamine with perylene dianhydride and another dianhydride in *m*-cresol with isoquinoline as a catalyst at 200°C. PFB5 was characterized by FTIR, EA, GPC, TGA, DSC, UV-vis, and PL. Because of the existence of the bulky diphenylfluorene units in the backbone, PFB5 showed high thermal stability and good solubility in common solvents such as chloroform. Solubility of PFB5 in low boiling point solvents allows direct spin coating of the polymer films, which exhibit intense photo- and electroluminescence (EL) in the visible range. This nonconjugated polymer could be used as emitting and electron-hole transporting layers in polymer electroluminescent devices (PELDs). EL properties of the unilayer ELDs based on PFB5 are discussed. The device emitted a greenish yellow light. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 786–791, 2003

Key words: polyimide; dye; light-emitting diodes

INTRODUCTION

Organic or polymeric electroluminescent devices (ELDs) have received much attention in recent years because of their color tunability, low operating voltages, ease of fabrication, and especially potential application for self-emitting a full color plat panel display.[1] However, one of the serious problems of organic or polymeric ELDs is the poor durability under operation owing to the intrinsically flexible and soft characteristics of the organic materials. The emission layer of ELDs can be easily relaxed by Joule heating during operation and can eventually lead to device destruction.[2] To fabricate ELDs with high stability, much research has been performed to improve the stability of organic materials and the interface between the metal electrode and the organic thin film.[3]

Polyimides have various outstanding characteristics such as good adhesion to metal, high thermal stability, low thermal expansion, excellent film-forming properties, and especially a high T_g of above 200°C, in general, which make them potentially useful as stable materials for ELDs.[4] ELDs with a polyimide thin film as emissive or hole transporting layers have been successfully fabricated.[5] Among the polyimides, the perylene-containing polymer appears to be one of the highest thermal stability because of a condensed aromatic perylene ring.[6] Perylenediimides represent one of the most widely studied classes of organic semiconductors with possible application in electrophotographs, electroluminescent (EL) displays, and photovoltaic cells.[7] But two factors hamper perylenediimides to be an effective luminescent material for ELDs: One is that the solubility of perylenediimides is similar to that of polyimides and is even low. For ELDs, processability and especially film formation is a prerequisite. Another is that the fluorescent quantum efficiency of pure perylenediimide film is low, which results from its self-quenching due to the high dye concentration within the thin film,[8] while the EL efficiency of a luminescent material depends directly on its quantum efficiency of fluorescence.[9]

To overcome these problems, we designed a novel fluorene-based Cardo copolyimide-containing perylene unit in the main chains. It is well known that polyimides containing a fluorene moiety (so-called Cardo-type polymers) have good thermal stability, mechanical properties, and solubility in common solvents.[10] Therefore, 4,4′-(9H-fluoren-9-ylidene)bisphenylamine (FBPA) was chosen as a Cardo diamine to polymerize with a perylene dianhydride to form a Cardo polyimide. The Cardo structure may increase the solubility and thermal stability of the resulting polyimide. Another advantage of the Cardo structure is the bulky side groups that could inhibit the packing of chains, which would eliminate the interchain quenching effects of chromophores. Furthermore, owing to the similar chemical structure of fluorene to

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carbazole, the incorporation of fluorene units into the macromolecular backbone of polyimide would increase its hole-transporting ability.[11] To circumvent self-quenching, our strategy was to introduce a second dianhydride, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), to dilute the perylene content in the polyimide.

In this article, the synthesis and characterization of copolyimide containing a low percentage of perylenediimide units is described. The solubility, thermal stability, optical behavior, and EL of this novel polyimide are discussed.

EXPERIMENTAL

Materials

FBPA (Aldrich) and BTDA (Aldrich) were purified by sublimation. 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA; Aldrich) was purified according to ref. 12. *m*-Cresol was stored over 4 Å molecular sieves and distilled before use. Isoquinoline (Acros) was used as received. 2-(4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was purchased from Sigma. ITO-coated glass substrates [sheet resistance ≤ 50 Ω/□, purchased from Jinlai Films Co. Ltd. (China)] was patterned and cleaned before use. All other organic solvents were commercially obtained and purified by standard distillation methods.

Synthesis of PFB5

A typical procedure is as follows: In a 50-mL three-necked flask fitted with a magnetic stirrer, a thermometer, and an argon inlet and outlet tube, 348.3 mg (1 mmol) of FBPA, 6 mL of *m*-cresol, and 0.2 mL of isoquinoline were added. After complete solubilization of diamine, 19.6 mg (0.05 mmol) of PTCDA was added. The reaction mixture was heated to 200°C and purged with a gentle argon flow for several hours (about 8 h) until the dye was completely attached between two diamine molecules (TLC control). After cooling, 306.1 mg (0.95 mmol) of BTDA was added. The reaction mixture was heated again to 200°C for 20 h. During cooling, the mixture was diluted with *m*-cresol. Then, the solution was poured dropwise into 400 mL of methanol. The precipitate was filtrated, dried, and extracted in methanol for 24 h. Then, the product was dried under a vacuum at room temperature for 4 h and at 260°C for 6 h. The product was a red powder with a 94% yield.

ANAL: Calcd for PFB5 $(C_{43.35}H_{21.1}O_{4.95}N_2)_n$ (637.5)n: C, 79.72%; H, 3.47%; N, 4.39%. Found: C, 78.85%; H, 3.72%; N, 4.20%.

Fabrication of the EL devices

Prior to use, ITO-coated glass substrates were patterned and cleaned. A 6 mg/mL PFB5 chloroform solution was used for film formation. The solutions were spin-coated onto ITO-coated glass substrates under an ambient atmosphere at 2500 rpm for 30 s. Then, the PFB5-coated substrates were loaded into a vacuum chamber. The aluminum (Al) layer was evaporated onto the PFB5 layer from a tungsten filament under a pressure of about 2×10^{-3} Pa. Two types of unilayer device, (a) ITO/PFB5/Al and (b) ITO/PFB5 + 9 wt % PBD/Al, were fabricated. The thickness of the film of the polymer layer and the Al layer were 60 and 100 nm, respectively. The active area of the device was 12 mm^2.

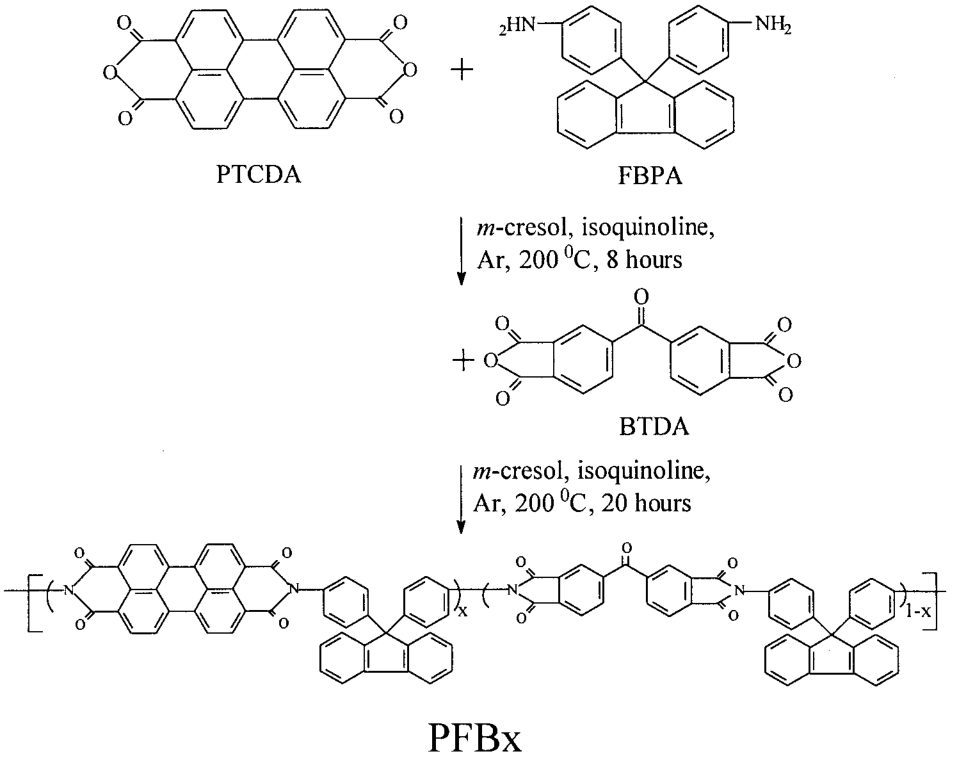
Measurements

Element analysis (EA) was determined on a ThermoQuest Italia S.P.A. EA 1110. The FTIR spectrum was recorded on a Bruker Vector 22 IR spectrometer (KBr pellet). The weight-average molecular weight (M_w) and molecular weight distribution (MWD) were measured on a Waters 208 gel permeation chromatograph (GPC) at 30°C using THF as the eluent and standard polystyrene as the reference. The temperature of decomposition (T_d) and the glass transition (T_g) were determined with a Delta series TGA7 and a Perkin–Elmer Pyris 1 DSC in nitrogen at a heating rate of 10°C/min, respectively. The UV-vis absorption spectrum was recorded on a Varian Cary 100 Bio UV-vis spectrophotometer in a chloroform solution. The photoluminescence (PL) and EL spectra were recorded on a Hitachi F-4000 fluorescence spectrophotometer. The thickness of the films was determined with a Dektak^3 profilometer. The current density (J)–voltage (V)–EL intensity (L) characteristics were measured using a photomultiplier tube (PMT) (Hamamatsu Photonics Co.) and an electrometer (Keithley 6517) controlled with a personal computer. All measurements were carried out under air at room temperature.

RESULTS AND DISCUSSION

Synthesis of PFB5

Scheme 1 shows the synthetic route of PTCDA–FBPA–BTDA polyimide (abbreviated as PFBx). PFBx was synthesized by a one-step polycondensation of a diamine, FBPA, and two dianhydrides (in different molar ratios), PTCDA and BTDA, in *m*-crersol with isoquinoline as a catalyst at 200°C. In the case of the two dianhydrides with different reactivity, a twice addition of dianhydride monomers is necessary to achieve a random incorporation of the comonomers. Owing to the low solubility of PTCDA in *m*-cresol at room temperature, the high temperature may increase its solubility. The argon flow could remove water and make the balance move to the polyimide. The extract of PFBx in methanol may remove the high boiling point



Scheme 1 Synthetic route of PTCDA–FBPA–BTDA copolyimide (PFBx).

solvent and catalyst. When the molar ratio of PTCDA to BTDA is 5:95, the perylene content of the polyimide (PFB5) is 1.97 wt %.

Characterization of PFB5

The completion of the imidization of PFB5 was confirmed by FTIR analysis and element analysis. As shown in Figure 1, the absorption bands at 1779 and 1724 cm^{-1} are related to the symmetric and asymmetric stretches of the carbonyl of the imide group, respectively, while the absorption bands at 1091 and 721 cm^{-1} are the vibrations of the imide structures. Also, the absorption at 1370 cm^{-1} is of C—N groups.[5c] The molecular weight of PFB5 was measured by GPC to be M_w = 27,000 with a molecular weight distribution (MWD) of 2.58. The above experimental results suggested the successful formation of polyimide PFB5.

Table I lists the solubility behavior of PFB5 (10 mg/mL) in different solvents at room temperature. PFB5 was completely soluble in chloroform, dichloromethane, *m*-cresol, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrroli-

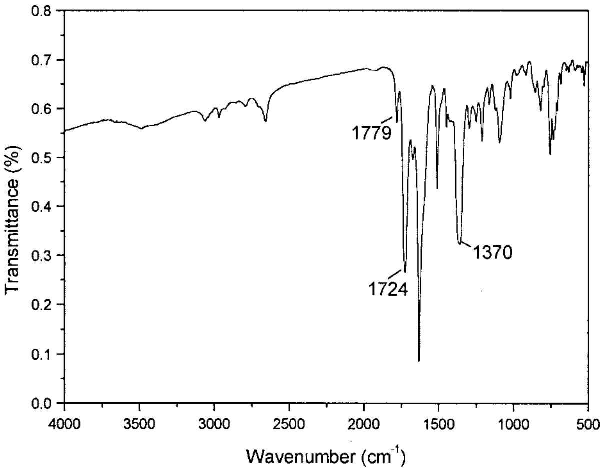


Figure 1 FTIR spectrum of PFB5 (KBr pellet).

TABLE I
Solubility of PFB5 (10 mg/mL) at Room Temperature

Solvent	Solubility[a]	Fluorescence[b]
Chloroform	+	g-y
CH_2Cl_2	+	g-y
m-Cresol	+	g-y
NMP	+	g-y
DMF	+	g-y
DMAc	+	g-y
DMSO	+	g-y
Pyridine	+	g-y
Cyclohexanone	±	y-g
THF	±	y-g
DCE[c]	±	y-g
Toluene	−	
Nitromethane	−	

[a] +, soluble; ±, partly soluble; −, insoluble.
[b] g–y, yellow is dominant; y–g, green is dominant.
[c] DCE, 1,2-dichloroethane.

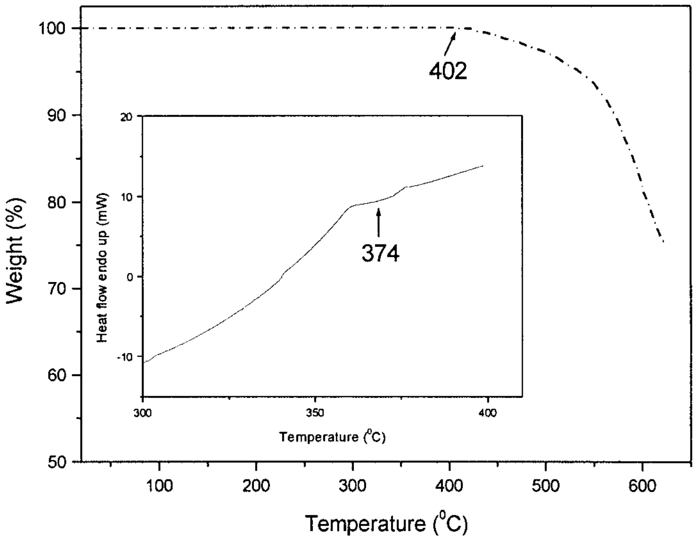


Figure 2 (Dash-dot line) TGA and (inset figure) DSC cures of PFB5 at a heating rate of 10°C/min in nitrogen.

done (NMP), dimethyl sulfoxide (DMSO), pyridine, etc. PFB5 was partly soluble in tetrahydrofuran (THF), 1,2-dichloroethane, and cyclohexanone. PFB5 was almost insoluble in toluene and nitromethane. The excellent solubility could be attributed to two factors: First, PFB5 has bulky diphenylfluorene groups in the main chains, which brings high steric hindrance to decrease the molecular interactions and also provide an easier solvation pathway. Second, the presence of carboxyl groups from benzophenone sequences increases the affinity of the chain to polar solvents. Due to this remarkable solubility, a thin film of PFB5 could be easily prepared by directly spin coating its chloroform solution.

The thermal stability of PFB5 was evaluated using TGA and DSC analysis under a nitrogen atmosphere at a heating rate of 10°C/min. The TGA and DSC results are shown in Figure 2. The temperature of the onset of the weight loss and the temperature of 5 wt % loss are 402 and 532°C, respectively. The glass transition temperature (T_g) was 374°C. The high thermal stability of PFB5 resulted from the existence of a bulky diphenylfluorene moiety in the polymer backbone.

The crystallinity of PFB5 was evaluated by a wide-angle X-ray powder diffraction measurement. Figure 3 illustrates its X-ray diffractogram. The polymer displays an amorphous structure, which is due to the kinked bulky 9,9-fluorenylidene structure. The steric repulsion of the bulky 9,9-fluorenylidene unit twists the rings dramatically out of plane. The resulting twisted conformation inhibits chain packing and crystallinity.[13]

The UV-vis absorption spectrum of PFB5 in chloroform is shown in Figure 4. The absorption spectrum exhibited three typical peaks at 461, 496, and 529 nm as well as a shoulder at 434 nm. The peak integral increased with the wavelength. These peaks could be assigned to the S_1 (0–2), S_1 (0–1), and S_1 (0–0) transition of the highest occupied bonding energy levels of perylenediimide.[14] The peak at 308 nm could be attributed to the absorption of the fluorene moiety. The powder of PFB5 shows a strong orange–red fluorescence under ultraviolet light radiation. At a high concentration, the solution of PFB5 exhibits greenish yellow fluorescence and yellow is the dominant color. While at a low concentration, it shows yellowish green fluorescence and green is the dominant color (see Table I). The PL spectrum of PFB5 in chloroform at an excitation wavelength of λ_{exc} = 496 nm is also shown in Figure 4. The emission spectrum shows three bands at 542, 582, and 628 nm from the singlet excited states of perylenediimide.[14e] The PL spectrum is homologous to the absorption spectrum of perylenediimide

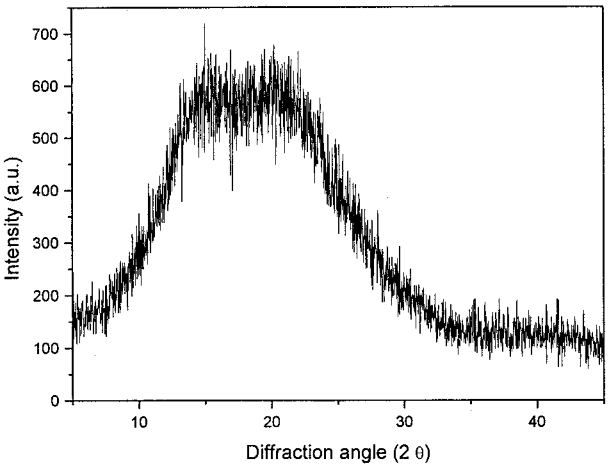


Figure 3 Wide-angle X-ray diffractogram of PFB5 powder.

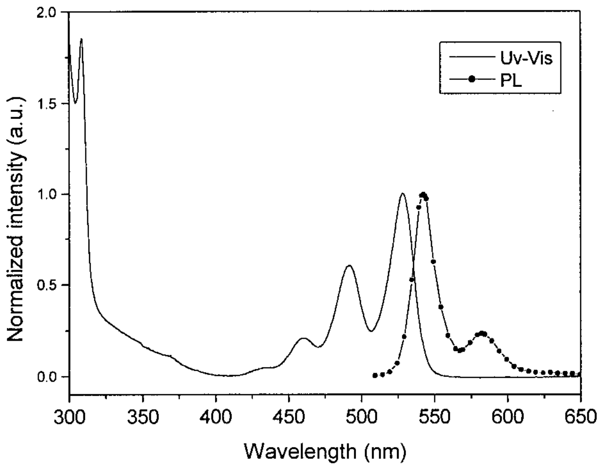


Figure 4 UV-vis absorption and PL spectra (λ_{exc} = 496 nm) of PFB5 in chloroform solution.

and the dominant PL maximum is only very slightly stokes-shifted (approximately 14 nm).

EL devices of PFB5

The presence of the diimide groups in the backbone makes the materials electronically conductive, while arylene (9,9′-diphenylfluorene) moieties play the role of hole-transporting sites in PFB5.^{5a} Therefore, the polyimide may exhibit an electron/hole dipolar transporting ability.

By using PFB5 as a light-emitting material and PBD as an electron-transporting material, aluminum (Al) as the cathode, and indium–tin oxide-coated glass substrates (ITO) as the anode, two unilayer EL devices were fabricated. Their structures are as follows: (a) ITO/PFB5 (60 nm)/Al (100 nm) and (b) ITO/PFB5 + 9 wt % PBD (60 nm)/Al (100 nm). The current density and voltage characteristics of devices (a) and (b) are shown in Figure 5. Both (a) and (b) showed diode behaviors. The turn-on voltage (the voltage at which light could be seen by the naked eye in the dark) of both (a) and (b) are 11.8 V and 10.5 V, respectively. Device (a), without electron-transporting PBD, showed a weaker EL intensity and was much less stable than the device (b). The reason may be that (b) is more efficient for electron transporting than (a), and the recombination of charges in (b) is more balanceable than in (a).

Device (a) emitted blue light. Device (b) emitted a greenish yellow light. At the forward 18-V dc voltage, the emission light of (b) could be seen in daylight. Their EL spectra are shown in Figure 6. The EL spectrum of (a) differs much from the PL spectrum of PFB5. According to ref. 11, the light may originate from the emission of the fluorene moiety, while the EL spectrum of (b) is at 545 nm with a shoulder peak at 580 nm. In comparison with the PL spectrum of PFB5 (Fig. 4), the light belongs to the emission from perylenedimide structure units. For (b), although the molar ratio of perylene to fluorene is 5 : 100, the EL spectrum constitutes almost 100% of peryleneimide and the emission of fluorene completely vanished, that is, fluorene moieties only acted as the hole-transporting site and perylenediimide units were the recombination sites of electrons and holes.

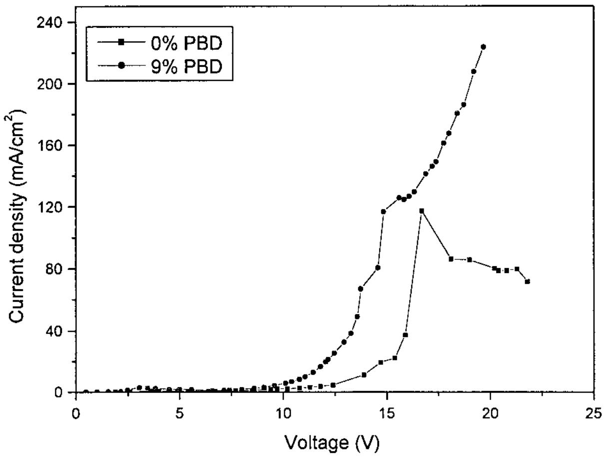


Figure 5 Current density and voltage characteristics of the device doped with or without PBD at a forward dc bias voltage.

CONCLUSIONS

A novel fluorene-based Cardo copolyimide-containing perylene (PFB5) was synthesized via a simple route. PFB5 is amorphous in nature and readily soluble in chlorinated aliphatic hydrocarbons, such as CH_2Cl_2 and $CHCl_3$, as well as aprotic polar solvents such as DMF, DMAc, and NMP. PFB5 showed a glass transition temperature at 374°C and no weight loss

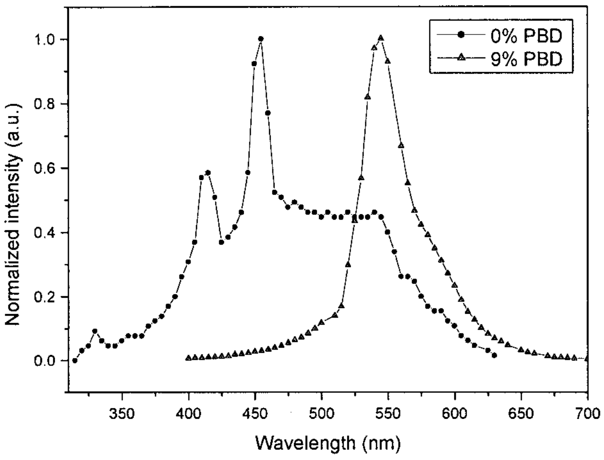


Figure 6 EL spectra of the device doped with or without PBD at the forward 18-V dc voltage.

below 402°C under a nitrogen atmosphere. PFB5 showed film formability, a hole/electron-transporting ability, and a light-emitting ability. The turn-on voltage of the device, ITO/PFB5 (60 nm)/Al (100 nm), was 11.8 V and the device emitted blue light, while the turn-on voltage of the device, ITO/PFB5 + 9 wt % PBD (60 nm)/Al (100 nm), was 10.5 V and emitted a yellow–green light. Further research in this field is necessary to study the suitable perylene content. Other research in this field is to design a new fluorene-based polyimide containing new aromatic amine and dianhydride for application in organic molecular electronics.

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