



## AFM, SEM and GIXRD studies of thin films of red polycarbazolyldiacetylenes

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### Abstract

In this paper we report the results of a morphological and structural investigation on film properties of a soluble polydiacetylene, the poly[1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD-HS). The red films of this polymer, prepared by standard spin-coating techniques, revealed absence of linear dichroism and birefringence in contrast with the ordered mesophases detected by powder X-ray studies. In order to interpret the optical behavior of this polymer, we performed AFM and SEM studies of polyDCHD-HS films spun on hydrophilic and hydrophobic glass substrates. We found the presence of surfaces organized in rod-like particles, more regularly oriented on the hydrophilic substrate. GIXRD studies, carried out on films sufficiently thick to allow the observation of the diffraction pattern, revealed the presence of a lamellar structure with a spacing of 3.22 nm. The low intensity of the diffraction peaks and the isotropic linear optical properties of the films show that the lamellar mesophases are not extended over large areas. These findings were compared with the data obtained from AFM and SEM studies on films of two other polydiacetylenes, the poly[1-(3,6-dihexadecyl-*N*-carbazolyl)-6-(*N*-carbazolyl)-2,4-hexadiyne] (polya-DCHD) and the poly[1,6-bis(3,6-dipalmitoyl-*N*-carbazolyl)-2,4-hexadiyne] (polyDPCHD), spun on hydrophilic glass substrate. The results confirmed the presence of nodular morphologies which seem to be a general characteristic of this class of materials. The particles organization appears instead related to the chemical nature of the substituents on the carbazolyl rings.

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## 1. Introduction

Among the conjugated polymers, polydiacetylenes (PDAs) are of considerable interest owing to their possible applications in third order nonlinear optics. In recent years we have been involved in the study of a class of PDAs, the polycarbazolyldiacetylenes (PCDAs), and in particular of some derivatives of poly(di(*N*-carbazolyl)-2,4-hexadiyne), polyDCHD, suitably designed to combine its outstanding optical and electronic properties with the processability required for the preparation of thin films. Three among the various synthesized monomers show the highest polymer yield in the thermal topochemical polymerization. The chemical structure of the correspondent polymers is reported in Scheme 1 in comparison with that of the precursor. The monomer-free polymers consist of red microcrystalline powders.

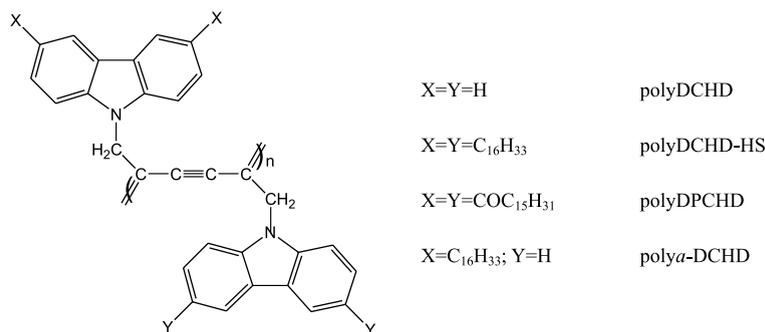
Among these polymers, polyDCHD-HS is the more interesting one, because its high solubility allows a complete molecular characterization and the preparation of films of different thickness by standard spin-coating techniques. The availability of homogeneous films permitted linear and non-linear optical characterizations of this polymer. Their electronic spectra match those of the correspondent dilute solutions [1] with an evident excitonic peak at 538 nm and not well resolved vibronic replica, thus indicating that the conjugated backbones are isolated also in the solid state. No linear dichroism was detected in all the films spun on glass or silicon wafers, thus showing the absence of preferential polymer chains orientation in the plane [2]. This result was supplemented by

the absence of birefringence in films of different thickness [3]. These findings were unexpected on the basis of the ordered form detected by powders X-ray diffraction [4], where a bidimensional columnar architecture, in which the columns formed by the conjugated skeleton with the carbazolyl substituents are assembled in a hexagonal array, was found. In order to understand the absence of any chain orientation in the films of polyDCHD-HS and their different behavior with respect to that of its powdered form, we performed an investigation by AFM, SEM and GIXRD techniques. The results obtained were supplemented with some data from the other two substituted polymers in Scheme 1.

## 2. Experimental section

The thin films of all the polymers of Scheme 1 were prepared in clean room by a spin-coating technique on glass substrates. The substrates consist of microscope glasses cleaned by using MilliQ water, high grade acetone and isopropyl alcohol. Hydrophobic surfaces were obtained by treating the cleaned hydrophilic glass with a 2% (V/V) hexamethyldisilazane solution in ethanol at pH = 4.5–5.5 for 20 h.

The thin films of polyDCHD-HS were prepared from a 20 mg/ml toluene solution, using a spinning rate of 3200/1000 rpm for hydrophilic/hydrophobic substrate. For the X-ray diffraction studies, where thicker samples are required, a multi-layer film of polyDCHD-HS was prepared by spin-coating of successive layers using a more dilute



Scheme 1.

toluene solution (5 mg/ml) and a deposition rate of 1500 rpm.

The thin films of poly $\alpha$ -DCHD were prepared on untreated glass from a 8 mg/ml toluene solution, using a higher spinning rate (6000 rpm). These different experimental conditions were due to the reduced solubility of this polymer with respect to polyDCHD-HS.

Being polyDPCHD only sparingly soluble in some organic solvents, films of this polymer were obtained by spin-coating of a 9 mg/ml monomer solution in chloroform, followed by thermal polymerization at 115 °C [5].

AFM measurements were performed using an Autoprobe CP Research Microscope equipped with a large area (90×90  $\mu\text{m}^2$ ) piezoelectric scanner, in noncontact mode with a NT-MDT cantilever operating typically at 280 KHz. All the acquired images were corrected for the tilt of the film faces subtracting a first order polynomial line by line in the faster scan direction by means of the microscope Proscan software. The surface roughness was evaluated through the mean square roughness,  $R_{\text{ms}}$  and the mean roughness,  $R_{\text{m}}$ , of the heights using the PSI ProScan Image Processing software on images up to a maximum scan area of 70×70  $\mu\text{m}^2$ .

SEM images were obtained using a LEO Microscope, model Stereoscan 440. The samples were fractured in liquid nitrogen in order to obtain the film thickness and then the surfaces were covered with a 20 nm thin gold layer to induce conductivity.

The GIXRD measurements were carried out with  $\text{CuK}\alpha$  (1.54 Å) radiation at room temperature using a Philips X'Pert system (PW3020 vertical goniometer and PW3710 MPD control unit) equipped with a focusing graphite monochromator on the diffracted beam and a proportional counter. The angle of incidence of the X-ray beam was fixed to 1° and the measurements were recorded (100 s  $\text{step}^{-1}$ ) with a step size of 0.05° on a 1.5–80° range.

### 3. Results and discussion

Figs. 1 and 2 report the results of the AFM studies as height- and error-images of the polyDCHD-HS films on the hydrophylic and hydrophobic substrates, respectively. Fibrous textures of rod-like particles with average diameter of about 250 nm are observed for both samples. However on the hydrophylic substrate the particles are more elongated (around 1000 nm) and oriented, while a more random distribution of length and orientation is observed when the polymer is coated on hydrophobic glass.

The two roughness parameters, related to a surface area of 10  $\mu\text{m}^2$ , resulted to be  $R_{\text{rms}} = 1.98/3.16$  nm and  $R_{\text{m}} = 1.22/1.88$  nm for the hydrophylic/hydrophobic substrates, respectively. The values refer to “flat” regions in order to minimize the contribution of bigger particles, whose sporadic presence has been found in images of larger scan area size (not reported).

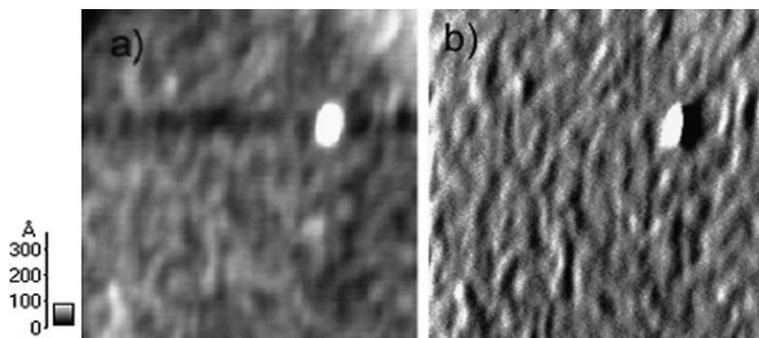


Fig. 1. Noncontact mode AFM images of polyDCHD-HS film on hydrophylic substrate: (a) height image; (b) error image. Scan size 3.5  $\mu\text{m}$ .

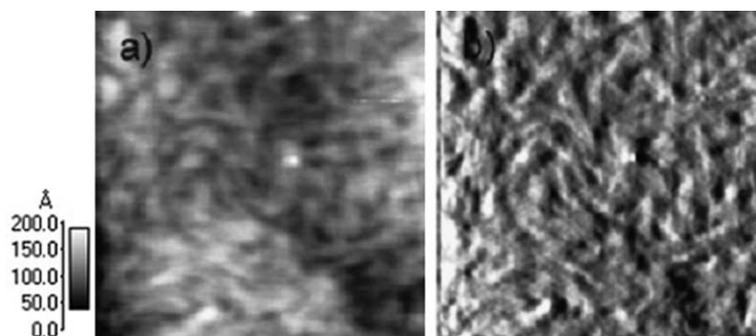


Fig. 2. Noncontact mode AFM images of polyDCHD-HS film on hydrophobic substrate: (a) height image; (b) error image. Scan size 4  $\mu\text{m}$ .

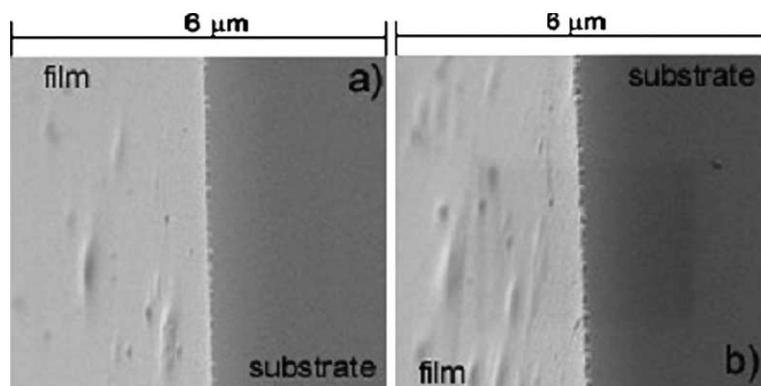


Fig. 3. SEM micrographs of polyDCHD-HS film: (a) hydrophilic substrate; (b) hydrophobic substrate.

SEM micrographs of the sections of the films are reported in Fig. 3, where the results from the two types of substrates are compared. The left sides of the micrographs represent the polymer film, while the right sides correspond to the bare glass. The average thickness, evaluated from the interface region, results  $150 \pm 20$  nm in both cases. Oriented polymeric structures having a diameter ranging from 150 to 600 nm and a length of 1–2  $\mu\text{m}$  protrude from an apparently uniform surface. In fact, owing to the 20 nm gold layer covering the surface to induce conductivity in the film, only the larger structures are visible. On the hydrophobic substrate the particles are more numerous and heterogeneous and, unlike the AFM images, they seem to have oriented disposition.

The main characteristic of the film morphologies derived from both AFM and SEM tech-

niques consists in the presence of elongated nanoparticles, although the nodular features, well evidenced by AFM, cannot be detected in the correspondent SEM micrographs. We remark that nodular structures were reported in the literature either for polyDCHD [6] and poly $p$ TS (poly [2,4-hexadiyne-1,6-diol]-bis( $p$ -toluenesulfonate)) [7] as results of AFM studies on the polymerization of monomer single crystals and were attributed to a random distribution of polymer nuclei. Although the experimental conditions in these works are quite different from ours, the trend to forming nodular morphologies seems to be a general characteristic of PDAs. However, the absence of linear dichroism and birefringence suggests that the fibrous oriented structure of polyDCHD-HS cannot be extended to the full area of the film [3], even when hydrophilic substrates are used.

In order to get a better insight on the film structure, grazing angle X-rays diffraction (GIXRD) studies were performed. This technique cannot be applied to the study of thin films because it is impossible to distinguish the scattering due to the supporting glass from the scattering due to the polymer. Measurements were then carried out on thick multi-layered samples. The diffraction patterns of the supported polymer, of the supporting glass and their difference are reported in Fig. 4.

The pattern of the film (difference) shows two peaks at  $s_0 = 0.31 \text{ nm}^{-1}$  and  $2s_0 = 0.62 \text{ nm}^{-1}$  that are the first and second order reflections of a lamellar structure with a spacing of 3.22 nm. This spacing is very close to the distance (3.3 nm) existing between the surfaces of the polydiacetylene chains separated by the long alkyl substituents in a liquid-like state as deduced from the structural data of Ref. [4]. The low intensity of the peaks indicates a random distribution of lamellar microdomains, which is in agreement with the observed absence of anisotropy in the electronic spectra.

The broad halo at  $s = 2.2 \text{ nm}^{-1}$  corresponds to a periodicity of 0.45 nm characteristic of melted paraffinic chains. It is clear from the spacing value that the lamellar structure is not determined by the multi-layer deposition because each layer corresponds to about 20 nm. It is also evident that during the spin-coating process the polymer loses its 2D-hexagonal organization. The SEM micrograph of the same sample, shown in Fig. 5, gives a thickness of  $450 \pm 20 \text{ nm}$ . One can notice on the surface the nodular structures typical of these polymers, but not the fibrous-like particles observed in thin films of polyDCHD-HS. This difference is presumably due to the different experimental conditions (concentration of the spun solution and spinning rate) used for the films preparation.

The results obtained on polyDCHD-HS stimulated further AFM and SEM investigations on the other two substituted polymers in Scheme 1, with the purpose of finding if the modulation of the chemical structure could modify the film morphology. Since more homogeneous films of

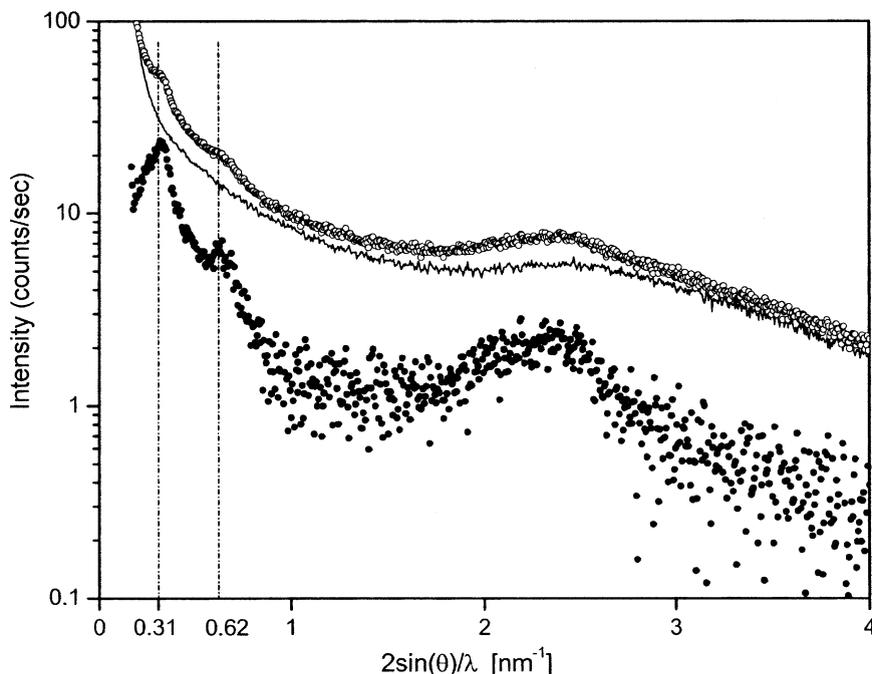


Fig. 4. GIXRD diffractogram of polyDCHD-HS multi-layer film on hydrophilic substrate: supported polymer (empty circles); supporting glass (full line); their difference (full circles).

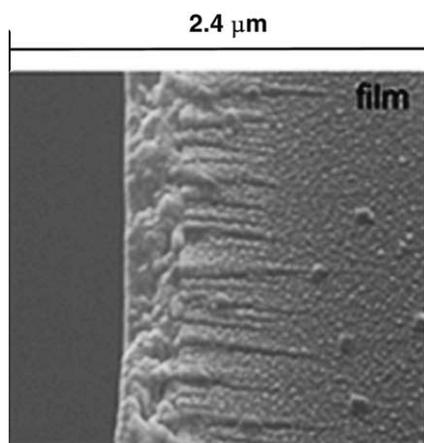


Fig. 5. SEM micrograph of polyDCHD-HD multi-layer film on hydrophilic substrate.

polyDCHD-HS were obtained on the hydrophilic substrate, results on the other two polymers are only given for this kind of support. AFM images and SEM micrographs are reported for polyDCHD and polyDPCHD in Figs. 6 and 7, respectively, and all the data on film thickness and roughness parameters related to a surface area of  $10 \mu\text{m}^2$  are collected in Table 1 together with those of the bare substrates.

The surface morphology, observed in the AFM image for the asymmetric polymer poly $\alpha$ -DCHD, differs from that of polyDCHD-HS, although nodular structures of average diameter around 150 nm are found with different degree of aggregation,

but without preferential orientation. Notice the presence of numerous hollows, that indicates the inhomogeneous distribution of the polymer even on the hydrophilic substrate. This fact can be attributed to the very low film thickness, as evidenced in the SEM micrograph, where the continuity of the film-substrate image at the separation line shows that the film thickness is smaller than the uncertainty ( $\sim 20 \text{ nm}$ ) of the method. Here again the polymer surface appears less homogeneous than that of polyDCHD-HS and, besides a few regions where very large aggregates are present, smaller nodular particles are observed. The film heterogeneity is consistent with the higher values of the roughness parameters of Table 1.

The AFM image of polyDPCHD film shows a regular arrangement of the partially oriented nodular structure. This result is in agreement with the very low values of  $R_{\text{rms}}$  and  $R_{\text{m}}$ . The large particle in the center of the figure is due to a dust bead. The polymer surface in the SEM micrograph is apparently homogeneous with locally oriented nanometric nodular threads, observable at higher magnification in Fig. 7. Notice the presence of numerous voids in the film, probably caused by a too fast evaporation of chloroform used for the monomer deposition. The large imperfections on the substrate surface are typical defects of glass. The film thickness is very close to that found for polyDCHD-HS.

At this point we would like to remark that the roughness of the substrates (reported at the

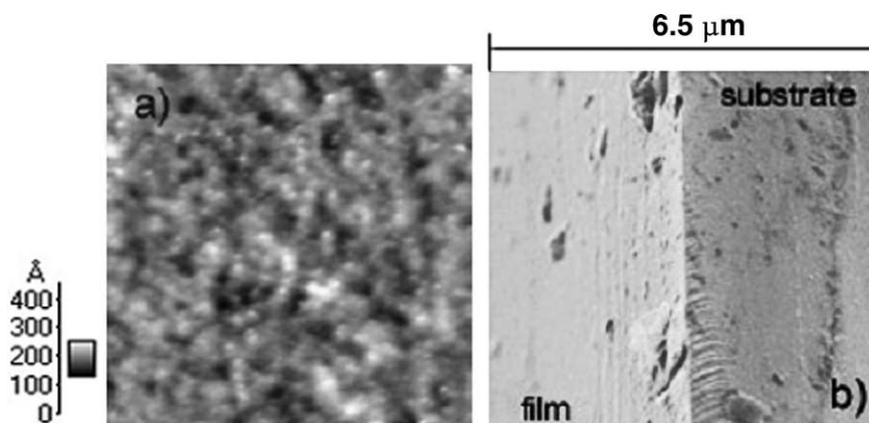


Fig. 6. Noncontact mode AFM image ((a); scan size  $5 \mu\text{m}$ ) and SEM micrograph (b) of poly $\alpha$ -DCHD film on hydrophilic substrate.

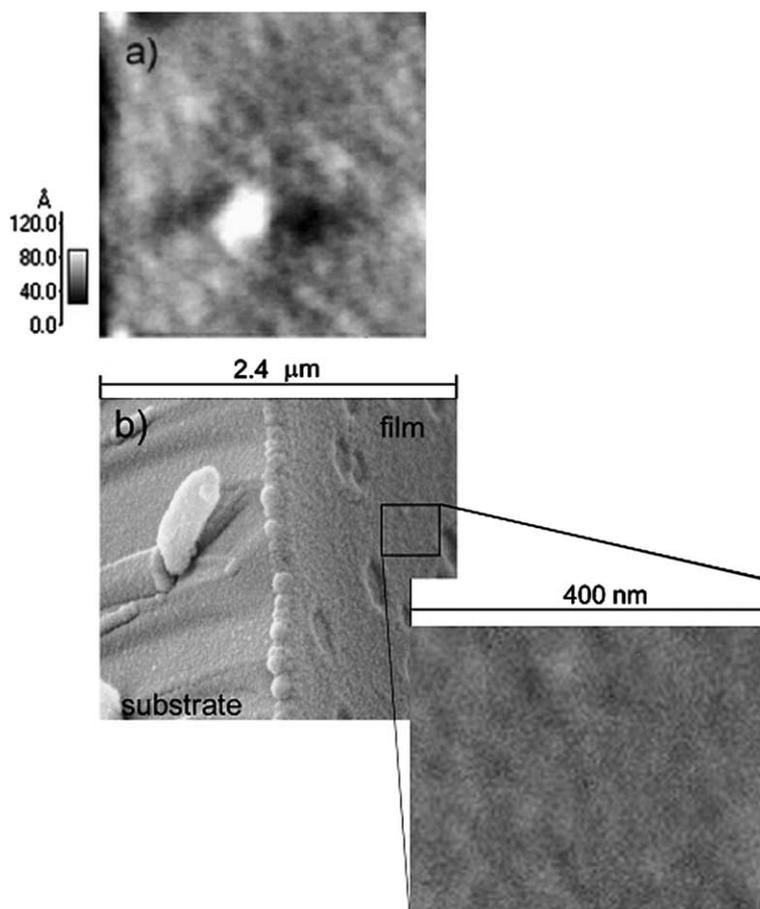


Fig. 7. Noncontact mode AFM image (a); scan size 3.5  $\mu\text{m}$ ) and SEM micrograph (b) of polyDPCHD film on hydrophilic substrate.

Table 1  
Surface roughness parameters (AFM) of PCDA films and their relative thickness (SEM)

Polymer	Substrate	Thickness (nm)	$R_{\text{rms}}$ (nm)	$R_{\text{m}}$ (nm)
PolyDCHD-HS	Hydrophilic	$150 \pm 20$	1.98	1.22
	Hydrophobic	$150 \pm 20$	3.16	1.88
Poly $\alpha$ -DCHD	Hydrophilic	<20	3.30	2.37
PolyDPCHD	Hydrophilic	$100 \pm 20$	1.26	0.78
Glass substrate	Hydrophilic	–	0.29	0.14
Glass substrate	Hydrophobic	–	0.14	0.07

The values of  $R_{\text{rms}}$  and  $R_{\text{m}}$  refer to a surface area of 10  $\mu\text{m}^2$ .

bottom of Table 1) should not affect the data on the polymers, when the film thickness is larger than 100 nm which is the case of polyDCHD-HS

and polyDPCHD. Indeed, our data show that the surface roughness is lower for the hydrophobic substrate than for the hydrophilic one while the

opposite is found for the polymeric films, and that the types of nanostructured clusters formed upon deposition on the different substrates are dependent on their chemical nature.

#### 4. Conclusions

In this paper we found that thin films of polycarbazolyldiacetylenes 3,6-substituted with long alkyl and acyl groups on the carbazolyl ring show the presence of nanosized nodules of similar diameter but organized in supra-aggregated particles whose length, shape and orientation depend on the type and the number of the substituents. In addition, also the surface properties of the substrate could determine the film morphology, as evidenced for polyDCHD-HS. Film thickness can play some role on the dimensions of supra-aggregates as testified by the comparison of the SEM micrographs of thin and thick samples of polyDCHD-HS, prepared under different experimental conditions. The diffraction measurements carried out on multi-layer films of the same polymer having a sufficient thickness for GIXRD experiments show the presence of local lamellar mesophases. The low intensity of the diffraction peaks agrees with the absence of long-range order in the films deduced from the isotropic optical characteristics previously detected. It is likely that the local lamellar structure may be a general property

of these PCDA's also when the film thickness is smaller.

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