Optical waveguiding in doped poly(methyl methacrylate)

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Poly(methyl methacrylate) doped with the photoinitiators benzil and benzildimethylketal is dissolved in the monomer MMA. From the solutions, planar waveguides and optically-recorded strip waveguides are fabricated on quartz substrates. Mode spectra and total losses are investigated and indicate a minimum loss value of about 0.015 dB mm^{-1} for photoinitiator concentrations of about 10%. The results also point to a considerable influence of surface irregularities.

(Keywords: optical waveguiding; poly(methyl methacrylate); photopolymerization; optical losses; strip waveguides)

INTRODUCTION

Refractive index patterns can be recorded in transparent organic materials using u.v.-light, either via standard photoresist techniques with masks or via laser beam writing[1,2]. For sufficiently large index changes these patterns may be utilized for waveguiding structures in integrated optical devices.

Poly(methyl methacrylate) (PMMA) films doped with the photoinitiators benzil or benzildimethylketal were investigated in a previous paper[3]. Refractive index changes up to 5×10^{-2} have been obtained by u.v.-illumination, demonstrating the capabilities of the material.

In this paper we study the applicability of these highly-doped PMMA films as strip waveguides recorded by light. The losses in planar waveguiding films are investigated with particular attention to the influence of the photoinitiator. On the basis of these results strip waveguides are optically recorded and examined.

EXPERIMENTAL

PMMA blocks were fabricated by polymerization of methyl methacrylate (MMA) at 50°C using the initiator azobisisobutyronitril (AIBN) in low concentrations (200 mg dm^{-3}). The blocks were heated to 100°C to decompose residual AIBN and then polymer solutions [0.5–1.0 wt%] were prepared by dissolving the blocks in purified MMA. Benzil or benzildimethylketal was added to the solutions in the concentration range 3–50 wt% (related to polymer plus photoinitiator). The refractive index of the solutions was measured with an Abbe refractometer.

The solutions were purified using a filter of 0.5 μm pore size. The polymer films were deposited on quartz glass plates, 2.5×7.5 cm^2, by evaporating the solvent for 72 h in a desiccator under a clean bench. The waveguides were considered to be 'dry' when the weight loss due to monomer evaporation was $< 1\%$ per day.

Strip waveguides in these films were fabricated by u.v.-illumination using photomasks with strip widths of 11–100 μm and strip lengths of ≈ 50 mm. Keeping the samples at 100°C for 24 h increased the refractive index difference Δn between illuminated and dark areas. Using this method, Δn-values up to 5×10^{-2} have been obtained[3].

The photoinitiator concentrations in the polymer films were determined from the absorption spectra recorded with a Cary 17D spectrometer. These measurements yielded additional information on the film thicknesses.

Waveguiding measurements were carried out using a 15 mW HeNe laser (632.8 nm) for both polarization states, TE and TM. Refractive index and film thickness of the planar waveguides were determined from the mode spectra[4]. Film thicknesses varied between 2 and 5 μm, so that at least two coupling angles for guided modes were obtained. The values of refractive index, n, and thickness, d, were fitted according to the mode equation, to the experimental data, assuming a constant value of n across the film thickness.

Loss was measured by the two prism method without using a liquid for index matching. Light was coupled out of the waveguide by a prism brought to various positions. A simpler method was also used: the attenuation was estimated by measuring the light scattered out of the waveguide with the help of an array camera containing 1024 pixels in^{-1}. However, this method was very sensitive to additional stray light and misalignments of the optical system. However, with this method, no contact behind the incoupling prism was needed to prevent polymer scratching or other damage.

RESULTS

Planar waveguides

The results from measuring optical losses in planar waveguides by the two prism method are shown in *Figure 1* for different TE modes. The measured intensity values can be fit rather well on straight lines, indicating a constant efficiency for the various positions of the out-coupling prism. The attenuation values are deduced from the slopes of these straight lines. Standard deviations between 2 and 20% were obtained, strongly depending on the quality of the waveguide.

The preparation conditions of the planar waveguides indicate a marked influence of the film surface (the

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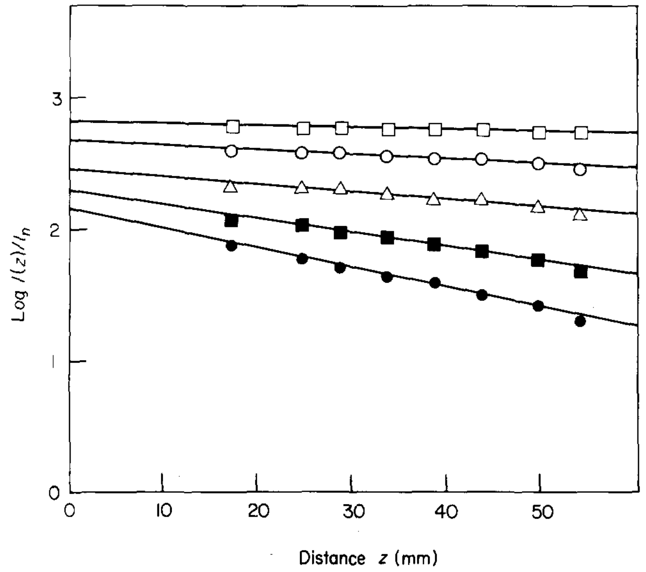

Figure 1 Logarithmic plot of relative intensity vs. distance z in a planar PMMA-waveguide doped with 10% benzil: □, TE mode 0; ○, TE mode 1; △, TE mode 2; ■, TE mode 3; ●, TE mode 4. The normalizing intensity I_N is chosen as 1 mW mm^{-2}

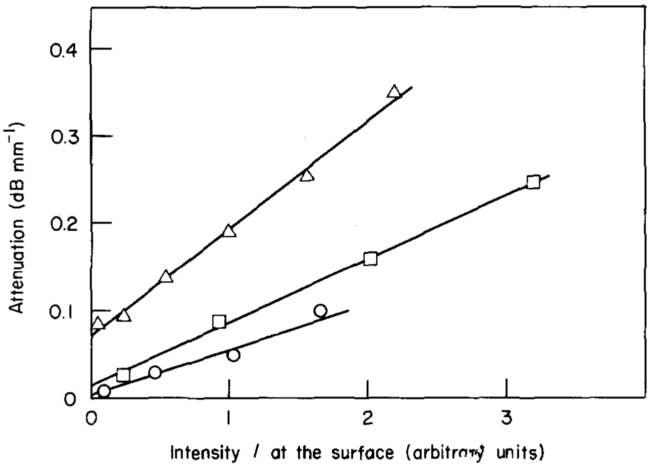

Figure 2 Light attenuation (TE modes) in different planar waveguides vs. light intensity I_s at the surface (boundary film/air): ○, PMMA+10wt% benzil; □, PMMA+20wt% benzil; △, PMMA+30% benzil

boundary film/air), because in this region refractive index fluctuations are produced by evaporation of the monomer. To check this the electrical fields, E_s, and the intensities, I_s, of the modes at the surface were calculated from the mode equation. The attenuation values of different modes were then plotted for several waveguides as a function of the intensity, I_s, at the surface, examples are given in *Figure 2*. The dependence may be approximately described by a linear increase of attenuation with increasing intensity, I_s, indicating that a considerable part of the losses results from surface scattering.

Light scattering also leads to intermodal coupling, diminishing the intensity of a certain mode. We confined ourselves to weak coupling effects and to a two-mode waveguide. If mode 0 (intensity I_0) is propagating in the waveguide then mode 1 (intensity I_1) is excited by intermodal coupling. Rough estimation yields for the intensities $I_0(z)$ and $I_1(z)$ the expressions[5]:

$$I_0(z)=A_0\exp[-(a_{00}+a_{01})z] \tag{1}$$

$$I_1(z)=A_0\{a_{01}/(a_{00}+a_{01})\}\times\{1-\exp[-(a_{00}+a_{01})z]\} \tag{2}$$

The parameters a_{00} and a_{01} describe the attenuation of mode 0 and the intermodal coupling, respectively. If we start with the propagating mode 1 the numbers 0 and 1 should be changed to 1 and 0 in the above equations.

Experimental results are summarized in the *Figures 3* and *4*. The intensities I_0 and I_1 are measured as a function of the distance z starting with propagating modes 0 and 1, respectively. The solid lines represent a fit to the experimental data according to the equations (1) and (2) with

$$a_{00}=1.09\cdot10^{-2}\,\mathrm{mm}^{-1}$$
$$a_{01}=6.8\cdot10^{-4}\,\mathrm{mm}^{-1}$$
$$a_{11}=1.88\cdot10^{-2}\,\mathrm{mm}^{-1}$$
$$a_{10}=2.7\cdot10^{-3}\,\mathrm{mm}^{-1}$$

The results indicate that losses due to intermodal coupling are relatively small. However, it should be noted that the strong influence of surface scattering is also confirmed by these measurements, i.e., scattering from mode 0 into mode 1 is considerably smaller than from

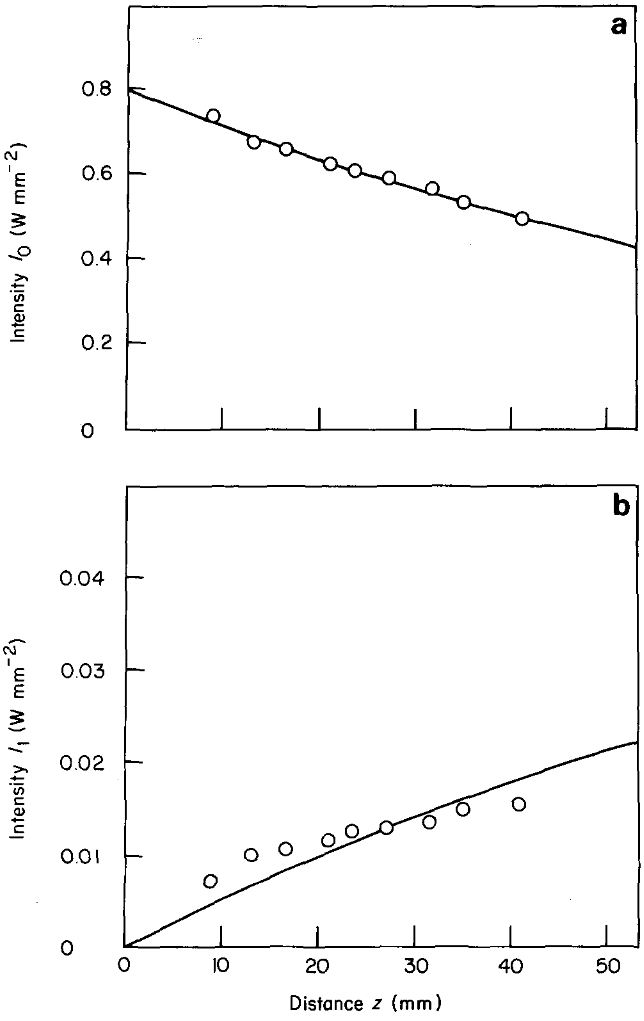

Figure 3 Intensity I_0 of a propagating mode 0 (a) and intensity I_1 of mode 1 excited by intermodal coupling (b) vs. distance z in a planar PMMA-waveguide with 7wt% benzildimethylketal. ○, Measured values; ——, lines drawn according to the equations (1) and (2)

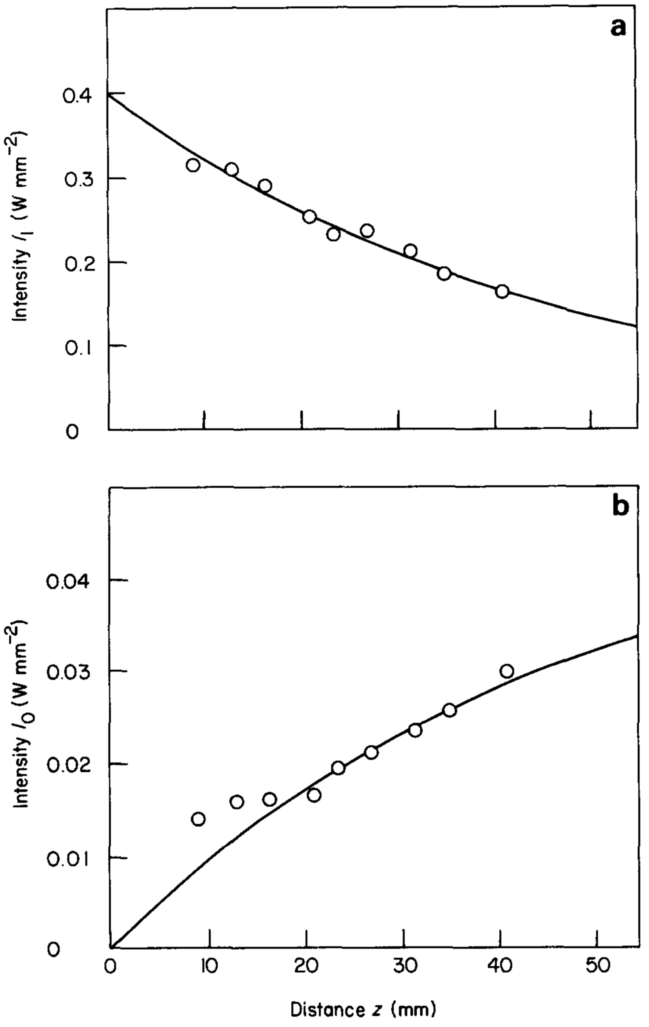

Figure 4 Intensity I_1 of a propagating mode 1 (a) and intensity I_0 of mode 0 excited by intermodal coupling (b) vs. distance z in a planar PMMA-waveguide with 7wt% benzildimethylketal. ○, Measured values; ———, lines drawn according to the equations (1) and (2)

mode 1 into mode 0.

Of great importance for optically-recorded waveguiding structures is the influence of the photoinitiators, benzil and benzildimethylketal, on the losses. During the illumination of benzildimethylketal there is some evidence of temporary formation of benzil, so that both photoinitiators may be treated similarly. The final photochemical products are of interest for optical applications, because they show a large increase in refractive index, are less volatile than pure MMA in PMMA-films and lower the tendency to crystallize[3].

The attenuation in doped PMMA films as a function of photoinitiator concentration is shown in *Figure 5* before illumination. The results relate to TE 0, the behaviour of higher modes is analogous. It is clearly seen that the smallest losses, of the order of 0.015 dB mm^{-1}, are obtained for a photoinitiator concentration of $\approx 10\%$. In the case of pure PMMA films (no photoinitiator) the attenuation values are always larger than 0.05 dB mm^{-1}.

Similar results are obtained after u.v.-illumination (*Figure 6*). The exposure time is chosen to be large enough to allow full photochemical reaction. For all photoinitiator concentrations no significant changes compared to the behaviour before illumination were obtained.

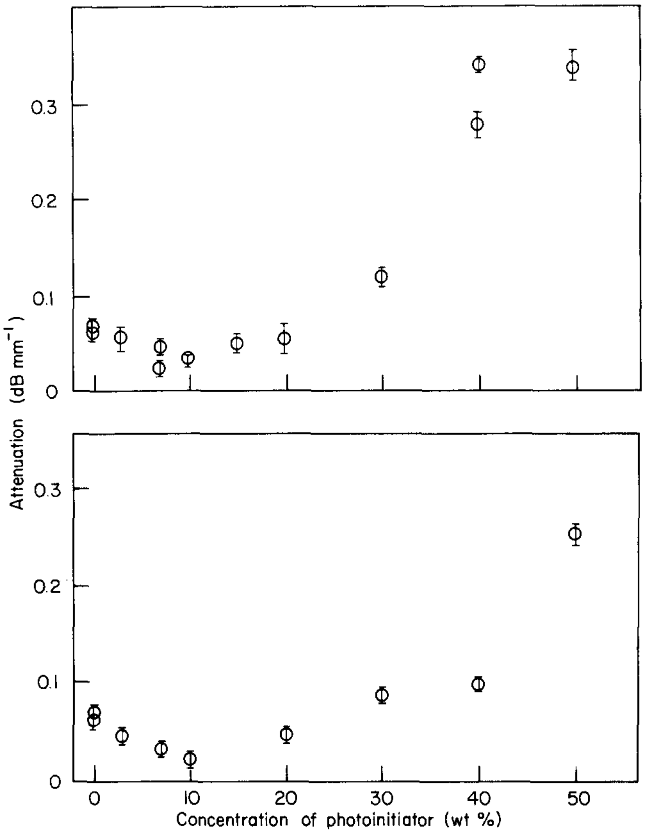

Figure 5 Light attenuation of mode TE 0 in a planar waveguide vs. concentration of the photoinitiators benzildimethylketal (a) and benzil (b) before u.v.-illumination

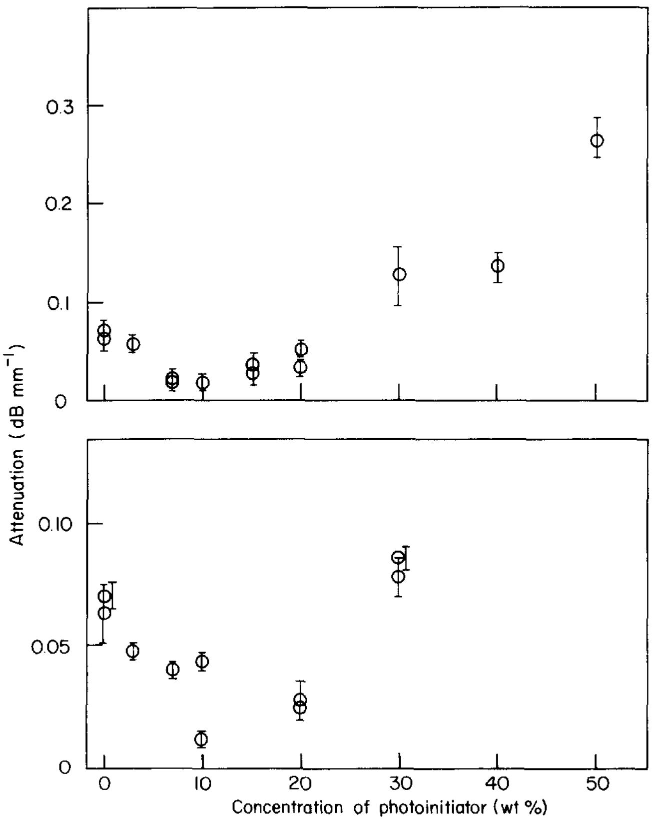

Figure 6 Light attenuation of mode TE 0 in a planar waveguide vs. concentration of the photoinitiators benzildimethylketal (a) and benzil (b) after u.v.-illumination

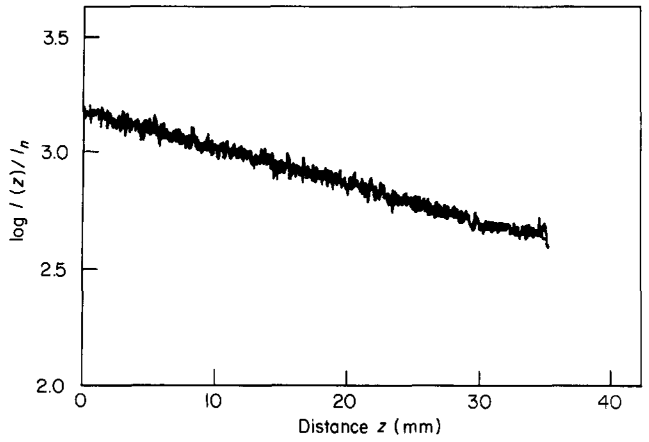

Figure 7 Logarithmic plot of relative intensity $I(z)/I_N$ (I_N in arbitrary units) of scattered light vs. distance z for the lowest mode in a strip PMMA-waveguide doped with 15 wt% benzildimethylketal (thickness, $d = 2.6\,\mu m$; width, $w = 30\,\mu m$)

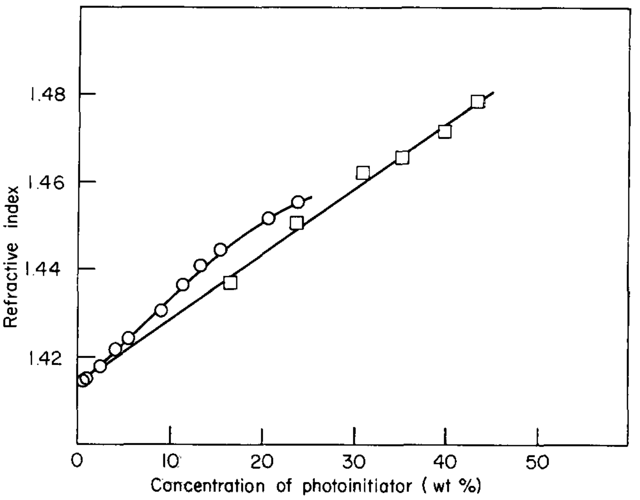

Figure 9 Refractive index of solutions vs. photoinitiator concentration: ○, MMA/benzil; □, MMA/benzildimethylketal. The index values relate to $\lambda = 589$ nm

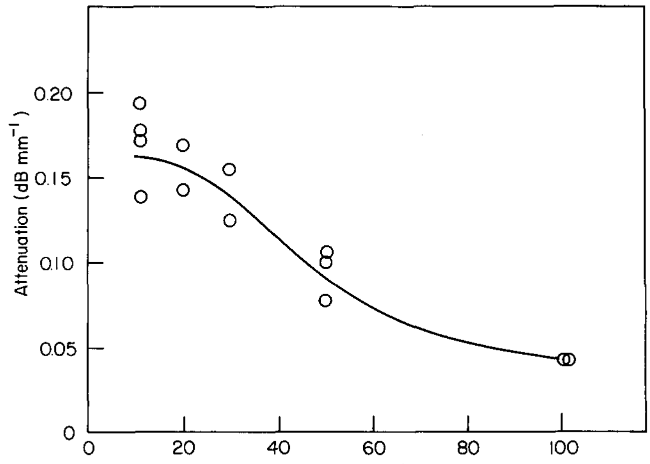

Figure 8 Light attenuation of the lowest mode in strip PMMA-waveguides doped with 15 wt% benzildimethylketal vs. strip width

Strip waveguides

The results obtained for planar waveguides are utilized for optical recording of strip waveguides. In these cases, measuring the attenuation with the help of the two prism method is unfavourable because the strips are easily damaged by the outcoupling prism. Therefore, the attenuation was deduced from the scattered light monitored by an array camera (see *Figure 7*). This method leads to standard deviations between 5 and 20%.

For the optically-recorded strip waveguides we choose PMMA containing 15% benzildimethylketal. The photoinitiator concentration of 10%, which leads to the smallest losses in planar guides, was not used because rather low refractive index changes were obtained.

The losses of the fundamental mode in strip waveguides with widths from 11 to 100 μm are given in *Figure 8*. The thicknesses of the samples varied between 2.5 and 3 μm. The losses decreased with increasing strip width, as expected. For strips of 11 μm width, attenuation values of about 0.17 dB mm^{-1} were obtained.

DISCUSSION

The experimental results clearly point to a considerable influence of surface irregularities on the attenuation in planar PMMA waveguides. By doping with photoinitiators of suitable concentrations ($\approx 10\%$ benzil or benzildimethylketal) the losses may be reduced to values of ≈ 0.015 dB mm^{-1} for the TE 0 mode. The reduction seems to originate from surface as well as from bulk effects. A similar behaviour, as indicated in *Figure 2*, is observed in most cases. Waveguides with small loss values of mode 0 also yield the smallest slopes of attenuation with increasing mode number.

There are some plausible reasons for this behaviour. Dissolving benzil or benzildimethylketal in MMA increases the refractive index of the solution with concentration, as illustrated in *Figure 9*. For saturated solutions the index values approach that of solid PMMA ($n = 1.49$). Additional investigations show that the boiling point of the saturated photoinitiator/MMA solution is raised to 120°C making MMA less volatile.

The usual 'dry' samples deposited from MMA solutions contain up to 20 wt% residual MMA. The photoinitiator content is about the same order of magnitude and the refractive index of the saturated solution is almost the same as that of solid PMMA. Thus fluctuations of the refractive index are reduced and scattering losses are less because of index matching of the liquid phase to the solid phase. Photochemical reactions seem to have little influence on the optimal concentration.

Furthermore the so-called photolocking process of the index matching phase should be mentioned. The final reaction products are less volatile and reduce surface irregularities by diminishing monomer evaporation. For large photoinitiator concentrations, however, crystallization processes also have to be taken into account, especially with respect to surface effects.

Strip waveguides recorded optically in these films exhibit loss values of the order of 0.17 dB mm^{-1} for strips of 11 μm width. The difference, compared with planar structures, indicates considerable influence of guide geometry and, again, of surface effects on light attenuation.

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