

# Orientation of flexible probes dissolved in deformed networks

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The orientation of 9,10-di-n-alkylanthracene probes dissolved in *cis*-1,4-polyisoprene networks was determined at different degrees of network extension. Orientation measurements were carried out by the fluorescence polarization method. The orientation of network chains containing anthracene groups was determined independently. Results of the measurements show that the n-alkyl probes are orientationally coupled to the network chains. The degree of coupling increases linearly with the length of the probe chain and is independent of the extension ratio over a wide range. This observation differs from the results of recent orientation measurements of rigid rods dissolved in similar networks, in which the degree of orientational coupling is inversely proportional to rod length and increases strongly with the extension of the network.

(Keywords: *cis*-1,4-polyisoprene; fluorescence polarization; fluorescent probes; segmental orientation; local orientational coupling)

## INTRODUCTION

Local orientational correlations between neighbouring chain segments and between solvent and chain segments in an amorphous polymeric system have been studied by various experimental techniques. The existence of orientational correlations has been observed in depolarized Rayleigh scattering<sup>1-3</sup>, strain<sup>4-12</sup> and electric<sup>13,14</sup> birefringence, deuterium n.m.r.<sup>15-18</sup> and fluorescence polarization<sup>19</sup> experiments. Analysis of data from the various experiments shows that (i) intermolecular orientational correlations between chain segments are significant in amorphous polymeric systems in the bulk state and diminish strongly upon dilution with isotropic solvents and (ii) orientational correlations of solvent molecules with segments of the polymer chains depend predominantly on the shape anisotropy of the solvent molecule. The extent of correlations among the solvent molecules and the chains has been observed to be significant even with solvent molecules of low anisotropy and at high degrees of dilution. This latter effect is of special interest because various aspects of intermolecular correlations may be analysed by varying the type and size of the solvent molecule. A permanently crosslinked network forms a suitable medium for such an analysis inasmuch as the equilibrium orientations of chains can be adjusted by the application of a macroscopic state of strain. Furthermore, the amount of solvent molecules may be controlled precisely in a network.

The specific aim of this study is to analyse orientational correlations between unattached flexible probes of different lengths and network chains at various degrees of uniaxial extension of the network. The strength of

orientational correlations may be described conveniently by the 'coupling function',  $f$ , defined as<sup>20</sup>:

$$f = S_u/S \quad (1)$$

where  $S_u$  and  $S$  are the orientation functions of the unattached flexible probes and the network chains, respectively. The orientation function is defined in general as:

$$S = (3\langle \cos^2\theta \rangle - 1)/2 \quad (2)$$

where  $\theta$  is the angle between the direction of stretch and the direction of the segment whose orientation is under study, and the angular brackets denote averaging over all such segments. In the present experimental investigation the function  $S$  of equation (1) is obtained by averaging over the orientations of 9,10-dimethylanthracene groups attached to a few of the network chains (Figure 1a).  $S_u$  is obtained by averaging over the orientations of the anthracene groups of the 9,10-di-n-alkylanthracene ( $C_n$ ) molecules (Figure 1b).

## MATERIALS AND METHODS

Samples were generously provided by Manufacture Michelin.

The polymer was an anionic commercial polyisoprene (Shell IR 307) with a high *cis*-1,4 configuration (92% *cis*, 5% *trans*) ( $T_g(\text{d.s.c.}) = -60^\circ\text{C}$ ) of high molecular weight ( $M_n = 46.3 \times 10^4$ ,  $M_w = 182 \times 10^4 \text{ g mol}^{-1}$ ). Samples were moulded and crosslinked with dicumyl peroxide. Crosslinking densities obtained by adjusting the curing time and temperature were characterized by the average molecular weight  $M_c$  of network chains (between adjacent junctions) derived from measurements of the equilibrium swelling ratio in cyclohexane and through the classical Flory-Rehner equation. After crosslinking, polymer

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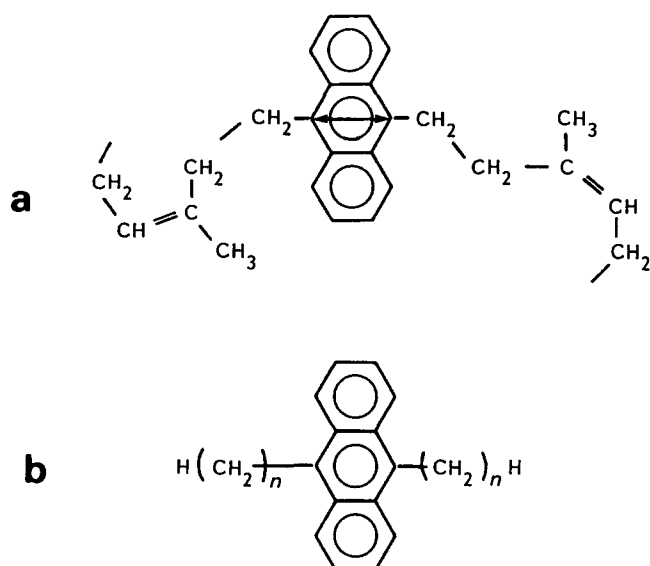
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sheets (2.4 mm thick) were carefully extracted with acetone for 15 h and then dried *in vacuo*.

#### Fluorescent probes

Crosslinked polymers characterized by an  $M_c$  value of  $1.6 \times 10^4 \text{ g mol}^{-1}$  were swollen with solutions of the probes in benzene and then dried *in vacuo*. The final probe concentration in bulk samples was approximately  $2 \times 10^{-5} \text{ M}$ .



**Figure 1** (a) 9,10-Dimethylanthracene-labelled polyisoprene; (b) 9,10-di-n-alkylanthracene,  $C_n$

#### Fluorescent label

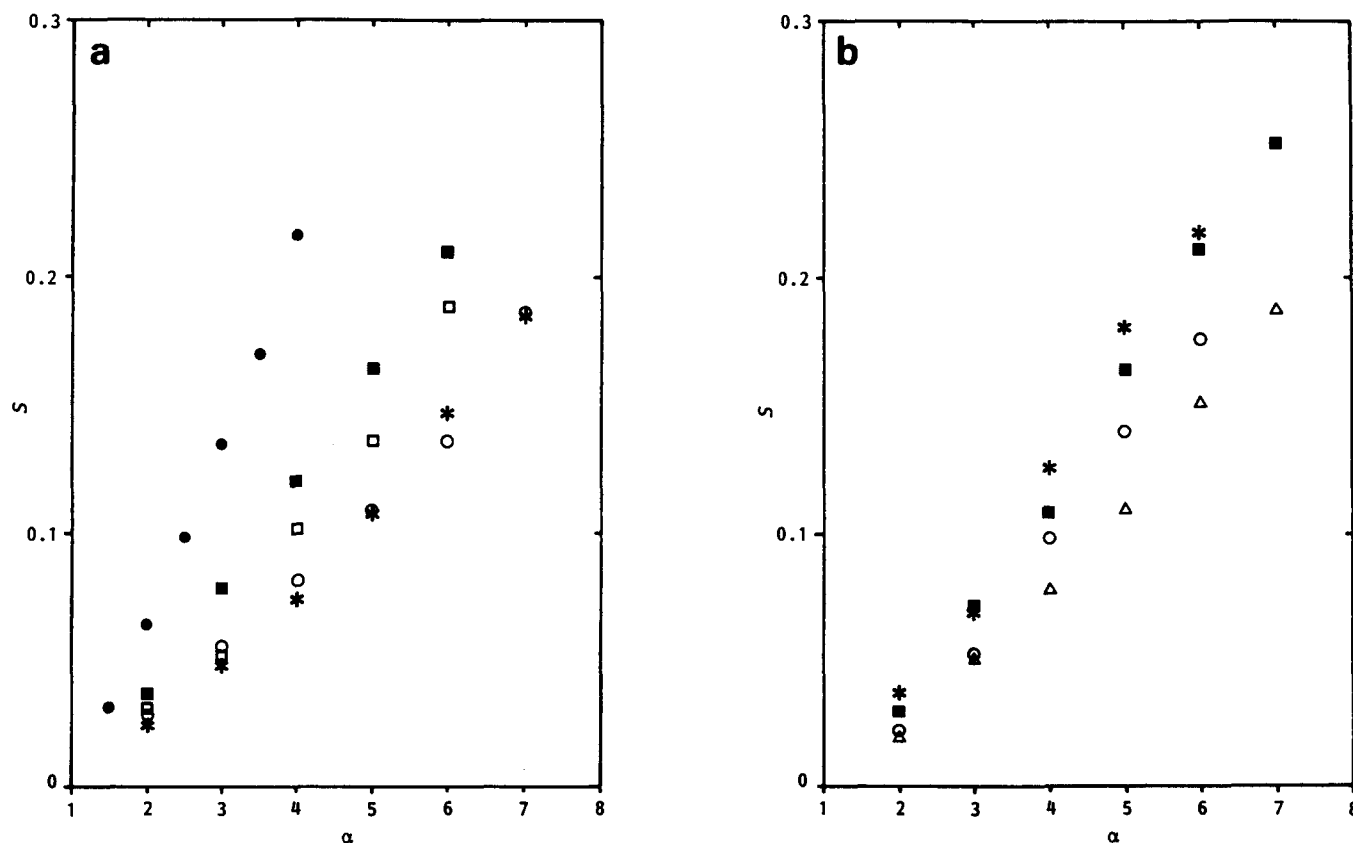
Polymer chains containing a dimethylanthracene (DMA) fluorescent group in the middle were prepared through monofunctional anionic chains deactivated with 9,10-bis(bromomethyl)anthracene<sup>21</sup>. Samples were obtained by mixing 1% of the labelled chains with 99% of IR 307.  $M_c$  values for these networks were  $1.5 \times 10^4 \text{ g mol}^{-1}$ .

The fluorescence polarization apparatus has been described elsewhere<sup>22</sup>. Measurements of fluorescent label and probe orientation  $S$  as a function of extension ratio  $\alpha$  (defined as the ratio of the deformed length to the undeformed length of the sample) were done during uniaxial stretching at constant crosshead speed,  $V = 50 \text{ mm min}^{-1}$ , and a temperature of 298 K. The reference dimensions of the samples employed in stretching were ca.  $50 \times 20 \times 2 \text{ mm}^3$ . Within experimental accuracy, no relaxation of  $S$  with time was observed when the samples were held at a fixed  $\alpha$  value. Thus the orientation function  $S$  can be considered to be measured at equilibrium.

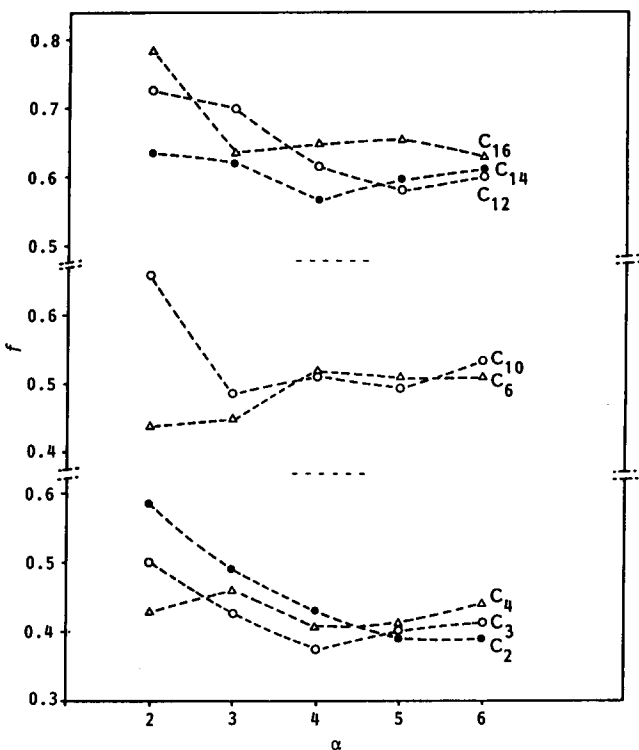
#### RESULTS AND DISCUSSION

Orientation functions  $S$  of anthracene label and probes are reported in *Figures 2a* and *2b* as a function of extension ratio  $\alpha$ .

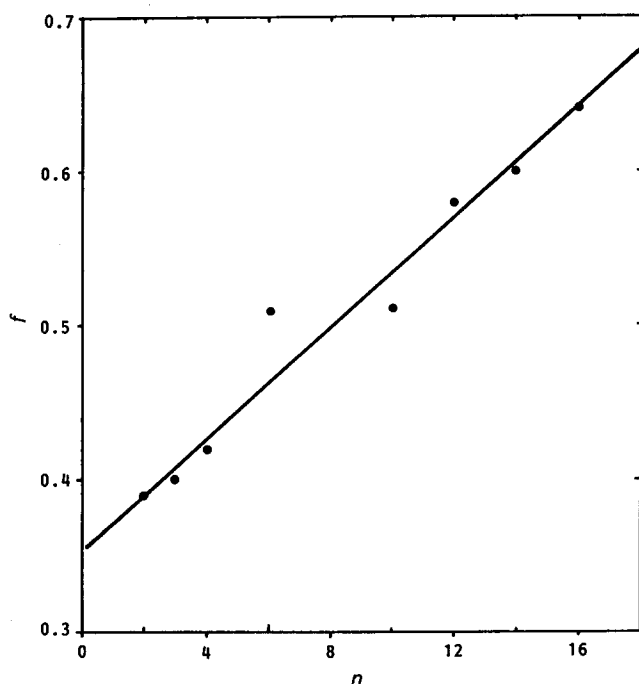
Values of the coupling function  $f$ , obtained as the ratio of the measured orientation function of the free probes to that of the network chains, are presented in terms of the extension ratio  $\alpha$  in *Figure 3*. Points denote the experimentally obtained values. Points belonging to each  $C_n$  group are connected by broken lines to guide the eye.



**Figure 2** Orientation function  $S$  presented in terms of extension ratio  $\alpha$ : (a) 9,10-dimethylanthracene-labelled polyisoprene network (●) and 9,10-di-n-alkylanthracene probes  $C_2$  (○),  $C_3$  (\*),  $C_{10}$  (□) and  $C_{12}$  (■); (b) 9,10-di-n-alkylanthracene probes  $C_4$  (△),  $C_6$  (○),  $C_{14}$  (■) and  $C_{16}$  (\*)



**Figure 3** Values of the coupling function  $f$  in terms of the network extension ratio  $\alpha$ . Points denote experimental data for the various  $C_n$  probes identified on the right-hand side of the figure. Experimental points belonging to the same  $C_n$  are joined by dotted lines



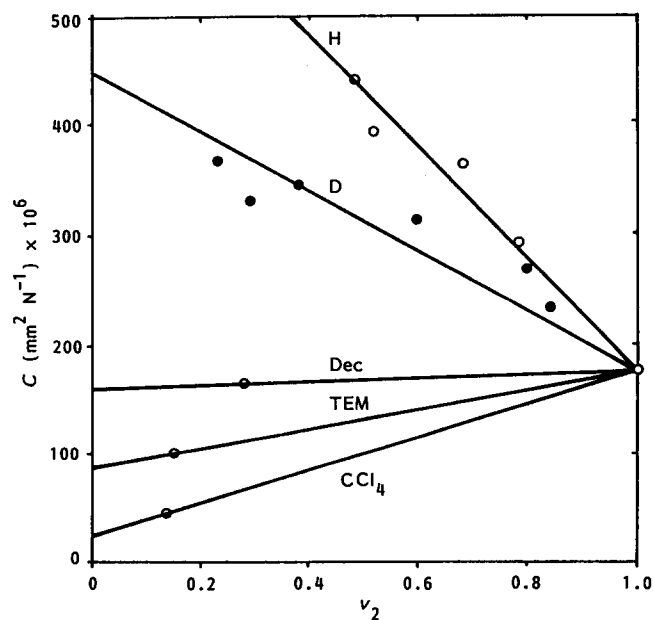
**Figure 4** Values of  $f$  obtained from the high extension part of the data of Figure 3, presented as a function of probe length  $n$ . The straight line is the least-squares line through the experimental points

Results are presented in three sets for the sake of clarity. In general, values of  $f$  tend to a constant value at high strains. Discrepancies observed at low values of  $\alpha$  for the various  $C_n$  probes could possibly originate from inaccuracies of the fluorescence polarization measurements at low deformations. Thus, within experimental accuracy, it can be concluded from Figure 3 that  $f$  is

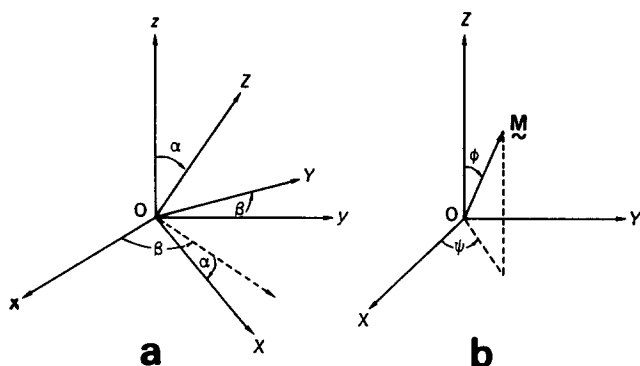
independent of  $\alpha$  for  $\alpha \geq 3$ . Values of  $f$  at high  $\alpha$ , obtained from Figure 3, are shown in Figure 4 as a function of the number of carbon bonds. Points denote the experimental data. In this high  $\alpha$  range an accuracy around 10% of  $f$  can be obtained. The full line is obtained by a least-squares fit to the data points. That the degree of coupling is proportional to the length of the probes can be clearly seen from Figure 4.

Review of the literature cited in the 'Introduction' shows that the coupling of the free probes to network chains essentially originates from and can be analysed in terms of orientational correlations between a single network chain and a single probe. This conclusion is supported by the data shown in Figure 5, reproduced from ref. 12. Ordinate values denote stress-optical coefficients of poly(dimethylsiloxane) (PDMS) networks obtained at various degrees of swelling in solvents of different shape anisotropies. The volume fraction of polymer,  $v_2$ , is shown along the abscissa. The solvents used are denoted on each curve in the figure. It is worth while to notice that the behaviour obtained with the isotropic carbon tetrachloride solvent leads to an intercept at  $v_2=0$  which may be considered as the stress-optical coefficient of a single network chain free of orientational correlations. Differences in the stress-optical coefficient  $C$  in the highly swollen state, i.e. low values of  $v_2$ , are indicative of orientational correlations between solvent and network molecules. Inasmuch as correlations between network chains are reduced to a minimum in the highly swollen state, the enhancement of  $C$  at this state can be attributed mainly to the solvent-network chain interactions. It is interesting to note from Figure 5 that the two solvents, tetraethylmethane and decalin, with relatively low anisotropies of shape enhance the  $C$  values significantly.

Oriental correlations between a chain and a solvent molecule can be analysed if the orientation



**Figure 5** Effect of solvent on the stress optical coefficient  $C$  of PDMS networks.  $v_2$  is the volume fraction of polymer present during the experiment. The solvents used are: H, hexadecane; D, dodecane; Dec, decalin; TEM, tetraethylmethane; and  $\text{CCl}_4$ , carbon tetrachloride (from ref. 12)



**Figure 6** Various coordinate systems for describing the orientation of the probe molecule.  $Oxyz$  and  $OXYZ$  are the laboratory- and network-chain-fixed systems, respectively.  $M$  denotes the direction of the probe

function of the probe can be expressed in terms of the orientation function of the network. Let the  $Oxyz$  coordinate frame in *Figure 6a* be the laboratory fixed frame where the  $z$  axis denotes the direction of extension of the network. Let the  $OXYZ$  coordinate system be affixed to the network chain whose interaction with a solvent molecule is being investigated. We assume that the  $Z$  axis contains the major axis of the chain segment at the point of contact with the solvent molecule. The system  $OXYZ$  is related to  $Oxyz$  by the Euler angles  $\alpha$  and  $\beta$ . They are chosen such that the axes  $zZX$  form a plane. The axis of cylindrical symmetry, i.e. the major axis of the solvent molecule, is denoted by the vector  $M$  in *Figure 6b*. The angles  $\phi$  and  $\psi$  denote the azimuthal and polar angles, respectively, of the vector  $M$  with respect to the coordinate system  $OXYZ$ . The chain segment performs orientational motion relative to the fixed reference frame as a result of which the angles  $\alpha$  and  $\beta$  change. The solvent molecule performs orientational motion relative to the chain, as a result of which the angles  $\phi$  and  $\psi$  change.  $S_u$  may be expressed in terms of the angles  $\alpha$ ,  $\phi$  and  $\psi$  by the use of Wigner rotation matrices<sup>23</sup> as:

$$S_u = \langle (3 \cos^2 \alpha - 1)(3 \cos^2 \phi - 1)/4 \rangle + \frac{3}{4} \langle \sin^2 \alpha \sin^2 \phi \cos(2\psi) \rangle - 3 \langle \sin \alpha \cos \alpha \sin \phi \cos \phi \cos \psi \rangle \quad (3)$$

The angle  $\beta$  does not appear in the averages in equation (3) for uniaxial deformation. If the angular variables  $\alpha$ ,  $\phi$  and  $\psi$  are uncorrelated, equation (3) reduces to the simple form:

$$S_u = \langle 3 \cos^2 \alpha - 1 \rangle / 2 \langle 3 \cos^2 \phi - 1 \rangle / 2 = f_0 S \quad (4)$$

where

$$f_0 = \langle (3 \cos^2 \phi - 1) / 2 \rangle \quad (5)$$

Here  $f_0$  denotes the orientation of the unattached probe relative to the chain segment. It reflects the degree of coupling of the probes to the chains and is identical to the coupling function  $f$  defined previously, provided that the angular variables  $\alpha$ ,  $\phi$  and  $\psi$  are uncorrelated. If the probe is rigidly attached to the chain segment in such a way that its major geometrical axis lies along the  $Z$  direction, then  $f_0 = 1$  and  $S_u = S$ . In the opposite extreme, if the major

geometrical axis of the probe is always directed perpendicular to the chain segment, then  $f_0 = -\frac{1}{2}$  and  $S_u = -\frac{1}{2}S$ .

It is worth noting that, depending on the experimental technique used to measure the probe orientation, the direction of the vector involved in the technique considered (e.g. transition moment in fluorescence polarization, C-D bond in deuterium n.m.r.) may deviate from the major geometrical axis of the probe molecule. In this case, equation (5) should be modified to:

$$f_0 = [(3 \cos^2 \chi - 1)/2] \langle (3 \cos^2 \phi - 1)/2 \rangle \quad (6)$$

where  $\chi$  specifies the direction of the vector under consideration relative to the major geometrical axis of the probe.

The simple expression given by equation (4) obviously is not valid when the angles  $\alpha$ ,  $\phi$  and  $\psi$  are correlated. Such correlations would result, for example, if the coupling of the probe to the chain increases with orientation of the network. In this case,  $S_u$  in equation (3) may be expressed in powers of  $S$  as:

$$S_u = f_0 S + f_1 S^2 + f_2 S^3 + \dots \quad (7)$$

where the coefficients  $f_1, f_2, \dots$  represent deviations from equation (4) due to correlations among the angles  $\alpha$ ,  $\phi$  and  $\psi$ . Equation (7) may be represented in the form of equation (1) by dividing both sides by  $S$ , i.e.

$$f = S_u/S = f_0 + f_2 S^2 \quad (8)$$

in which  $f_1$  is equated to zero inasmuch as minimum coupling should be obtained in the undistorted state of the amorphous network.

According to the data presented in this paper,  $f_2 = 0$ , denoting that correlations of probes are independent of the state of orientation of the network chains, and hence that the angular variables  $\alpha$ ,  $\phi$  and  $\psi$  are uncorrelated. Recent experimental data<sup>20</sup> presented on the orientation of rigid rods dissolved in similar networks show, however, that the  $f_2$  term in equation (8) is not small. According to experiments  $f_2$  is positive and is independent of the length of the three diphenyl polyene probes used. Contrary to the results of flexible probes,  $f_0$  was found to vary inversely with length of the rigid probes. Estimates based on statistical analysis of polyethylene chains<sup>24</sup> show that the average lengths of the  $C_n$  probes along the major direction vary in size between 0.8 and 1.7 nm for  $n = 2$  to 16. The lengths of the rigid polyene probes on the other hand were 1.15, 1.40 and 1.65 nm. This comparison indicates that the main difference between the observed behaviour of the  $C_n$  and polyene probes is in the flexibility of the former and stiffness of the other. Such stiffness could lead to selective correlations of the rod probes with specific configurational sequences of the *cis*-1,4-polyisoprene chains of the network<sup>20</sup>.

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