Stress Optical Behavior of Partially Fluorinated Aliphatic Polyesters

Regina C. Reiss-Nunes, Evaristo Riande,* Julio Guzmán, and Nelson A. Chavez

Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006 Madrid, Spain

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ABSTRACT: Thermoelastic networks were prepared by end-linking hdroxyl-terminated poly(neopentylglycol hexafluoroglutarate) using tris(*p*-isocyanate phenyl) thiophosphate as cross-linking agent. The plot of birefringence versus stress exhibits negative deviations from linearity at elongation ratios larger than 1.9. The value of the optical configuration parameter Δa is 2.98 Å^3 at 5 °C. Theoretical calculations carried out using the rotational isomeric state model give for this parameter the value of 2.24 Å^3, in fair agreement with the experimental results. The cause of the strong discrepancies between the theoretical and experimental results observed for the optical configuration parameter of polyesters containing phenyl groups in the acid residue is discussed.

Introduction

There is growing interest in the synthesis of polymers containing fluorine atoms in their structure. This interest arises from the desirable properties that the fluorine atoms confer to polymers, among them low surface energy, thermal stability, excellent dielectric properties, good chemical resistance, low water absorption, and weatherability. When incorporated into copolymers, fluorinated comonomers are usually enriched at the surface, thus reducing the surface energy of the material. Fluorinated moieties have been incorporated into polyurethanes, polyacrylates, silicones, polyimides, poly(aryl ether)s, etc.[1]

Fluorinated polyesters can be prepared by polycondensation of fluorinated dicarboxylic acid derivatives with either aliphatic or fluoroaliphatic diols. Some drawbacks of these polyesters are the relatively low amount of fluorine they possess and their hydrolytic instability.[2] This instability can, in principle, be circumvented by using diols of low acidity in the synthesis of polyesters. For example, diols of type $HOCH_2CH_2$-$(CF_2)_nCH_2CH_2HO$ can be used to obtain fluorinated polyesters with improved stability.[3]

Despite the obvious interest of fluorinated polymers, the studies on the conformational properties of these materials are scarce. Results have been reported showing that diesters obtained by esterification of fluorinated diacids have higher polarity than their hydrogenated counterparts.[4] This behavior arises from differences in the modulus and orientation of the dipoles rather than from differences in the rotational populations about their respective skeletal bonds. The comparative analysis of the dipole autocorrelation coefficients of poly(neopentylglycol hexafluoroglutarate) (PNGHFG) and poly(neopentyl glycol glutarate) (PNG) confirmed these results.[5] In this work, these studies are extended to the experimental and theoretical determination of the optical configuration parameter, Δa, of PNGHFG networks. Earlier theoretical calculations of Δa of polyesters containing ether groups in their structure, such as poly(diethylene glycol terephthalate) (PDET), carried out using the valence optical scheme (VOS), led to theoretical values of the optical configuration parameter much lower than the experimental ones.[6] Similar discrepancies were observed for other symmetric polymer chains. However, the analysis of the optical configuration parameter of poly(methyl acrylate)[7] and poly(vinyl acetate)[8] shows that the VOS reproduces both the negative sign and even roughly the values experimentally found for Δa. Good agreement between theory and experiment was found for the optical configuration parameter of poly(3-methyltetrahydrofuran).[9] To investigate whether the discrepancies between the theoretical and experimental values of Δa is a common characteristic of polyesters, we have undertaken in this work the experimental determination of the optical configuration parameter of PNGHFG. The value obtained for Δa is critically interpreted in terms of the rotational isomeric state model. Attention is also paid to the elastic characteristics of PNGHFG networks.

Experimental Section

Neopentyl glycol was purified by successive crystallizations from solutions of acetone/hexane (1/1) (mp 131 °C; lit. 130 °C). Hexafluoroglutaric acid was distilled at reduced pressure (bp 140 °C, 10^{-2} mmHg) obtaining a solid of melting point 89 °C.

Hydroxyl-terminated poly(neopentyl glycol hexafluoroglutarate) was synthesized by the standard melt phase procedure from stoichiometric quantities of neopentylglycol and hexafluoroglutaric acid, using tetraisopropyl titanate as catalyst. The reaction was carried out at 130 °C for 4 h, under magnetic stirring, and the water formed was eliminated by means of a continuous stream of dry nitrogen. Then an excess of neopentyl glycol was added to the reaction medium, and the polycondensation was allowed to proceed at 170 °C for an additional 6 h. The polyester was dissolved in chloroform, precipitated with methanol, and, finally, dried overnight, at 50 °C, in a vacuum oven. The number-average molecular weight of the polymer, measured in chloroform with a Knauer vapor pressure osmometer, was 7600. The glass transition temperature was measured with a DSC-7 Perkin-Elmer calorimeter at 10 °C/min. The value of T_g taken at the onset of the baseline was −17 °C.

Polymer networks were prepared by end-linking the hydroxyl-terminated PNGHFG chains with tris(*p*-isocyanate phenyl) thiophosphate. A solution of equivalent amounts of polymer and cross-linking agent in dried chloroform was cast in a Teflon mold. Once the solvent was removed by evaporation in a dried atmosphere at room temperature, the mixture of polymer and cross-linker was kept at 60 °C for 12 h in a vacuum. The soluble fraction of the resulting network was 0.21.

Thermoelastic and Birefringence Measurements. Strips of the network were mounted between two clamps, the lower one fixed and the upper attached to a Statham strain gauge.

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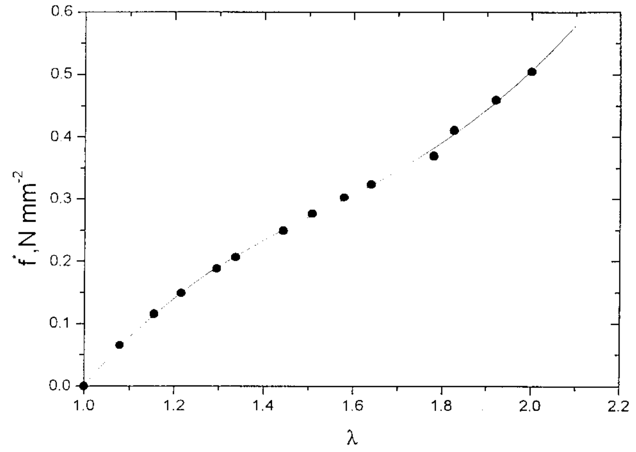

Figure 1. Dependence of the elastic force of poly(neopentylglycol hexafluoroglutarate) networks on the elongation ratio.

Stress–strain isotherms were obtained at 5 °C for a sequence of increasing values of elongation ratios, λ, and the elastic forces were recorded when they became sensibly constant.

Strain-birefringence experiments were performed using a 2 mW, 632.8 nm He–Ne laser. The analyzer and polarizer were Glan-Thompson prisms, and the compensator was of the Babinet Soleil type (Karl-Lambert K1148). The experiments were also carried out at 5 °C for a sequence of increasing values of λ, and the elastic forces and the birefringence for each elongation ratio were recorded when the stretched strips were completely relaxed.

Results

Values of the elastic force per undistorted cross-sectional area, f^*, are plotted as a function of the elongation ratio in Figure 1. It can be seen that the shape of the isotherm is similar to that of rubbery networks, though at high elongations, the modulus experiences an anomalous increase.Values of f^*, were also expressed in terms of the reduced stress $[f^*]$ or modulus defined as[10]

$$[f^*] = \frac{f^*}{\lambda - \lambda^{-2}} \tag{1}$$

where $\lambda = L/L_i$, L and L_i being respectively the lengths of the stretched and unstretched strips. Usually the reduced force for rubbers fits to the Money-Rivlin expression

$$[f^*] = 2C_1 + 2C_2\lambda^{-1} \tag{2}$$

where $2C_1$ and $2C_2$ are constants independent of the strain but dependent on the chain length between cross-linking points. An illustrative Money-Rivlin plot for PNGHFG networks is shown in Figure 2. It can be seen that $[f^*]$ is a linear function of λ^{-1} for relatively low values of the elongation ratio. However, for values of $\lambda^{-1} < 0.5$, the reduced force experiences an upturn or anomalous increase in the reduced force caused by either the development of crystallinity or maximum chain extensibility.

Strain-birefringence isotherms were analyzed in terms of the equation[11,12]

$$\frac{\Delta n}{\lambda - \lambda^{-2}} = 2B_1 + 2B_2\lambda^{-1} \tag{3}$$

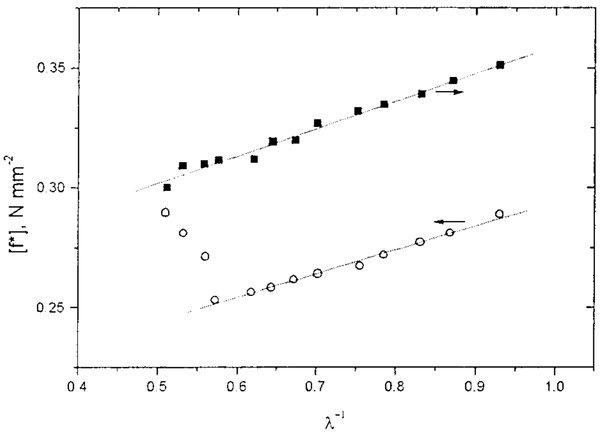

Figure 2. Mooney-Rivlin plots for the reduced force (○) and the reduced birefringence (■) of poly(neopentylglycol hexafluoroglutarate) networks.

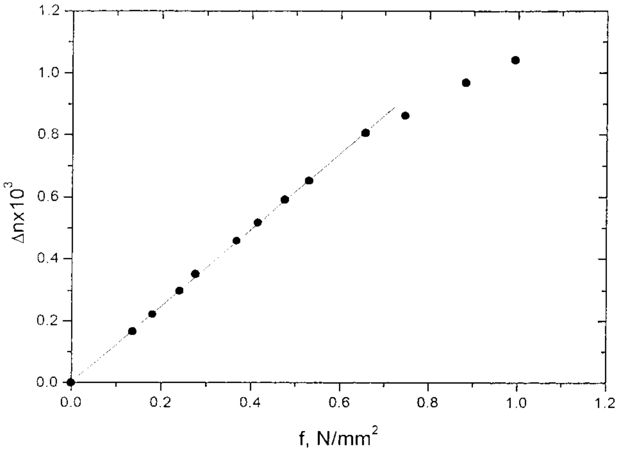

Figure 3. Illustrative plot showing the variation of the birefringence with the true stress of poly(neopentylglycol hexafluoroglutarate) networks at 5 °C.

where Δn is the birefringence referred to the stretched thickness of the sample and $2B_1$ and $2B_2$ are constants independent of the elongation ratio. In fact, these constants would correspond to the reduced birefringence of phantom and affine networks, respectively. As can be seen in Figure 2, the birefringence is a linear function of the reciprocal of the elongation ratio in the whole range of the values of λ measured. This behavior suggests the absence of crystalline entities in the stretched networks because their presence presumably would enhance the birefringence. Therefore, the upturn observed in the modulus at high elongations might be due to maximum chain extensibility rather than to reinforcing effects of crystalline entities.

Values of Δn against the true stress, f, are shown in Figure 3. It can be seen that the birefringence is a linear function of f until an elongation ratio is reached above which the results lie below the straight line. From the slope of the straight line, the stress optical coefficient C ($=\Delta n/f$) is obtained. The value of this quantity for PNGHFG networks is 1.22×10^{-10} cm^2/dyn at 5 °C.

The optical configuration parameter Δa is related to the stress optical coefficient by the standard equation[13,14]

$$\Delta a = \frac{45 k_B n T}{2\pi(n^2 + 2)^2} C \tag{4}$$

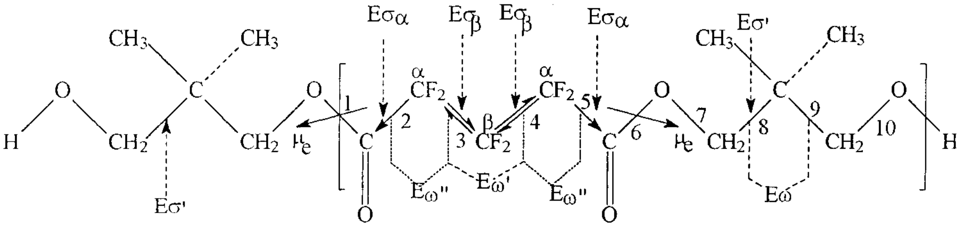

Figure 4. Schematic representation of hydroxyl-terminated poly(neopentylglycol hexafluoroglutarate) in all-trans conformation. First- and second-order conformational energies associated with gauche states about the skeletal bonds are indicated. Dipole moments corresponding to the ester moieties and the CF$_2$ groups are shown by arrows.

where k_B is the Boltzmann, T is the absolute temperature, and n is the index of refraction of the network. The value obtained for Δa at 5 °C is 2.98×10^{-24} cm^3.

Theoretical Calculations and Discussion

A schematic representation of the repeating unit of PNGHFG in its all-trans conformation is shown in Figure 4. The bond angles required in the calculations of the optical configuration parameter were defined as $\angle$CCO = 113°, $\angle$C*OC = 114°, and $\angle$C*CC = $\angle$CCC = 112°. The bond lengths used were $l_{C-C^*} = 1.51$ Å, $l_{C-C} = 1.53$ Å, $l_{C^*-O} = 1.36$ Å, and $l_{C-O} = 1.43$ Å. The rotational states for the C*$-$CF$_2-$CF$_2-$CF$_2-$C* bonds of the acid residue, calculated by using semiempirical potential functions, were taken to occur at 0°, ±120°. The same rotational angles were assumed for the C$-$C$-$C bonds of the alcohol residue, whereas the C*(O*)$-$O bonds of the ester group are restricted to the trans state.

The conformational energies used were taken from the analysis of the dipole moments of diethyl hexafluoroglutarate[4] and poly(neopentyl glycol hexafluoroglutarate).[5] Gauche states about CF$_2-$C*(O*) bonds of the acid residue have an energy $E_{\sigma\alpha}$ ca. 0.5 kcal mol^{-1} below that of the alternative trans states. However, the energy $E_{\sigma\beta}$ of gauche states about CF$_2-$CF$_2$ bonds is 0.7$-$1 kcal mol^{-1} above that of the corresponding trans states. The critical interpretation of the dipole autocorrelation coefficients of poly(neoptenyl glycol adipate)[15] and poly(neoptenyl glycol glutarate)[5] suggests that gauche states about the CH$_2-$C(CH$_3$)$_2-$CH$_2$ bonds of the alcohol residue have an energy $E_{\sigma'}$ 0.6 kcal mol^{-1} below that of the alternative trans states. Moreover, since gauche states about the CH$_2-$O bonds of the alcohol residue gives rise to strong repulsive interactions between a methyl and a carbonyl group, these bonds were considered to be restricted to the trans states. Finally, the second-order energies E_ω , $E_{\omega'}$, and $E_{\omega''}$ indicated in Figure 5 were assumed to have an energy 1.2 kcal mol^{-1} above that of the corresponding tt states.[5]

The optical configuration parameter is given by[13,14]

$$\Delta a = \frac{3}{2}\frac{\langle \mathbf{r}^T \hat{\alpha} \mathbf{r}\rangle}{\langle r^2\rangle_0} \tag{5}$$

where, as usual, brackets denote conformational averages, $\mathbf{r}$ is the end-to-end vector of the chains, $\mathbf{r}^T$ its transpose, and $\hat{\alpha}$ is the anisotropic part of the polarizability tensor. The evaluation of $\hat{\alpha}$ rests upon the additivity of the anisotropic polarizabilities of bonds or groups. The most important contribution to $\hat{\alpha}$ is associated with the diester part of the repeating unit that can be obtained from the traceless polarizability tensor of methyl acetate, as indicated below. This tensor is[16]

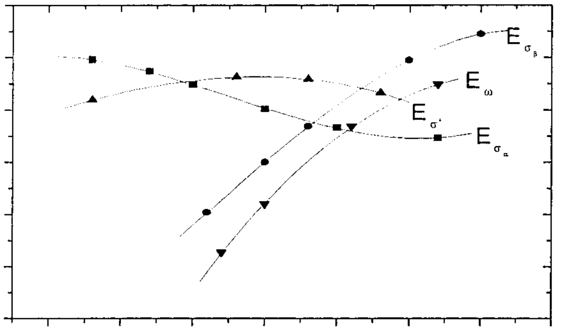

Figure 5. Theoretical results showing the variation of the optical configuration parameter of poly(neopentylglycol hexafluoroglutarate) networks with the values of the first- and second-order conformational energies.

$$\hat{\alpha}_E = \begin{pmatrix} 1.03 & -0.10 & 0 \\ -0.10 & 0.09 & 0 \\ 0 & 0 & -1.12 \end{pmatrix} = \Delta\alpha_E \mathbf{K} + \Delta\alpha_E^{+} \mathbf{L} + \begin{pmatrix} 0 & -0.1 & 0 \\ -0.1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{6}$$

where $\Delta\alpha_E = 1.545$ Å^3 and $\Delta\alpha_E^{+} = 1.21$ Å^3 in a coordinate system having the x axis in the direction of the C$-$C* bond and the y axis in the plane of the molecule. $\mathbf{K}$ and $\mathbf{L}$ are diagonal 3 × 3 matrices whose diagonal elements are ($^2/_3$, $-^1/_3$, $-^1/_3$) and (0, $^1/_2$,$-^1/_2$), respectively. Let us represent the traceless polarizability tensor of trifluoromethyl acetate as $\hat{\alpha}_{FE}$. If additivity holds, this tensor can be obtained as

$$\hat{\alpha}_{FE} = \hat{\alpha}_E - \hat{\alpha}_{CH_3} + \hat{\alpha}_{CF_3} = \hat{\alpha}_E + \hat{\alpha}_{C-H} - \hat{\alpha}_{C-F} \tag{7}$$

where, by symmetry, $\hat{\alpha}_{CH_4} = \hat{\alpha}_{CF_4} = \mathbf{0}$. The tensor $\hat{\alpha}_{FE}$ associated with bonds of type 2 or 5 corresponds to the polarizability of the group of atoms 1, 2, and 10 or 5, 6, and 7, respectively. Therefore,

$$\hat{\alpha}_1 = \hat{\alpha}_{10} = \hat{\alpha}_6 = \hat{\alpha}_7 = \mathbf{0} \tag{8}$$

For bonds of type 3 and 4,

$$\hat{\alpha}_3 = \hat{\alpha}_4 = \hat{\alpha}_{C-CF_3} - \hat{\alpha}_{C-F} = \hat{\alpha}_{C-C} - 2\hat{\alpha}_{C-F} \tag{9}$$

Here,

$$\hat{\alpha}_{C-C} = \Delta\alpha_{C-C}\mathbf{K} \quad \text{and} \quad \hat{\alpha}_{C-F} = \Delta\alpha_{C-F}\mathbf{K} \tag{10}$$

where $\Delta\alpha_{C-C}$ is[17] 0.96 Å^3 and the value of $\Delta\alpha_{C-F}$ will be discussed later.

The tensor associated with bonds of type 8 can be obtained by removing a C−H bond of methyl trifluoroacetate and substituting it by a $C-CH_3$ bond. Accordingly,

$$\hat{\alpha}_8 = \hat{\alpha}_{C-CH_3} - \hat{\alpha}_{C-H} = \hat{\alpha}_{C-C} - 2\hat{\alpha}_{C-H} \qquad (11)$$

where $\hat{\alpha}_{C-H} = \Delta\alpha_{C-H}\mathbf{K}$, $\Delta\alpha_{C-H}$ being equal[17] to 0.21 Å^3. Finally, the traceless polarizability tensor associated with bonds of type 9 is given by

$$\hat{\alpha}_9 = \hat{\alpha}_{C-C} - 2\hat{\alpha}_{C-H} + 2\mathbf{T}(\hat{\alpha}_{C-C} - 2\hat{\alpha}_{C-H})\mathbf{T}^{T} \qquad (12)$$

In this equation $\mathbf{T}$ and $\mathbf{T}^{T}$ are respectively the transformation matrix and its transpose, necessary to refer the polarizability tensors associated with the methyl groups to the reference frame corresponding to bond 9.

Values of Δa were computed by using matrix multiplication methods described elsewhere.[18,19] The following main set of statistical weights was used: $E_{\sigma\alpha} = -0.5$ kcal mol^{-1}, $E_{\sigma\beta} = 0.7$ kcal mol^{-1}, $E_{\sigma'} = -0.6$ kcal mol^{-1}, $E_{\omega} = E_{\omega'} = E_{\omega''} = 1.2$ kcal mol^{-1}. The large soluble fraction of the networks precludes the possibility of knowing the average molecular weight between cross-linking points. However, preliminary calculations showed asymptotic values of Δa are already obtained for chains whose degree of polymerization is larger than 12. Although the traceless polarizability tensor associated with C−F bonds, $\hat{\alpha}_{C-F}$, is not known, comparison of the values of $\Delta\alpha$[19] for Si−H (1.02 Å^3), C−H (0.21 Å^3), and Si−F (0.11 Å^3) suggests that $\Delta\alpha_{C-F}$ should lie in the interval $0 < \Delta\alpha_{C-F} < 0.11$. Therefore, the computation of Δa was carried out for the two extreme values of $\Delta\alpha_{C-F}$, 0 and 0.11.

Let us consider first the evaluation of the optical configuration parameter assuming that $\hat{\alpha}_{C-F} = \mathbf{0}$. The calculations show that for the all-trans conformation the optical configuration parameter reaches its maximum value, 83.3 Å^3. Departure from the trans conformation decreases the optical configuration parameter and its value, computed using the main set of conformational energies indicated above, is only 2.24 Å^3 at 5 °C. In general, Δa is nearly insensitive to the rotational population about the $CH_2-C(CH_3)_2-CH_2$ bonds of the alcohol residue. In changing $E_{\sigma'}$ from −1.2 to 0.8 kcal mol^{-1}, the optical configuration parameter only increases from 2.09 to 2.16 Å^3. This parameter is much more sensitive to the rest of conformational energies, as can be seen in Figure 5 where the dependence of Δa on $E_{\sigma\alpha}$, $E_{\sigma\beta}$, and $E_{\omega'}$ ($= E_{\omega''} = E_{\omega}$) is shown. For example, Δa augments from 1.02 to 2.72 Å^3 when $E_{\sigma\beta}$ increases from −0.4 to 1.5 kcal mol^{-1}. However, the optical configuration parameter shows a decreasing dependence on $E_{\sigma\alpha}$, its value declining from 2.48 to 1.72 Å^3 when $E_{\sigma\alpha}$ increases from −1.2 to 1.2 kcal mol^{-1}. On decreasing E_{ω} the chain coils back on itself, and as a result Δa, like the characteristic ratio C_n ($=\langle r^2\rangle_0/nl^2$), strongly decreases. The values of C_n and Δa grow from 0.57 Å^3 and 2.34, respectively, to 4.96 and 2.24 Å^3, respectively, when $E_{\sigma\alpha}$ increases from −0.3 to 1.2 kcal mol^{-1}.

If $\hat{\alpha}_{C-F} = 0.1 \times \mathbf{K}$, then the optical configuration computed using the main set of conformational energies is 2.00 Å^3, slightly lower than that calculated for $\hat{\alpha}_{C-F} = \mathbf{0}$. Therefore, the theoretical value of Δa must lie in the range 2.00−2.24 Å^3. An increase of temperature will increase the coiling of the chains, and as a result Δa will exhibit a negative temperature dependence. The value of this quantity, expressed in terms of $d \ln \Delta a/dT$, is -1.9×10^{-3} K^{-1}.

The closeness of the theoretical value of the optical configuration parameter of PNGHFG to the experimental one contrasts with the great differences observed among these values in the case of poly(diethylene glycol trepthalate) (PDET). Values[6] of Δa of the order of 20 Å^3 were found for this polymer at 30 °C whereas the value computed for this quantity, using the rotational isomeric state model, was only 4.0 Å^3. This significant difference must be attributed to intermolecular interactions that enhance the polarizability of the chains. Thus, we could envisage the PDET networks as formed by microdomains. In each of these microdomains the high polarizable terephthaloyl residues would be poorly ordered with respect to a local director. Obviously, the directors of the microdomains would be randomly oriented in the space. Therefore, the birefringence in excess of the PDET networks would arise from the orientations of the microdomains. Intermolecular interactions may not favor the formation of poorly ordered microdomains in PNGHFG networks and as a result the birefringence of these materials mainly arises from the orientation of the chains under the stress field and, hence, the relatively good agreement between the theoretical and experimental results.

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