

## CRYSTALLIZATION KINETICS OF SYNDIOTACTIC POLYPROPYLENE STUDIED BY TIME-DEPENDENT LIGHT ATTENUATION\*

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**Abstract** Crystallization kinetics of syndiotactic polypropylene (sPP) was observed by light attenuation measurements. The initial stages of temperature dependent sPP crystallization fall in the range of Rayleigh scattering and Rayleigh-Debye-Gans scattering. Initial time and growth time of crystallization were obtained, and the trend of crystallization temperature dependent linear attenuation coefficient on the radius and the index of the refraction of the spherulite were evaluated.

**Keywords:** Light attenuation; Crystallization kinetics; sPP.

### INTRODUCTION

Polymer crystallization processes have been studied for a long time<sup>[1–6]</sup>. Of these, the investigations of kinetics of polymer crystallization are usually carried out by differential scanning calorimetry or X-ray scattering in the wide- and small-angle range, sometimes also by light scattering, dilatometry or time dependent vibrational spectroscopy. Although based on different properties there is not much difference in the sensitivity of all these methods. Reliable data are only obtained from values of the crystallinity in the range of some percent of the final values. This means that for growing spherulites, which usually reach end sizes in the order of several micrometers, measurements start only at sizes of several hundred nanometers. This, however, is already far away from the initial stages. Nuclei have sizes in the order of several to ten nanometers and these, together with the small hedrites and spherulites existing at the beginning, cannot be observed. To study the objects in these initial stages, one can now use atomic force microscopy (AFM), but this technique has also some shortcomings. Observations by AFM principally refer to the development and growth of spherulites at the free surface of a melt, and conditions here may differ from those in the bulk. In addition, deriving global properties from observations of the development of single objects is sometimes difficult, because a certain selectivity is usually involved.

Presently, the work on polymer crystallization has given considerable attention to the possibility that the crystal phase in the final semicrystalline state could be preceded by a transient liquid phase with density different from that of the initial quenched bulk isotropic melt or annealed glassy state. A number of papers have explicitly criticized the spinodal hypothesis and associated experimental studies, favoring the traditional picture of nucleation and growth. Various studies have suggested that the denser transient phase involves chain orientation, and there are good reasons to assume a crystal nucleation and growth which include an intermediate phase in the form of a coverage of the whole volume by a prior mesomorphic phase developing by a mechanism which resembles a spinodal process<sup>[7]</sup>, or a nucleation into a mesomorphic phase<sup>[8]</sup>, or the existence of a

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mesomorphic phase in the front of a growing spherulites<sup>[9]</sup>. Being involved in this discussion we used an experimental tool with a sensitivity superior to the conventional methods and found that measurements of the attenuation coefficient of light can indeed have a large dynamical range. In the following we report some results obtained for syndiotactic polypropylene. The results are compared to crystallization isotherms measured by wide and small angle X-ray scattering.

Much is already known about the structure of semicrystalline *s*PP. Morphological studies showed that *s*PP forms both hedrites and spherulites, depending on the crystallization temperature  $T_c$ . At high  $T_c$ s one finds hedrites and often also single crystalline objects with rectangular, lath-shaped habit. For low  $T_c$ s, an increasing tendency of branching and splaying of growing lamellae continuously changes the hedrites into spherulites. The crystal structure has been analyzed in detail. Since the early work of Natta and Corradini, it has been known that the chain conformation corresponds to a  $t_2g_2$  sequence for each syndiotactic units per turn with a period of 0.74 nm. The stable structure of *s*PP (modification III) has a unit cell which includes two left- and two right-handed helices in a regular alteration along both the  $a$  and the  $b$  axes (space group  $Ibca$ ). In real crystals, the regular left-right packing is often perturbed, leading to lattice disorder. This disorder is known to increase with decreasing  $T_c$ . We had carried out a comprehensive study of the lamellar structure formed at different crystallization temperatures for samples of different tacticity and (octane-) co-unit content. It was therefore quite natural to use one of the samples now also in a light attenuation study of the crystallization process.

## EXPERIMENTAL

A *s*PP samples with 80% of syndiotactic diads, provided by Fina Chemical Co., Ltd., was used in this study without any further purification. *s*PP pellets were first dried under vacuum conditions at 110°C for 12 h. A film sample with 500  $\mu\text{m}$  thickness was then prepared by pressing the pellets between two coated quartz plates at 180°C, followed by cooling to room temperature. The samples were heated at 170°C for 5 min, and then inserted into the hot stage in the attenuation device at the various crystallization temperatures as soon as possible. Since the temperature of 170°C is well above the equilibrium melting point reported for a similar sample 160°C, it can be assumed that the crystallization starts from a relaxed equilibrated melt.

The time and temperature resolved light-attenuation measurements were carried out with a home-built apparatus<sup>[10]</sup>.

Synchrotron radiation experiments were made at HASYLAB am DESY in Hamburg, Germany (beamline A2,  $\delta = 0.15$  nm). There, WAXD and SAXS patterns can be measured simultaneously. The beam size at sample is about 2 mm  $\times$  3 mm, and the scattering angles range between 0.1° and 50°. The samples with thicknesses of about 1 mm were enclosed in Aluminum foil in order to keep the melt. The samples were first molten to 170°C and kept at that temperature for 3 min and then cooled to 100°C. The heating rate and cooling rate are 15 K/min. The scattering angles were calibrated by standard PET and a rat tandon tail sample for WAXD and SAXS, respectively.

## ANALYSIS OF LIGHT ATTENUATION RESULT<sup>[10, 11]</sup>

The attenuation of light after a passage through a plate-like sample with thickness  $D$  is described by the Lambert-Beer law

$$\frac{I}{I_0} = \exp(-AD) \quad (1)$$

where  $I_0$  denotes the flux of the light beam at the sample front,  $I$  gives the flux remaining after the beam has passed through the sample, and  $A$  is the linear attenuation coefficient. In general the attenuation can be due to both scattering and absorption of light. In our experiments on crystallizing polymers, measurements are conducted for samples cooled from the melt to the crystallization temperature. At the beginning they are still in the molten state but then spherulites or hedrites are nucleated and grow successively. The contribution of the

growing spherulites or hedrites to the linear attenuation coefficient  $A$  follows from

$$A = \frac{1}{D} \ln \frac{I(0)}{I(t)} \quad (2)$$

As long as the scattering objects are diluted in the matrix, which is always the case during the initial stages of the crystallization process,  $A$  is given by

$$A = \rho \sigma^2 \quad (3)$$

Here,  $\rho$  describes the number density of objects and  $\sigma^2$  is the total scattering cross section.  $\sigma^2$  is usually represented as

$$\sigma^2 = \pi R^2 Q \quad (4)$$

where  $Q$  represents a ‘scattering efficiency factor’. Expressions for  $Q$  are given in the literature, and one distinguishes here between three different ranges, addressed as

Rayleigh scattering

Rayleigh-Debye-Gans scattering

Mie scattering

Explicit expression exists for spherical scatters. Here, the scattering cross section depends on the radius  $R$  of the sphere and the indices of refraction  $n_m$ ,  $n_s$  of the melt and scattering object. The parameters included in the equations are the ratio of the indices of refraction

$$m = \frac{n_s}{n_m} \quad (5)$$

and a parameter  $\alpha$  which is proportional to the radius ( $\lambda_v$  denotes the vacuum wavelength)

$$\alpha = \frac{2\pi n_m R}{\lambda_v} \quad (6)$$

Rayleigh scattering is found for  $\alpha \ll 1$ . The scattering efficiency factor here is given by

$$Q_r = \frac{8}{3} \alpha^4 \left( \frac{m^2 - 1}{m^2 + 2} \right)^2 \quad (7)$$

In the next range, that of Rayleigh-Debye-Gans scattering, the scattering efficiency factor reads

$$Q_{RDG} = (m-1)^2 \left[ \frac{5}{2} + 2\alpha^2 - \frac{\sin(4\alpha)}{4\alpha} + \frac{7}{16\alpha^2} (1 - \cos(4\alpha)) + \left( \frac{1}{2\alpha^2} - 2 \right) (0.577 + \ln(4\alpha) + Ci(4\alpha)) \right] \quad (8)$$

with

$$Ci(x) = - \int_x^\infty \frac{\cos x'}{x'} dx' \quad (9)$$

Equation (8) includes Eq. (7) as a limiting case for  $\alpha \ll 1$ . The full equations to be used in the case of Mie scattering are rather involved, but there exists an approximate expression. It follows for the ‘anomalous diffraction model’ and has the form

$$Q_M \approx 2 - \frac{4}{\alpha'} \sin \alpha' + \frac{4}{(\alpha')^2} (1 - \cos \alpha') \quad (10)$$

where  $\alpha'$  is the modified variable

$$\alpha' = 2(m-1)\alpha \quad (11)$$

Reference [12] gave an example result of calculation of  $\alpha^2$  carried out for the case of a crystallizing polyethylene, setting  $n_m = 1.49$  and for  $n_s$  the relation

$$n_s = n_m + \phi_s(n_c - n_m) \quad (12)$$

With  $n_c = 1.54$ .  $\phi_s$  here describes the crystallinity within the spherulite. Calculations were carried out for  $\phi_s = 0.1$ . One can identify in the figure the three different ranges. The continuous curve was obtained by a combination of Eqs. (7), (8), (10) and includes the Rayleigh, the Rayleigh-Debye-Gans and the Mie region. The parts drawn with broken lines follow from applying Eq. (7) and Eq. (8) exclusively. The three ranges differ in the dependence of the scattering cross section  $\sigma^2$  on the object radius  $R$ . One finds in the Rayleigh range

$$\sigma_R^2 \sim (m-1)^2 R^6 \quad (13)$$

in the Rayleigh-Debye-Gans range

$$\sigma_R^2 \sim (m-1)^2 R^4 \quad (14)$$

and in the Mie range

$$\sigma_R^2 \sim (m-1)^2 R^2 \quad (15)$$

The transitions between the three ranges are rather sharp and located around 100 nm and 10  $\mu\text{m}$ . Experiments usually deal with objects in the central Rayleigh-Debye-Gans range where  $\sigma^2 \sim (m-1)^2 R^4$ .

As was already emphasized, these equations hold as long as the objects are isolated in the matrix. Application of the equations ends, when the objects touch each other. In fact, the attenuation factor then passes over a maximum and decreases again until homogeneity is reached when the sample is fully occupied by objects. Light attenuation then still exists due to the birefringence within the spherulites, but the main scattering following from the density difference between the melt and the spherulites has disappeared.

## RESULTS AND DISCUSSION

Figure 1 demonstrates an example of measured light attenuation result of *s*PP isothermal crystallized at the indicated temperature and the fluctuation of light attenuation at *s*PP melt temperature. From the plot in Fig. 1(a), one can obtain the initial time of *s*PP crystallization before the crystal growth and the half time of crystal growth. The method on how to define the initial time and the half growth time is shown in Fig. 1(a). The fluctuation of the light attenuation is about 0.1% compared with the light attenuation at the half time of the crystallization as shown in Fig. 1.

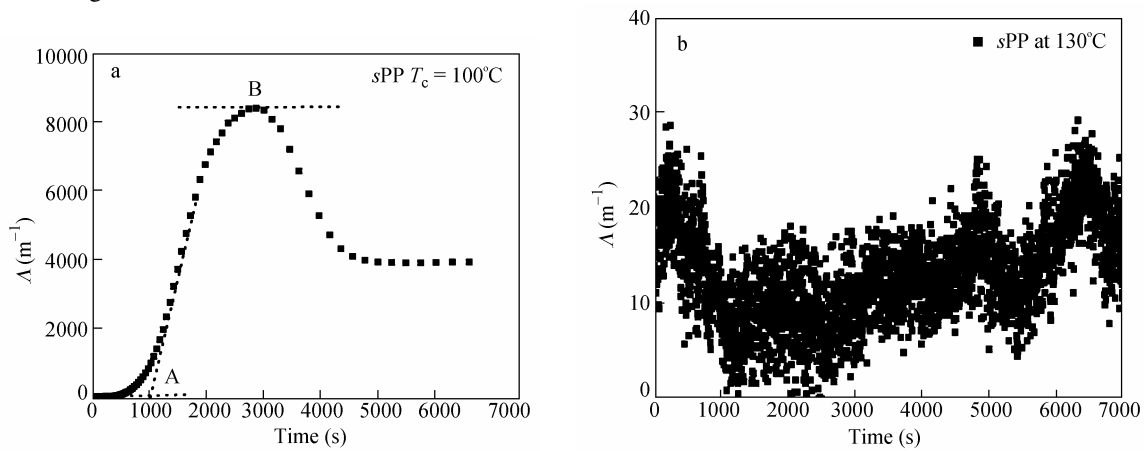


**Fig. 1** Typical measured light attenuation during *s*PP isothermal crystallization (a) and fluctuation of the device (b)

Figure 2 shows the compared results of *s*PP crystallized at 100°C measured by light attenuation, SAXS and WAXS, respectively. From the results in Fig. 2 one can find that the light attenuation measurement is more sensitive than SAXS and WAXS. As shown in Fig. 2, the initial time of *s*PP crystallized at 100°C detected by light attenuation, SAXS and WAXS was 1002 s, 1335 s and 1475 s, respectively.

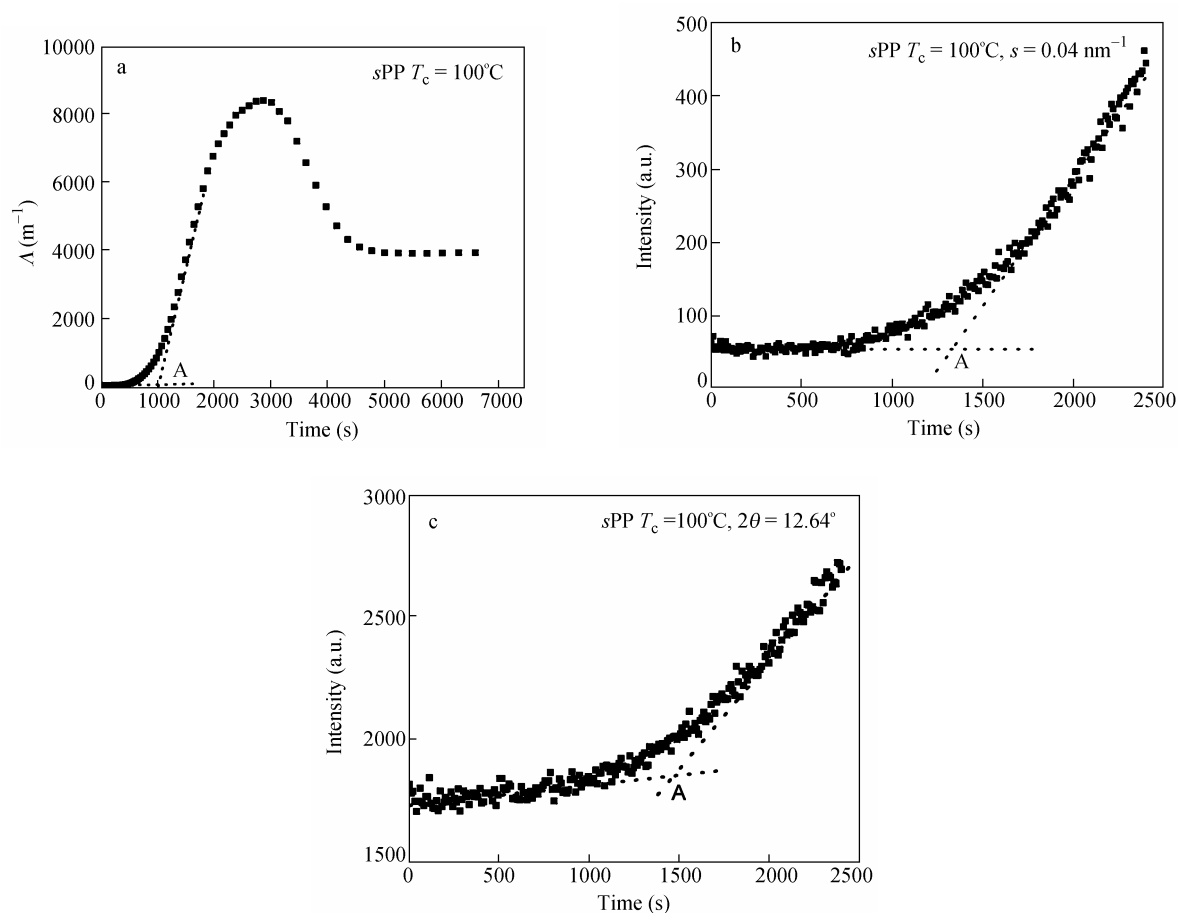


**Fig. 2** The transitions of *s*PP crystallization at 100°C measured by light attenuation (a), SAXS (b) and WAXS(c)

The measured light attenuation results of *s*PP crystallized at different temperatures are shown in Fig. 3. The results in this figure indicate the initial stages of crystallization and the further development of  $A$ , which passes over a maximum and then decays to a final value. From the results in Fig. 3 one can obtain the initial crystallization time and half crystallization time of *s*PP at different temperatures by the method shown in Fig. 1(a). A indicates the initial crystallization time, and B corresponds to the half crystallization time. The initial crystallization time and half crystallization time of *s*PP obtained from Fig. 3 are shown in Fig. 4 in the form of  $\lg(t)$ - $T$  plot. The results in Fig. 4 show good linear relationships, and the slopes in the  $\lg(t)$ - $T$  plots are a little different for the initial time and the half time of *s*PP crystallization.

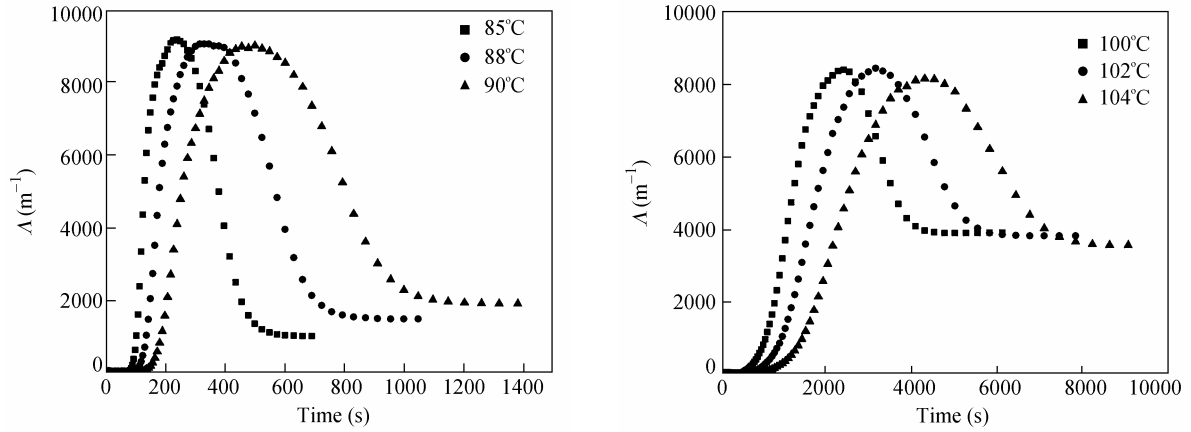


**Fig. 3** Light attenuation of sPP crystallized at the indicated temperatures

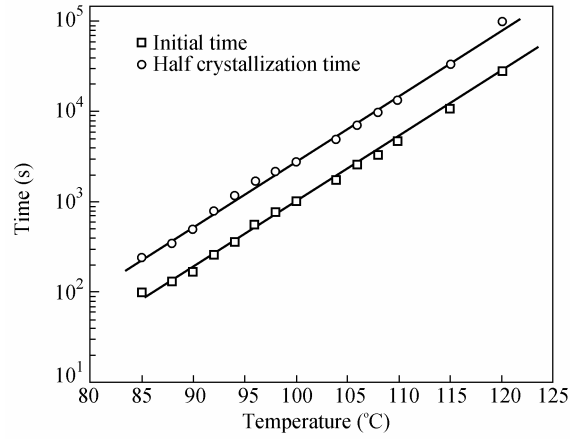


**Fig. 4** Initial time and half crystallization time of sPP during isothermal crystallization measured by light attenuation

As reported in studies on sPP isothermal crystallization by using time resolved dilatometer and attenuation<sup>[11, 13]</sup>, the slope of the lg-lg plots indicates that in the initial stage of the crystallization process the specific volume and the linear attenuation coefficient are proportional to time in logarithm. The results show that an increase in the crystallization temperature just results in a parallel shift of the curves to longer times. Such a behavior is expected if the growing object — hedrites or spherulites — increases in size with a constant growth rate, *i.e.*, for  $R \sim t$ . One therefore expects for the time dependence of the linear attenuation coefficient  $A$  an equation given by Eq. (14)  $A \sim R^4 \sim t^4$ . Figure 5 demonstrates the change of the linear attenuation coefficient  $A$  during isothermal crystallizations at the indicated temperatures. The slopes of the lg-lg plots in Fig. 5 show in Fig. 6. The slopes in the lg-lg plots indicate a decreasing exponent from 12 to 4 for the initial stages when the isothermal crystallization temperature is lower than 95°C. As soon as the temperature is higher than 96°C, the slope of the lg-lg plots indicates a constant exponent of 4 during the initial stages.

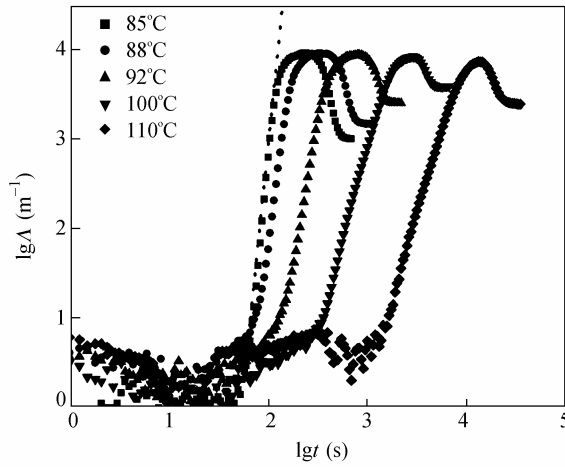


**Fig. 5** Time dependent light attenuation of sPP crystallization in lg-lg plot

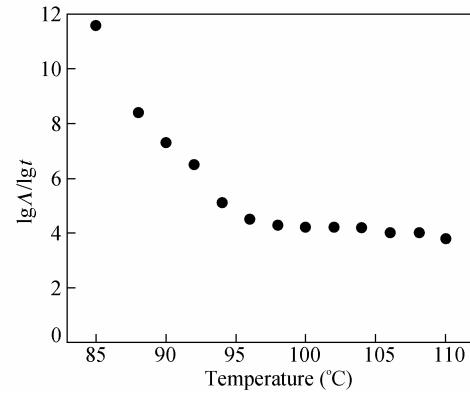


**Fig. 6** Temperature dependent slopes of light attenuation during isothermal crystallization

According to the AFM observations on the initial crystalline structure during sPP crystallization<sup>[14]</sup>, we can assume that the initial time of sPP crystallization for the growth of object at different temperatures and the size of object are related to the fixed crystallization temperatures. The result in Fig. 6 indicates that when the crystallization temperature is higher than 96°C  $\Lambda \sim R^4 \sim t^4$ , i.e., the attenuation of the crystalline sPP object is in the Rayleigh-Debye-Gans range, when the crystallization temperature is lower than 95°C that is roughly in the Rayleigh range, i.e.,  $\Lambda \sim R^6 \sim t^{lg\Lambda/lg t}$ . The calculated results according to Rayleigh scattering and Rayleigh-Debye-Gans scattering are shown in Fig. 7. From the results in Fig. 7 one can find that the size of sPP crystalline objects is constant at low crystallization temperatures, then the size of the object increases with temperature. One can also find a jump of the size of the objects increasing with temperature from Fig. 7. From the results in Figs. 6 and 7, one can find that the size of crystalline object is temperature dependent not time dependent, which maybe indicate that the initialization of sPP crystallization is from a spinodal related state.

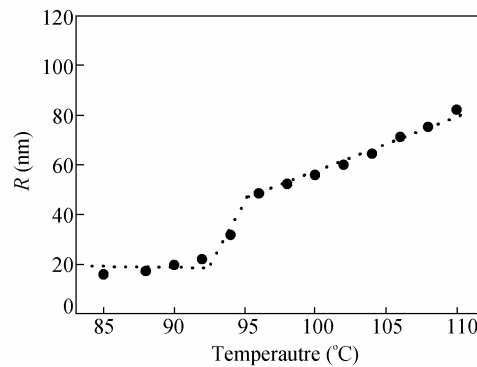


**Fig. 7** Temperature dependent object size related evaluation of sPP crystal according to light attenuation

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