Growth and Evolution of Particle Morphology: An Experimental & Modelling Study

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Summary: In order to fully understand the crucial issues of how particles grow during olefin polymerisation, how the morphology evolves, how fines are formed, as well as related key issues it is necessary to develop more sophisticated single particle models than those currently available. Such models should ideally allow us to calculate how force, or stress, develops and is released in the growing polymer particles. However, it is shown that before such models can be developed with confidence, it is necessary to develop experimental techniques that allow us to study particle growth under precise conditions. Parallel development of well-adapted experimental techniques and well-conceived models is proving to be a useful means of achieving the above-mentioned goals.

Keywords: nascent polymerisation; particle modelling; polymer properties; polyolefins; stopped-flow reactor

Introduction

Since the mid 1950s, a great deal of effort has been directed towards the development of ever-more efficient and sophisticated supported catalysts for the polymerisation of olefinic monomers.[1] At the same time, there has been an intense interest in attempting to understand the kinetics and mechanisms of the catalytic reaction. The resulting advances in organometallic chemistry have led to catalysts capable of polymerising at ever-higher rates, which in turn has serious implications in terms of reactor operation, productivity, monomer incorporation, fines generation, etc. As discussed previously (see e.g. Ray[2] or McKenna and Soares[3]), one can picture these ''implications'' as shown in Figure 1.

On the one extreme, (reactor scale) one needs to consider issues related to mixing in the reactor, bed stability, monomer and catalyst feed, product withdraw, etc.; all of which determine, and are determined by the bulk reactor conditions. On the other extreme, the chemical nature of the active sites will determine how the monomer and hydrogen (and eventually other molecules) that arrive at the active sites will react to form the (hopefully desired) product. In between is the particle. Any molecules that eventually reach the active sites must pass into and through the physical structure (pore space/polymer phase) of the particle. For a very short period of time (on the order of 10^{-1}–10^{2} seconds depending on the system in question – especially on the nature of the support), the particle is a continuous inorganic phase. As polymer builds up at the active sites, the inorganic phase suffers a build-up of stress at different points, and very quickly fragments into a series of unconnected substructures held together by a polymer phase. During this fragmentation step, the particle is ideally transformed into a continuous organic phase, throughout which the active catalytic sites are dispersed. In a perfect world, one supported catalyst particle will yield one polymer particle.

Regardless of whether we are considering the initial catalyst support, or the even more complex polymer particle, the system with which we are dealing is a two phase

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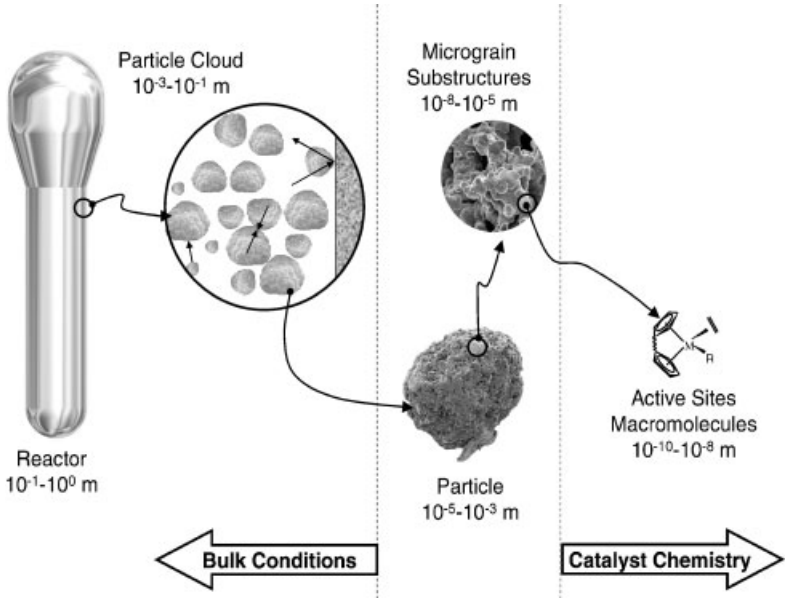

Figure 1.
The supported catalyst/growing polymer particle can be envisaged as a "filter" between the external process conditions and the conditions at the active site.

(polymer + pore) structure. It is evident that the morphology of the particle will have a strong influence on the rate at which monomers arrive from the bulk phase of the reactor to the active sites. For instance, in a polymer particle, the more it is necessary for monomer to diffuse through layers of polymer to get to the active sites, the more likely it is that the rate of reaction and chain microstructure will be limited by mass transfer.

Furthermore, the shape of the particles will have a strong influence on the way in which particles are modelled. Consider the following equation, which is the general form for the mass balance of monomer inside a growing polymer particle (of course to solve this, one needs to specify initial and boundary conditions[2]), where $\boldsymbol{C}_i$ is the monomer concentration in the particle as a function of time and spatial coordinates, $\boldsymbol{N}_i$ is the molar flux of monomer through the particle, and $\boldsymbol{R}_{p,i}$ is the rate of polymerisation of monomer i which is also a function of position and time:

$$\frac{\partial C_i}{\partial t} = \underbrace{\nabla \cdot N_i}_{\text{Form of } \nabla\cdot \text{ depends on transport mechanism and morphology}} \underbrace{- R_{p,i}}_{\text{Form depends on intrinsic kinetics}} \tag{1}$$

In this expression the first term on the right hand side, the mass transfer term depends, on the transport mechanism (e.g. convection and/or diffusion) *and* the morphology (e.g. cubic, plate-like, spherical . . .), whereas the second term depends on the intrinsic kinetics only. With a few exceptions, most authors will take this form of the equation, suppose that the particle to be

modelled is spherical and perfectly homogeneous, and that mass transfer is by diffusion only (some authors also allow for convection inside the particles[4,5]). The morphology of the particle will then either be assumed to be: (1) a pseudo-homogeneous medium where diffusion is characterised by a characteristic diffusion coefficient that is made up of weighted contributions of the diffusivity in the pore space and through the polymer layer surrounding the active sites; or (2) an amalgam of identical spherical sub-particles (micrograins), each with an individual crystal/grain of support material at the centre. In this case we will need to write coupled mass balances for mass transfer through the pore space and mass transfer through the polymer layers around the active sites. It should be mentioned here that a full model for particle growth would also include an energy balance, but discussion of this point is beyond the scope of the current paper. For a more detailed treatment of this last issue, as well as a for a fuller description of the state of the art in particle modelling, see McKenna and Soares.[2]

These models (PFM/MGM) can be used successfully to predict polymerisation rates, particle growth etc. if one is willing to treat certain quantities that *should* have a physical meaning as adjustable parameters. This concept is illustrated in Figure 2 for a set of isothermal polymerisations (adapted from Mattioli and McKenna[6]). This figure shows the dimensionless monomer concentration profile in growing particles of different idealised morphologies modeled using the polymer flow model (PFM) to calculate concentration profiles in the polymeric phase of growing particles. The white bands in each of the different idealised morphologies are macropores that are connected to the bulk phase of the reactor somehow, and that contain monomer at a concentration equation to that in the bulk. For the reaction conditions specified here, it can be see that for a physically realistic value of the effective diffusion coefficient, reaction rate and particle size, the PFM predicts that the concentration gradient is very strong, which leads to a certain value of the productivity after 300 seconds (profile 1). If we assume that there is one macropore in the centre (profile 2) of the particle, then the concentration in the middle of the particle is close to that of the bulk, the overall concentration gradient is

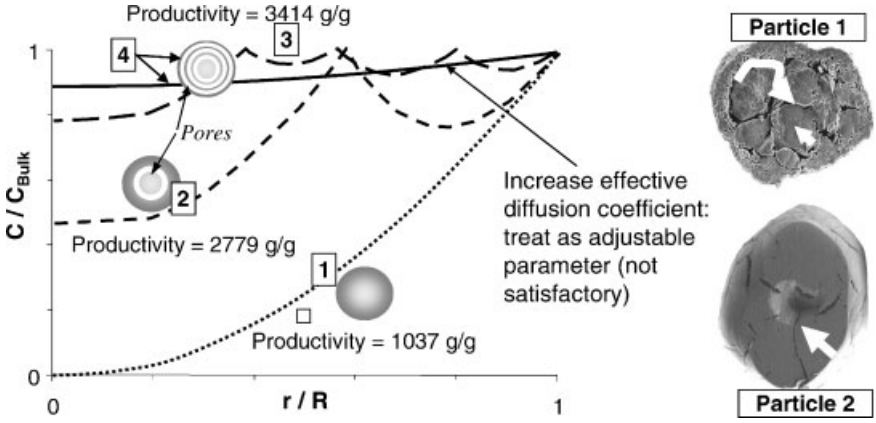

Figure 2.
Schema (simplified) of the role of particle morphology on mass transfer and observed productivity for different particle configurations. Calculations made using PFM model, for slurry polymerisation of ethylene in heptane at 6 bars of monomer, with initial particle diameter of 10 μm and an intrinsic activity of 25 kg PE/g CAT/h. Profiles 1–3 were calculated with an effective monomer diffusivity in the macroparticle of $D_{eff} = 10^{-10}$ m^2/s. Profile 4 was calculated with $D_{eff} = 10^{-8}$ m^2/s. Profiles 1–4 and the productivities indicated are dimensionless monomer concentration inside the growing particle after 300 s of reaction.

less significant than in the first case, and the observed rate of reaction higher. In the case of profile 3, there are several such pores and the observed activity (and therefore rate of reaction) will again be even higher. Note that the only thing that has changed between profiles 1, 2 and 3 is the particle structure. Finally, if one used the diffusion coefficient as an adjustable parameter and increased its value by two orders of magnitude, it would be possible to use the morphological representation without a pore (i.e. the original PFM) to predict similar productivities to those predicted with the morphology corresponding to profile 3 (this is profile 4, the solid line).

If one is interested in predicting the behaviour of a given catalyst in a well defined situation, this solution of adjusting D_{eff} to fit a set of data might be acceptable. However, if the morphology changes during the course of the reaction, then it might be difficult to obtain a meaningful prediction with this approach. This concept was used in early versions of the MGM model (e.g. Laurence and Chiovetta[7]) where fragmented and unfragmented parts of a catalyst particle wer assigned different values of D_{eff}. In a slightly different vein, Hutchinson and Ray[8] attempted to link D_{eff} with the degree of advancement of the polymerisation via a change in porosity. However, in neither case did the approach involve a prediction of the way in which the morphology might evolve. In addition (perhaps more importantly?), treating the diffusivity as an adjustable parameter makes it extremely difficult to differentiate with confidence chemical and physical effects (e.g. if we change the cocatalyst and see a change in rate is this due only to a change in the chemistry of the active sites? Or is it also due to a concurrent change in the particle morphology?).

Furthermore, we have not yet mentioned the fact that most particle growth models do not consider particle fragmentation (they assume it is complete and instantaneous), that all-important step when the particle is transformed from a continuous inorganic phase to a continuous organic matrix with the inorganic fragments dispersed within it. When they do include it (with very recent exceptions discussed below) it is usually to look at the influence of particle fragmentation on mass transfer and initial rates rather than on the structure of the particle. This is clearly a major lacuna since it is a well known fact that small changes in temperature or composition, or the use of different phases during the (admittedly short) fragmentation step can have a profound influence on the presence of fines in the reactor and the shape of the particle in general. This is also true of different types of reactions, for example in the case of impact copolymers, where it has been shown that accumulation of rubber in the pores of a polypropylene matrix can also lead to changes in mass transfer and bulk density.[9]

Particle Morphology Models

It seems clear that particle growth models that allow us to incorporate the continually changing nature of the morphological structure in the prediction of reaction rates, polymer properties, etc. would be a major asset. As we will discuss below, while certain progress has been made in this direction, we are still a long way from really understanding how to propose a useful version of such a model, and that part of the reason for this is that it is very difficult to accumulate experimental evidence of the evolution of morphology and properties during the nascent phase of polymerisation.

The basic premise upon which morphology models are being built is that it is necessary to calculate the build-up and dissipation of stress at different points in the particles, and that this will allow us to understand how the overall shape of the particles evolves. Building models of this sort means combining knowledge of the rates of polymerisation (rate of stress generation), with knowledge about the structural arrangement of the particle and the polymer properties at the point of stress (stress dissipation).[10–12] This is illustrated

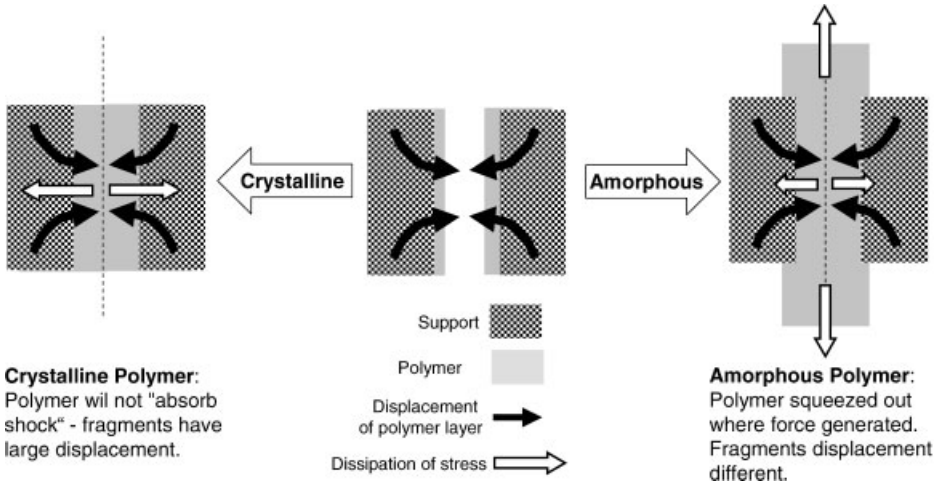

Figure 3.
Premise linking rates of stress generation and polymer properties.

in the schema in Figure 3. In the idealised 2D finite pore shown in this figure, polymer is formed at the surface of the support material and is displaced toward the centre of the pore as the reaction continues. As it accumulates it will enter into contact with the layer coming from the other side of the pore. In the case of a highly crystalline material that is produced relatively quickly, the stress that builds up at the interface will not be dissipated by provoking a displacement of the polymer, and will be "sent back" directly into the support matrix. On the other hand, in the case of a soft, amorphous material, the polymer at the interface will be more easily deformable, and can flow out of the pore to a certain extent. The force experienced by the support will be very different in this case, and thus the fragmentation in the initial instants, or the evolution of the particle morphology later on will be different in this case than in the precedent.

Fairly recently, a few models that look at the relationship between reaction rate, polymer properties and particle morphology have appeared in the literature. The earliest clear discussion of these concepts appears to have come from our research group.[10,13] These works were highly simplified in the sense that they looked at homogeneous particles,[13] or individual pores.[10] In the latter, it was demonstrated that increasing the rate of stress generation in the pore created conditions that favoured early fragmentation at low polymer yields, whereas conditions such as short relaxation times for the polymer that favoured rapid dissipation of energy and easy polymer deformation led to fragmentation at higher polymer yields. These models were improved upon in a recent paper by Di Martino et al.,[11] but the basic concept remains the same: simple particle morphology and evaluation of order of magnitude effects of energy accumulation due to reaction, dissipation due to a change in morphology as a function of polymer properties. Subsequently, the group of Pinto[14,15] used a similar approach, but focused on the fragmentation process from the energy balance angle. They analysed the fragmentation in terms of a balance between the mechanical energy accumulated inside the particle, and the energy dissipated both by the rupture of the catalyst support and by the deformation and flow of the accumulated polymeric material. In other words, the ability of the particle to dissipate the accumulated energy was decisive in defining the time and the locus of fragmentation. Based on the possible model responses, the authors defined different fragmentation

criteria that were highly dependent on the polymer properties and rates.

Perhaps the most sophisticated approach to looking at morphology modelling comes from the group of Kosek.[12,16] These authors treated the growing particles as an agglomeration of interconnected microstructures (N.B. these substructures do not directly correspond to the micrograins in the MGM; rather they tend to be somewhat larger and less numerous), imposed arbitrary rates of polymer production and polymer properties, and use a force balance between neighbouring structures to predict the morphology. The authors were able to build very useful working maps to predict different types of particle morphologies as a function or reaction rates and polymer properties. The interest of this contribution is undeniable, and certainly the most complete to date. Nevertheless, certain aspects are lacking, such as the ability of the microstructures to agglomerate into larger substructures, or means for assessing realistic physical property values. In addition, the model has not yet been validated experimentally for a number of good reasons.

On the one hand it is clear from these treatments that the polymer properties, rate of polymerisation and particle morphology are interdependent. However, none of the approaches proposed to date offers the possibility of doing more than offering generalities, and none have really been experimentally validated. To a certain extent, it would appear that morphology models themselves are in a ''nascent'' stage. Reasons for this include the fact that they are computationally demanding,[12] but also that it is very difficult to know how to construct them (we have a difficult time painting an accurate physical picture of the different phenomena involved), what properties to use, how the fragmentation step proceeds, how the physical properties of the polymer evolve, and what are the values of the important physical properties. In large part, difficulties associated with the experimental investigation of particle fragmentation in the case of real catalysts under realistic conditions (i.e. at a sub microscopic scale and in a fraction of a second) are serious obstacles on the road to developing a mechanistic description of the initial stages of catalyst activation and particle growth.

Experimental Part

As a partial solution to the above-mentioned limitations, it appears that stopped, or quenched flow reactors, suitably modified to allow the evaluation of kinetics, polymer properties *and* nascent morphology are ideal tools for this type of work. One of the approaches used by our research group, and recently described in the literature is a slurry phase quenched-flow reactor that has been developed.[17] It is based on the concept popularised by Keii and Terano[18] for olefin polymerisation, with the major differences being that the particles are captured in a quench vessel and poisoned with CO_2 to stop the reactor but preserve the morphology, and the residence times are as short as 40 ms, thereby allowing us to investigate the truly nascent structure of the macromolecules present before, and during fragmentation.

Experimental Procedure

As the experiments discussed here are described in detail in previous papers,[19,20] full details can easily be found elsewhere. Suffice to say that the set-up is composed of two upstream vessels that contain the reactants (catalyst, cocatalyst – TEA, monomer and hydrogen in different combinations, and are connected to a T-mixer that leads into a tubular reactor where the polymerisation takes place. By varying the pressure drop between the up-stream vessels, and the length of the tubular reactor we are able to accurately control the reaction time for durations as short as 40 ms. It is also possible to either contact the catalyst particles and the TEA before the reaction for controlled times, or alternatively to contact them in the T-mixer as the reaction begins. The resulting product was quenched in 250 cm^3 of CO_2-saturated heptane solution at ambient temperature. The mixture is

then degassed before sampling for off-line analysis.

Results

Results of a series of off-line analyses of the evolution of the crystallinity of a high density polyethylene (HDPE), polymerised at 4 bars of ethylene at 80 °C, no hydrogen and with precontacting of a commercial Ziegler-Natta catalyst and TEA in one of the upstream vessels (the other contained 8 bars of ethylene) are shown in Figures 4 and 5.[19]

It can be seen from these figures that the crystallinity and molecular weight are much lower than expected at times less than one second – in other words, the time scale for fragmentation of a Ziegler-Natta catalyst supported on $MgCl_2$ – and that the rates of reaction are extremely high at short residence times. The implications of these results are numerous, but, in terms of the theme of the current article, it can be seen clearly seen that particle behaviour during the critical initial time frame is not what is expected, and that the polymer properties change extremely rapidly during this period. For instance, at very short times, it is

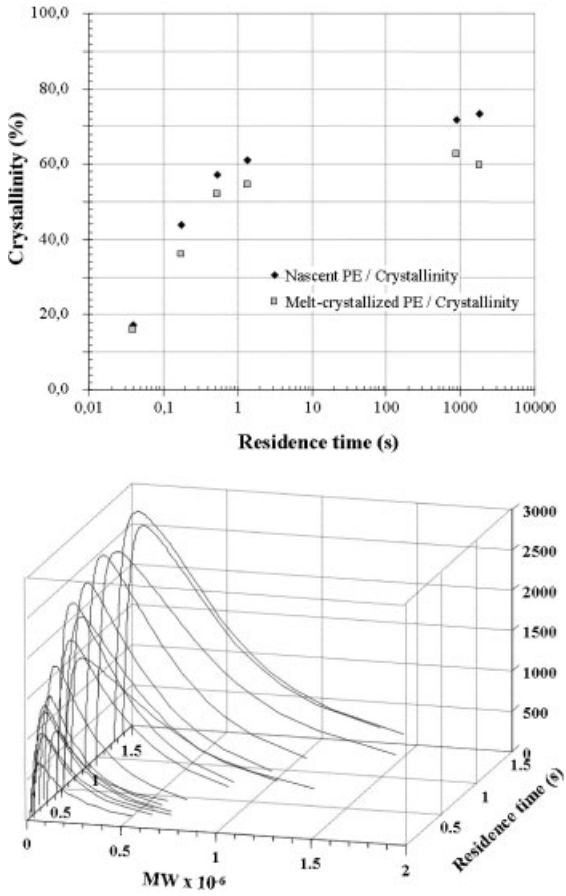

Figure 4.
The evolution of the crystallinity (top) and full molecular weight distribution (bottom) of a series of polymerisations run at different residence times. The properties vary tremendously, and in unexpected ways at very short time.

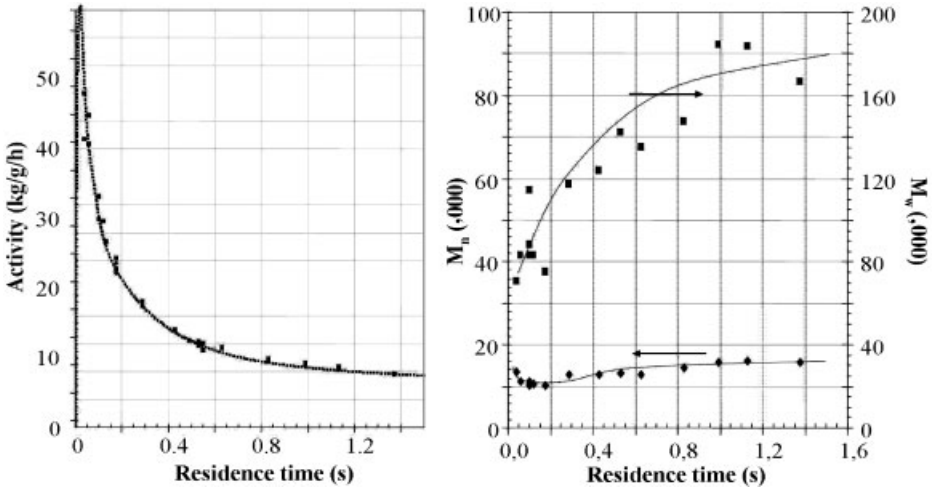

Figure 5.
Rate of reaction (left) and evolution of the number average and weight average molecular weights of the runs in Figure 4 as a function of reaction time.

possible that the rate of polymerisation is much faster than the rate of crystallisation, and the very short chains produced very rapidly form fairly amorphous material (which will fragment differently than crystalline material). It is only after a few seconds that the physical properties of the polymer and the rates of reaction change to more expected values.

If we reflect on the discussion about model building presented above, it should be evident that if one were to use physical properties and rate date obtained under longer reaction times than 1 second, it is possible that we would not be able to build a coherent description of the relationship between physical properties, reaction rate and morphology that we would like to obtain.

Conclusions

It should be clear from the preceding discussion that the relationship between particle morphology, rate of reaction and polymer properties is, to say the least, a complex one. If we focus on the evolution of particle morphology during the initial instants of polymerisation, then it is only by using experiments such as those shown here that we will be able to obtain a realistic picture of the evolution of particle morphology during the initial instants of the reaction, and to eventually decide upon how to model this critical phase of the reaction.

Furthermore, it is important to point out that the evolution of particle morphology, and its interdependent relationship with mass transfer rates, particle growth and polymer properties will continue throughout the entire production process at a more or less significant level depending on the reaction conditions and type of polymerisation in question (see e.g. Kittilsen et al.[9] for a discussion of the influence of rubber accumulation on reaction rates during the production of high impact polypropylene). In addition, heat transfer is also a key point that we have not discussed here due to space constraints. However, since heat transfer influences polymer properties and reaction kinetics it will clearly exert an influence on polymer particle structure.

In closing, we can say that while some interesting progress has been made in proposing means of linking morphology, rates and properties, significant amounts of work remain to be done before we can have a tool that predicts particle shapes and the evolution of the critical length scales for

mass transfer during a polymerisation reaction. If more progress is to be made in this direction, it is necessary to construct specially adapted experimental methods to help both provide visual insight into how things evolve, as well as to provide a methodology for the measurement of important physical properties.

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