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Influence of the Relative Humidity on the Demixing of Polymer Blends on Prepatterned Substrates

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ABSTRACT: Demixing of two polymers (polystyrene and poly(2-vinylpyridine)) in solution was studied on a substrate with a surface energy pattern for varying relative humidities and gaseous atmospheres. A good pattern transfer of laser-generated surface energy patterns could only be observed at medium relative humidity. An incomplete replication of the energy patterns at lower humidity and a netlike (nanoporous) structure, especially in the PVP phase, at higher humidity was observed. The control of the water content in the solvent (tetrahydrofuran/THF) turned out to be a second important factor for the templating process. So a fine balance including both parameters, the humidity in the process gas and the content of water in the solution, is critical for the quality of surface energy pattern transfer into polymer blends during spin-coating.

The demixing of polymer solutions on structured substrates[1−3] and patterns of different surface energy[4,6] is a promising route to generate nanostructures by means of a versatile, fast, and inexpensive bottom-up technique. For a controlled and predictable generation of nanostructures out of ternary[1−5] polymer/polymer/solvent or binary[7,8] polymer/solvent blends, it is important to understand the interactions of the polymers and solvent during the demixing process.

Flory et al.[9] have illustrated in their theory of demixing that polymers, depending on their interaction parameter χ between each other and the solvent and the volume fraction of the polymers, are only miscible at a low enough concentration of polymers in solution.[9,10] When spin-casting the solution on a substrate, the solvent evaporates and the polymers start to demix at a critical concentration. The generated structures depend on both the initial concentration of polymers in solution and the rotation speed of the spin-coater.[2] A similar approach on polymer mixing has been used by Hansen,[11] who defines the interaction parameter χ as a function of three Hansen solubility parameters (HSP) for every polymer and solvent. With these HSP the polymers and solvents can be plotted in a three-dimensional Hansen plot, and a polymer is miscible in a solvent if it is in a certain radius of interaction around the solvent.

Böltau et al.[4] have shown that spin-casting these ternary solutions on a chemically patterned substrate with commensurate structure sizes[2−4,12−14] leads to a replication of the chemical pattern by the polymers. The discussed phase separation of the polymer blends due to interfacial instabilites[15] has been supported by time-resolved simulations of spinodal decomposition[16,17] and recent experimental results of Heriot et al.[18] The development of the morphology in the course of such surface instabilities has been investigated by Kargupta et al.,[19] showing U-shaped structures in the last, hydrodynamic stages of the pattern-induced structure formation.

The influence of the humidity in the atmosphere during polymer demixing has been described in earlier publications.[8,15,20,21] Hecht et al.[20] showed that demixing of polymers at high humidities leads to additional holes in the polymer films. This effect has been attributed to interactions between the polymer molecules and water[15,22] and a condensation of water droplets on the evaporatively cooled polymer solution.[21,23] However, the mechanism for the formation of the structures during spin-coating of polymer blend solutions at higher humidity is still under discussion.[7,20] Widawski et al.[8] have shown that a binary system of solvent and polymer at moist conditions can be used to generate periodic honeycomb structures or breath figures.[7,24,25]

Additionally to the polymers, which tend to swell with increasing water content in a humid atmosphere,[22] the presence of water influences the solvent as well. Metteoli et al.[26] have shown with Kirkwood−Buff integrals[27] that the addition of water to tetrahydrofuran (THF) leads to an increase in the binding energy of the THF molecules. This effect can be seen in the higher density of the water−THF mixture—higher than expected from the arithmetically calculated density of the single components involved.[28]

In this paper we investigate the process of demixing on patterned substrates and the issue of breath figures at higher humidities. Spin-coating of blends of polystyrene and poly(2-vinylpyridine) demixing in the same humidity-controlled environment and solvent gives new insights into the mechanism of demixing of polymer solutions at different humidities.

Experimental Section

As a template for demixing a ternary polymer blend, consisting of poly(2-vinylpyridine) (PVP), polystyrene (PS), and tetrahydrofuran, we used a surface energy pattern of hydrophilic and hydrophobic self-assembled monolayers (SAMs) on gold. In order to generate the surface energy pattern, we first evaporated an adhesive layer of 1 nm chromium and 25 nm gold onto a (111) silicon wafer, which had been cleaned by the RCA method and an oxygen plasma prior to evaporation. The surface energy pattern consisted of alternating stripes of 11-mercaptoundecanol (MUD, Aldrich) and 1-octadecanethiol (ODT, Aldrich) generated by single pulse laser interference lithography (SPLIL):[6] The interference of two laser pulses with a duration of 10 ns in SPLIL generates a thermal line pattern, locally desorbing molecules of

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Table 1. Characteristics of the Used Polymers Purchased from PSS, Mainz

polymer	M_w ($\times 10^3$) [Da]	M_n ($\times 10^3$) [Da]
PS	9.58	9.32
PVP	11.1	10.7

the MUD SAM on the substrate. The substrate areas from which MUD has been removed are backfilled by ODT molecules, generating a pattern with a high surface energy contrast. As the patterning is done by a thermal process, there is a laterally limited transition zone with a medium surface energy between the areas with a SAM of MUD or ODT.[6] The central line of maximal intensity is marked by a rounded, slightly elevated dorsum, which stems from the local melting process of the gold film during laser irradiation.

In order to replicate this energy pattern by demixing poly(2-vinylpyridine) and polystyrene (purchased from PSS, Mainz) (Table 1), a solution of 0.5 wt % of each polymer in tetrahydrofuran with 3000 rpm was spun-cast on the energy-patterned substrates. The polymer demixing was carried out in a spin-coater with adjustable relative humidity (RH) from 15% to 70%, measured above the substrate, and a temperature of 24 °C. The gases had a starting humidity of below 15%. By directing the gas flow over a water surface of a constant temperature, the relative humidity of the atmosphere could be adjusted. In the experiments presented here we used both air and nitrogen as process gas atmosphere. To avoid an influence of possible residuals in the compressed air on the results, we have filtered the air and used nitrogen as a reference atmosphere.

In the experiments with water-free tetrahydrofuran, the THF was dried over sodium and stored and handled in a dry nitrogen atmosphere, thus being saturated with nitrogen. To minimize the water uptake of the hygroscopic THF, the used polymer solutions were prepared in a nitrogen atmosphere. The water content of the used tetrahydrofuran, stored under ambient conditions (THF_{st}), was measured with a ATAGO refractometer using water-free tetrahydrofuran (THF_{wf}) as a reference ($n_D^{20} = 1.408 \pm 0.0005$). The measured refractive index for the THF_{st} was 1.40735 ± 0.0005, corresponding to a water content of $1.8 \pm 0.2\%$.[28]

After the demixing process, PVP and PS can be selectively dissolved by ethanol and cyclohexane, respectively, without altering the other polymer and revealing the desired polymer pattern. These patterns were imaged by AFM operated in non-contact mode (Digital Instruments Nanoscope IIIa) before and after the selective dissolution of one of the polymers.

Results

By changing the relative humidity in the experiment, five different regimes for the replication of the surface energy pattern can be seen (Figure 1, air and THF_{st}). At a relative humidity lower than 26% the polymer solution with the standard tetrahydrofuran does not show a good reproduction of the surface energy pattern (Figure 1A). This changes at a relative humidity of 26% in air (Figure 1B), although the profile of the PVP stripes following the energy pattern shows a U-shaped structure with elevated walls and a lower plateau in the middle (Figure 2). With increasing humidity (28% RH, Figure 1C), the structure of the PVP is transformed to a more rectangular shape. At a relative humidity of 38% the area of the profile is highest, and the PVP shows a pronounced netlike structure (Figure 1D). The profiles of the generated PVP structures at different humidities are shown in Figure 2 (left). If the relative humidity is further increased, bigger holes of micrometer diameter appear, and the structure of the energy pattern is not reproduced very well (Figure 1E).

The same humidity regimes for good pattern replication as in air could be verified in a nitrogen atmosphere as can be seen in the AFM image in Figure 1F,G. The PS−PVP patterns before the removal of the PS at 40% RH (Figure 3, left) shows smaller holes in the PVP and bigger holes in the PS. The normalized distribution of the hole diameter in the polystyrene and poly(2-vinylpyridine) in Figure 2 (right) was measured with the program Gwyddion. This gives a Gaussian distribution of the holes in PS with a average diameter of 23.3 ± 1.3 nm and a full width at half-maximum (fwhm) of 30 nm, which is significantly larger in diameter and has a broader distribution than in PVP with 18.4 ± 0.5 nm and a fwhm of 12 nm. Furthermore, a gap between the PVP and PS structure has formed.

In the next experiments we have used water-free tetrahydrofuran as a solvent for the immiscible polymers. As can be seen in Figure 1H,I, the necessary relative humidity for the same structure shapes as in the first experiments is increased by more than 10%. The best structures are now acchieved with 51.5% RH, and the patterns began to form at 39.5% RH.

Discussion

As the strong dependency of the generated structures on the water content in the atmosphere and in the solvent shows, water plays a major role in the pattern formation process.

The netlike structure for RH above 38% (Figure 1) is very similar to breath figures observed by spin-coating polymer films in moist atmospheres of over 50% RH[7] or if solvents containing a high amount of water are used.[24] These figures were explained as condensation of water droplets on top of the polymer solution due to the temperature drop resulting from the loss of latent heat of the evaporating solvent.[7] Whereas this model might explain the netlike structure for higher humidities, it does not account for the influence of the water content in the solvent and the U-shaped structure for lower humidities. This leads us to an alternative explanation for the structure generation in our case: The replication of the surface energy pattern with ternary polymer solutions depends apart from other factors on the given time for the polymers to form the desired structures,[16,19] and too short a time leads to an incomplete structure formation as the polymer phases are drying during the process of demixing and dewetting. In this picture, the U-shaped structures can be seen as PVP frozen during the movement from the hydrophobic into the hydrophilic areas during the demixing process. A transient top layer of the polystyrene phase could have been trapped on top of this U-shaped profile, which later on, in the hydrodynamic regime of the phase segregation process, could have been flown down to the PS-covered region. In Figure 1A,B,F,H the reminiscent traces of such a flow mechanism can be seen in the graphs of 26% RH and below. A similar U-shaped structure has been found by molecular dynamic simulations of Kargupta et al.[19] for short times during the dewetting process of polymers on chemically patterned substrates. So this means for a good profile the solvent THF_{st} evaporates too fast below a humidity of 26%. Above 28% humidity the ternary solution has enough time to demix and arrange on the pattern. The reason for the slower evaporation involves water enrichment of the hygroscopic solvent tetrahydrofuran, which can be explained by Raoult's law, which says that adding additional substances to a solvent leads to a reduced vapor pressure. This simple picture is supported by the increased binding energy of the THF molecules in the presence of water.[26,28]

In this picture a higher humidity is needed in the case of water-free THF to give the demixing and dewetting process enough time as the water uptake has to compensate the lower water content in the solution at the beginning. This coincides with the experimental results for water-free THF (Figure 1H,I).

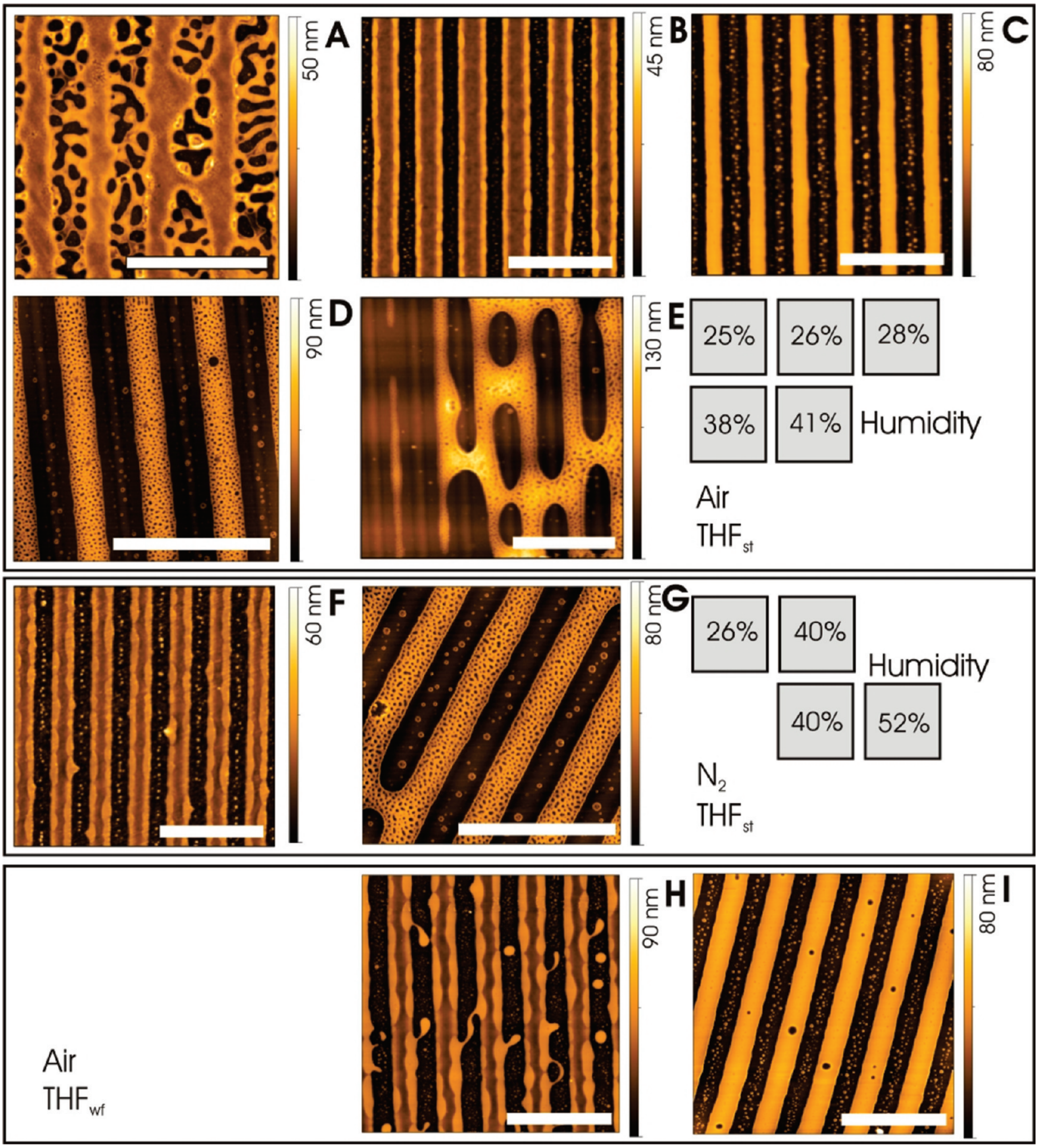

Figure 1. Template-directed demixing of two immiscible polymers (PVP, PS) out of a ternary system with THF as solvent for different relative humidities and atmospheres on chemically patterned substrates. The PS component has been removed by cyclohexane. Relative humidity in the atmosphere (air) influences the structure formation significantly. A very good pattern replication is reached at a medium humidity of about 28% (C). If the same solution is spun in a pure (also humid) nitrogen atmosphere, the result is similar (F, G: 26% and 40%; compare B, D: 26% and 38%). If water-free THF (THF$_{wf}$) is used to prepare the solution, the humidity has to be increased to obtain a good structuring (51.5% instead of 28%). The scale bar in the AFM images is 4 μm. (The width of the template stripes slightly varies from sample to sample.)

The water concentration influences not only the time scale of demixing but also the process of demixing itself, as the interaction between the polymers and the solvent is altered. In Figure 4, a two-dimensional cut through a HSP plot with the parameters for polystyrene, poly(2-vinylpyridine), water, and THF (Table 2) is shown. Due to lack of an experimental value for the HSP of PVP, we calculated them from their group contributions, using the Hoftyzer–Van Krevelen method.[31] The values are shown in Table 2. Both PS and PVP are inside the radius of interaction of the THF, and water on the other hand is outside; hence, the polymers are only soluble in THF. As the THF absorbs water during the process of polymer demixing and THF evaporates faster than water, the solvent shifts in the HSP plot toward water, indicated by the arrow in Figure 4. In case of a high humidity during the demixing process, the water uptake of the solvent leads to a shift of the solvent out of the radius of the polymers. This leads to a phase separation into a THF–water and THF–polymer phase and ultimately water droplets in the polymer structure

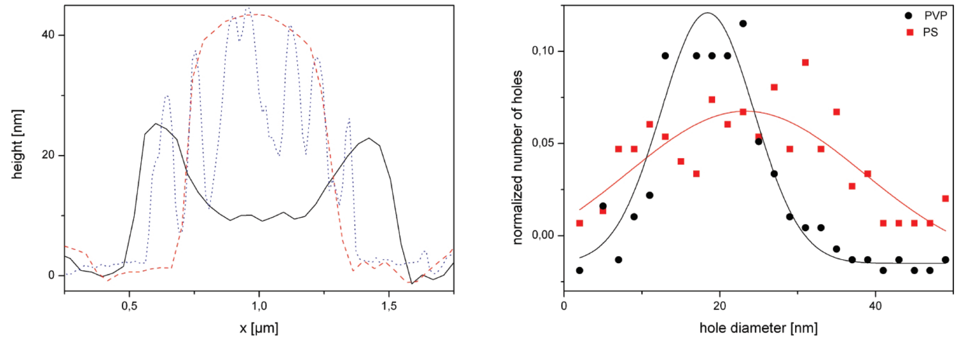

Figure 2. Profiles taken from Figure 1 of the poly(2-vinylpyridine) structures generated at 26% (black), 28% (red, dashed), and 38% (blue, dotted) relative humidity in air (left). The distribution of the diameter of the holes in the PS and PVP taken from Figure 3 is shown in the right graph.

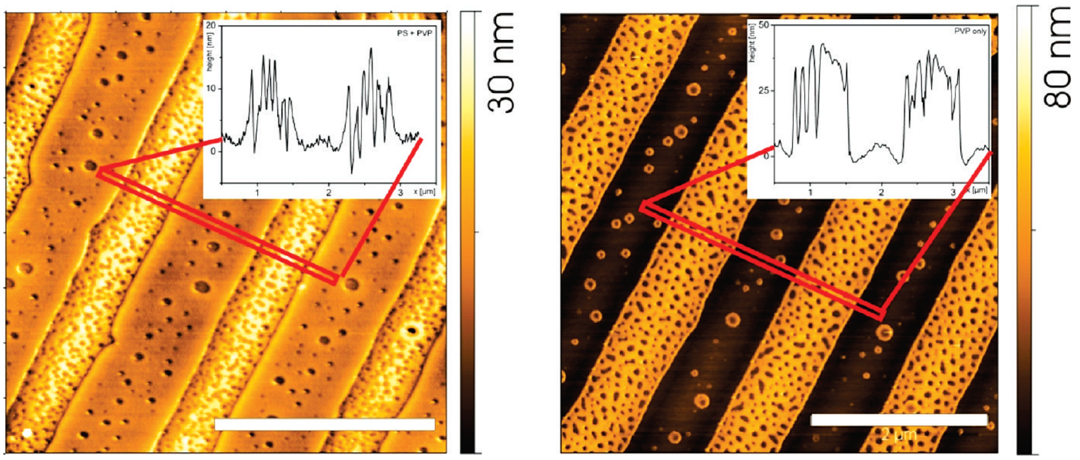

Figure 3. Demixing PS and PVP at a humidity of 40% in nitrogen and THF$_{st}$ as a solvent leads to porous structures in both polymers. The porosity in PVP can be seen before (left) and after PS has been dissolved (right). The scale bar is 2 μm.

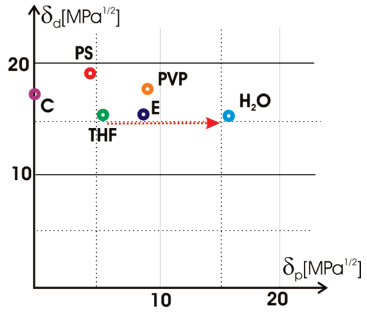

Figure 4. HSP plot of the polymers polystyrene (PS) and poly(2-vinylpyridine) (PVP) with the solvents cyclohexane (C), ethanol (E), tetrahydrofuran (THF), and water (H_2O) from Table 2. The arrow indicates the movements of the solvent in the HSP plot due to a higher water content.

are formed. By the clear confinement of the netlike structure in the single polymer phase in Figure 3 at an only slightly higher relative humidity than in the case of well-defined polymer structures it seems to be justified to assume that the phase separation between one polymer and the water in the solution takes place after the polymers have demixed.

As Jaczewska et al.[22] have shown, PVP is able to swell more in the presence of water than PS. This influence can be seen in Figure 3 in the gap between the PVP and PS formed by a shrunken PVP structure and the smaller distribution of the hole diameters in PVP than in PS, as the water droplets had less time to merge due to the water uptake of the swollen PVP (Figure 3). This is a similar effect as in the case of the breath figures.

Table 2. Hansen Solubility Parameters for the Used Solvents and Polymers

polymer/solvent	δ_d	δ_p	δ_H	ref
ethanol	15.8	8.8	19.4	11
cyclohexane	16.8	0	0.2	11
THF	16.8	5.7	8.0	11, 30
water	15.5	16.0	42.3	11
PS	18.64	4.5	2.9	11
pyridine	19.0	8.8	5.9	11, 29
$CH_2{=}CH{-}$	−1.06	0		11
PVP	17.9	8.8	5.9	

In case of lower humidities of 36% and less, the water content in the solvent is low enough to be absorbed by the highly concentrated polymer solution. At very high humidities above 40% much bigger water droplets are formed and the whole polymer structure is disturbed, leaving a visibly opaque film, due to so-called blistering.[11]

Conclusion

We have demonstrated a strong dependence of the structure of demixed polymer blends on the water content in the atmosphere and in the solvent on both ends of a window for very good pattern replication (28%−36% RH, Figure 1) and proposed a model explaining the influence of the water on the demixing process of polymer blends. This model includes the changes of the water−solvent interaction with different water content in the solvent, which influences the evaporation rates and thus the time for demixing of the polymer phases. A consequence of this is the incomplete or U-shaped polymer structure formation for relative humidities below 28%. On the other hand, the water content in the solvent tends to demix from the solvent in addition to the polymers and small water droplets are formed, giving rise to the shown netlike structure in the polymer film at a relative humidity above 38%. Another remarkable result is that pattern transfer works only poor in the extreme dry case: The presence of water in the system may increase the difference in polarity of the PS and PVP phase because it will preferentially accumulate in the PVP phase and though increase the driving force to draw the PVP phase on the polar COOH-terminated MUD regions of the substrate pattern. So humidity is not only a disturbing factor but an important prerequisite for surface energy pattern templating into polymer blends.

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