# Nitroxide-Mediated Controlled Free Radical Polymerization of the Chelate Monomer 4-Styryl-tris(2-pyridyl)borate (StTpyb) and Supramolecular Assembly via Metal Complexation

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S Supporting Information

ABSTRACT: The reaction of 4-(dibromoboryl)styrene with 2-pyridylmagnesium chloride resulted in the formation of 4-styryl-tris(2-pyridyl)borate free acid (StTypb), a new polymerizable nonpyrazolyl "scorpionate" ligand. StTypb did not undergo self-initiated polymerization under ambient conditions and proved to slowly polymerize through standard radical polymerization at 90 °C. Nitroxide-mediated polymerization (NMP) of StTypb at 135 °C proceeded with good control, resulting in a polymer of M_n = 27400 and PDI = 1.21. The TEMPO-terminated homopolymer successfully initiated the polymerization of styrene, generating an amphiphilic block copolymer with DP_n of 1200 and 78 for the PS and the StTypb block, respectively. A similar block copolymer with DP_n of 29 and 20 for the PS and the StTypb block respectively was obtained in a reverse polymerization procedure from a PS macroinitiator. The self-assembly of these block copolymers was examined in selective solvents and preliminary metal complexation studies were performed.
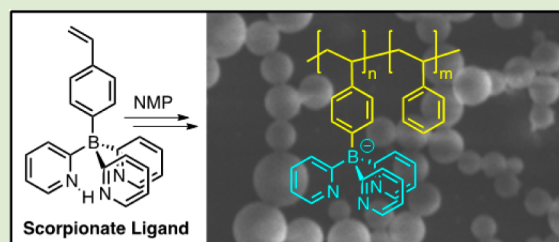
Transition metal-induced self-assembly is a powerful tool to generate supramolecular self-assembled materials such as supramolecular polymers, rings, and metal–organic frameworks.[1,2] Incorporation of polyfunctional pyridines into monomers and polymers has allowed researchers to generate supramolecular polymers with unique physical and chemical properties. For example, polymers that contain terpyridine and related ligands have been reported to display desirable optical, magnetic, stimuli-responsive, self-healing, and ion exchange properties.[3] Significant attention has also been paid to chelate-ligand functionalized polymers for recovering precious organometallic catalysts.[4]

While there are many examples of polymers that are functionalized with N-donor ligands, applications of tris(1-pyrazolyl)borates (Tp, also referred to as "scorpionate" ligands[5]) in polymer chemistry remain limited.[6] This is surprising considering the typically high binding strength associated with these powerful negatively charged chelate ligands. Indeed, molecular Tp ligands have been exploited successfully in numerous fields including catalysis, enzyme modeling, and materials chemistry.[6,7] An issue that has almost certainly mired broad utilization in polymer sciences is the tendency of Tp ligands to undergo degradation via B–N cleavage and rearrangement reactions.[8]

We have recently discovered that by replacing the 1-pyrazolyl groups with 2-pyridyl groups we can generate a more stable tris(2-pyridyl)borate (Tpyb) ligand with overall similar bite angles and electronic structure as the Tp ligands.[9] It is our intention to introduce these more robust Tpyb ligands as new versatile building blocks in supramolecular polymer chemistry.

Herein, we report on the synthesis and polymerization of 4-styryl-tris(2-pyridyl)borate (StTpyb). We also discuss the formation of the first Tpyb-functionalized block copolymers[10] and provide preliminary insights into their metal complexation behavior. The ultimate goal of these studies is to generate metal-containing responsive nanostructured materials.

Boron/silicon exchange[11] is a versatile method to introduce boron onto organic frameworks and generally proceeds with high selectivity. With that in mind, we designed the synthesis of our target Tpyb ligand utilizing a B/Si exchange between 4-(trimethylsilyl)styrene and BBr_3 in toluene to generate 4-(dibromoboryl)styrene. The latter can be further purified by sublimation under high vacuum. However, to avoid unnecessary loss due to thermally induced autopolymerization during purification, the reaction mixture of 4-(dibromoboryl)styrene was placed under vacuum to remove solvent and the byproduct Me_3SiBr, redissolved in toluene and then reacted directly with 2-pyridylmagnesium chloride. Since the Grignard reagent[9] contains 3.5 equiv of THF, it is important that the 4-(dibromoboryl)styrene is added to the 2-pyridylmagnesium chloride to minimize ring-opening of THF at the reactive boron center. Following aqueous workup, purification by chromatography, and recrystallization, StTpyb monomer was isolated in a moderate yield of about 20% (Figure 1A).
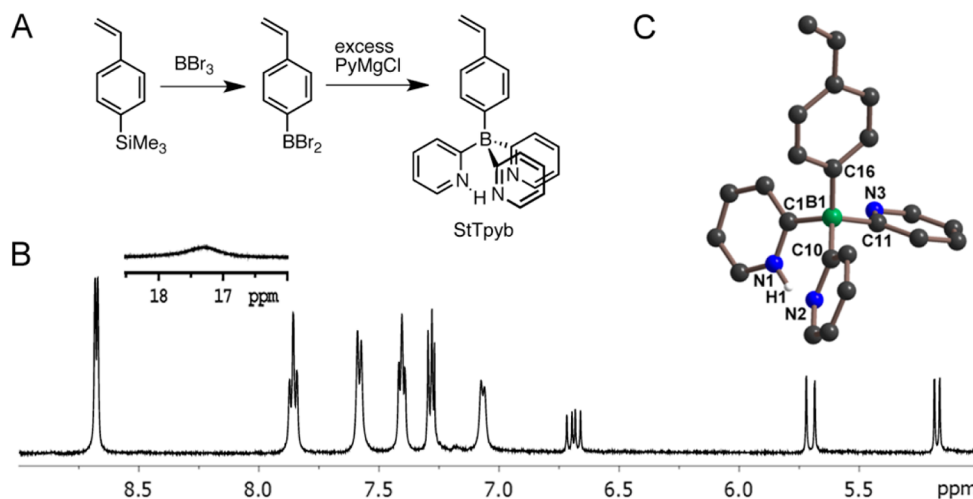
Figure 1. (A) Synthesis of StTpyb. (B) ^{1}H NMR spectrum of StTpyb in CDCl$_3$; the acidic proton at 17.3 ppm is shown as inset. (C) Ball-and-stick representation of the molecular structure of StTpyb (H atoms are omitted except for the acidic N−H proton).
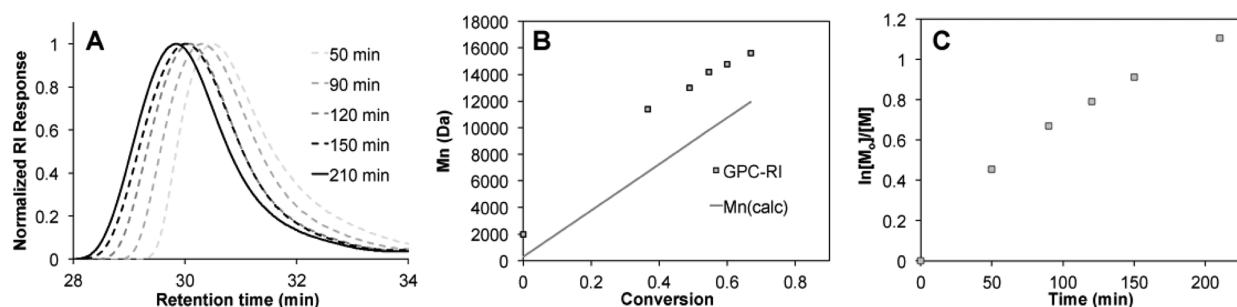
Scheme 1. (A) Nitroxide-Mediated Polymerization of StTpyb and Chain Extension with Styrene; (B) Nitroxide-Mediated Polymerization of Styrene and Chain Extension with StTpyb
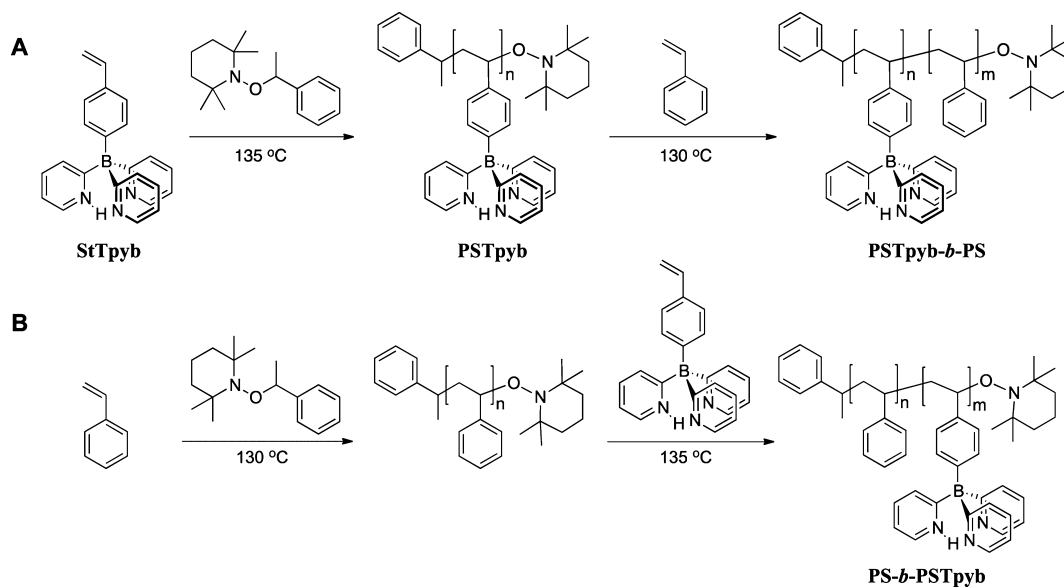
High resolution MALDI-MS and multinuclear NMR established the successful synthesis of the monomer StTpyb. ^{11}B NMR is arguably the most useful characterization method to confirm the formation of the product. The ^{11}B NMR of 4-(dibromoboryl)styrene displays a broad signal at 56 ppm. After reaction with 2-pyridylmagnesium chloride the ^{11}B NMR resonance shifts to −11.0 ppm and becomes significantly sharper (Figure S1); this chemical shift is characteristic of tetra-coordinate boron bound to four carbons. In the ^{1}H NMR the pyridyl protons give rise to the expected pattern of two sets of doublets and two sets of pseudotriplets between 8.68 and 7.41 ppm, while the acidic pyridyl NH proton resonates at about 17.3 ppm (Figure 1B). Single crystals of StTpyb suitable for X-ray diffraction analysis were grown by slow evaporation of an acetone solution. According to the X-ray crystal structure of StTpyb (Figure 1C), the pyridinium proton is shared between two of the pyridine groups which point toward each other (interplanar angle of 35.0°); both rings are almost perpendic-ular to the third pyridyl group (88.2, 83.7°), which in turn is

oriented perpendicular to the phenyl plane (88.2°) of the styryl moiety. All B−C bonds fall in a narrow range from 1.634(2) to 1.645(2) Å, which is typical of a tetracoordinate boron environment.

The availability of the olefin grants the potential for direct polymerization, but in the solid state StTpyb proved to be stable and did not undergo self-initiated polymerization under ambient conditions. To indicate the ability for StTpyb to undergo free radical polymerization, the monomer was reacted with AIBN in DMF at 90 °C for 40 h. The resulting white material (PSTpyb) showed broad resonances in the ^{1}H NMR spectrum, typical of atactic polymers (see Figure 3A), which can be ascribed to the nonstereospecific nature of the free radical polymerization process. The ^{11}B NMR displayed a similarly broadened resonance at −10.8 ppm, a chemical shift that is almost identical to that of the molecular tris(2-pyridyl)borate precursor. Gel permeation chromatography (GPC) of PSTpyb in DMF containing 20 mM NH$_4$[PF$_6$] at 60 °C revealed a relatively broad major trace (PDI = 1.57) with

Figure 2. (A) GPC RI traces (0.5 mL/min, DMF, 20 mM $NH_4[PF_6]$) for the nitroxide-mediated polymerization of StTpyb at progressive polymerization times ([M]/[I] = 50:1; DMF; 135 °C). (B, C) Corresponding kinetic plots (conversion determined by ^1H NMR integration of the olefinic resonances relative to 1,4-dimethoxybenzene as an internal standard).

a $\overline{M}_n$ of approximately 35000 Da relative to narrow PS standards. These results demonstrate that StTpyb is polymerizable and can potentially undergo controlled free radical polymerization (CFRP), which provides an avenue for block copolymer synthesis and the targeted development of metal-containing nanostructured materials.

The formation of metal-containing block copolymers has seen much progress in recent years as CFRP methods have proven highly versatile in the development of new functional materials.[12] However, our initial attempts at atom transfer radical polymerization (ATRP)[13] and reversible addition–fragmentation chain transfer (RAFT)[14] polymerization of StTpyb proved unsuccessful. We attributed this to the presence of the strong chelate ligand that could interfere with the catalyst/mediator system used in ATRP and RAFT polymerization. Another contributing factor could be the strong electron-donating effect of the borate moiety. Nitroxide-mediated polymerization (NMP)[15] is generally well suited for polymerization of various (functional) styrene derivatives, and was therefore explored for the controlled radical polymerization of StTpyb. Using 2,2,6,6-tetramethyl-1-(1-phenylethoxy)-piperidine[16] as a unimolecular initiator StTpyb was successfully polymerized in DMF at 135 °C (Scheme 1A).

Gel permeation chromatography of the resultant polymer (PSTpyb) using narrow PS standards gave a monomodal distribution with a $\overline{M}_n$ of 27400 Da and a relatively low PDI of 1.21 (Figure 2), demonstrating good control of the polymerization. Kinetic studies of the nitroxide-mediated polymerization confirmed chain extension; with increasing conversion there was a slight deviation from pseudo-first-order kinetics of the polymerization. The latter is attributed to some termination due to chain–chain coupling processes at high monomer conversion. We found that the molecular weights for PSTpyb are generally about 1.5 times higher than the calculated molecular weights, which is likely due to the particular monomer structure and possibly some interactions with the column material. Consistent is that the monomer StTpyb itself (MW = 349 Da) gives a similarly overestimated $\overline{M}_n$ of 1350 Da by GPC under otherwise identical conditions.

Encouraged by these results, we decided to explore the utility of PSTpyb ($\overline{M}_n$ = 27400 Da) as a macroinitiator in the formation of block copolymers. A chain extension reaction with styrene (7.4 g; [PSTpyb]/[St] = 1:31400) as a second monomer was conducted at 130 °C for 3.5 h in the presence of 2 mL of DMF to solubilize the macroinitiator PSTpyb (Scheme 1A). The product was precipitated into hexanes repeatedly to recover the block copolymer PSTpyb-b-PS. The

^1H NMR spectrum of PSTpyb-b-PS shows broad resonances due to the PS block at 7.03, 6.57, 1.86, and 1.43 ppm (see Figure 3B). Because of the large size of the PS block most of
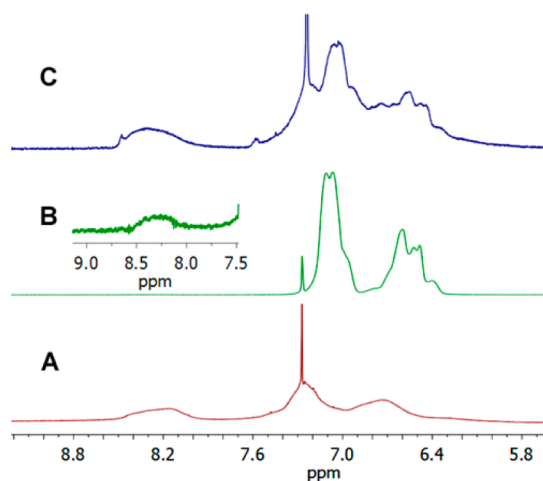

Figure 3. Aromatic region of the ^1H NMR spectra of (A) PSTpyb homopolymer, (B) PSTpyb-b-PS block copolymer, and (C) PS-b-PSTpyb block copolymer; all data in $CDCl_3$.

the resonances due to the StTpyb block are overlapped and overshadowed by the PS resonances; however when examined closely there is a weak resonance between 8.89 ppm and 7.81 ppm that can be clearly assigned to the pyridyl groups of the StTpyb block. A resonance at −11.1 ppm in the ^{11}B NMR further confirms the presence of the StTpyb block (see the Supporting Information, Figure S1).

GPC analysis in DMF with 20 mM $NH_4[PF_6]$ revealed a single monomodal trace corresponding to a $\overline{M}_n$ of 150 kDa and a PDI of 1.5 (Figure 4A). This would indicate that the PS block possesses a DP_n of approximately 1200, assuming a PSTpyb block of 78 units. As noted above, the block length of PSTpyb is likely overestimated; this is consistent with ^1H NMR integration and elemental analysis results, which indicate a much higher ratio of about St/Stpyb = 200/1.

We also investigated a reverse block copolymerization protocol in which the StTpyb monomer was polymerized using nitroxide-terminated PS. To prepare the PS macroinitiator, styrene was reacted in bulk with 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine at 130 °C, which gave a polymer with M_n = 3000 Da and a PDI of 1.21 (Scheme 1B). This macroinitiator was then used to polymerize StTpyb at 135 °C in DMF to give a polymer with M_n = 11500 Da and a PDI of
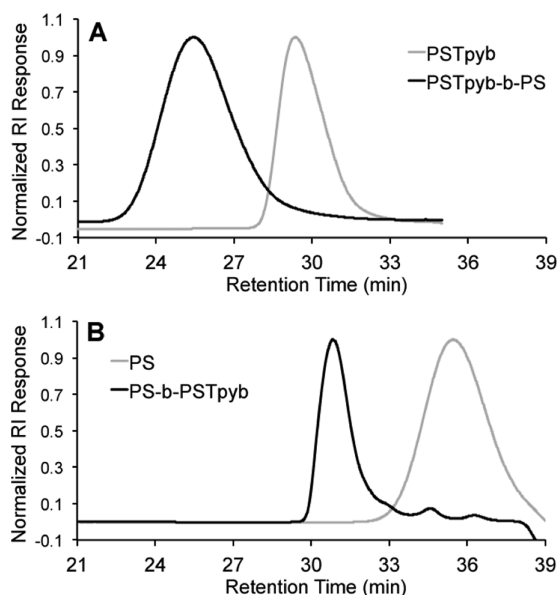
Figure 4. (A) GPC-RI traces of PSTpyb and PSTpyb-*b*-PS; (B) GPC-RI traces of PS-macroinitiator and PS-*b*-PSTpyb (20 mM $NH_4[PF_6]$ in DMF, 0.5 mL/min, 60 °C).

1.10 based on GPC-RI detection (Figure 4B).[17] This corresponds to an average of about 29 styrene and 24 StTpyb repeating units. ^{1}H NMR analysis (see Figure 3C) indicated a block ratio of approximately St/StTpyb = 2:1, corresponding to an average of 15 StTpyb units, which is as expected somewhat lower than the GPC result.

The block copolymers PSTpyb-*b*-PS and PS-*b*-PSTpyb are amphiphilic and therefore expected to undergo self-assembly in block-selective solvents. To explore the self-assembly behavior a sample of PSTpyb-*b*-PS was dissolved in CH_2Cl_2 (or DMF) and dialyzed with methanol to give a solution that according to

dynamic light scattering (DLS) analysis consisted of relatively regular (PDI = 0.100) polymer aggregates with an average hydrodynamic diameter of $D_{h,app}$ = 445 nm (Figure 5). These aggregates are thought to consist of a ligand-functionalized PSTpyb shell and a PS core. The relatively large size is consistent with imaging results from scanning electron microscopy (SEM; Figure 5B; see also Figure S3 in the Supporting Information for TEM data from $CHCl_3$/MeOH = 1:10). Reverse micelles were generated by dialysis of a CH_2Cl_2 solution of the polymer with THF. In this case, the features that are evident in the DLS histogram ($D_{h,app}$ = 35 nm; Figure 5A) and SEM (see the Supporting Information, Figure S4) are expected to consist of PSTpyb cores surrounded by PS shells. Qualitatively similar results were obtained for the polymer PS-*b*-PSTpyb, but DLS analysis revealed less regular size distributions (see the Supporting Information, Figure S5). The number-averaged hydrodynamic diameters of about 200 nm in MeOH as the solvent and about 23 nm in THF are relatively smaller, as expected, given the much shorter PS block.

We also performed preliminary studies on the metal complexation of the aggregates. Based on a reactivity test with a molecular model compound, complexation of the *t*-butylphenyl-tris(2-pyridyl)borate ligand to Cu(II) using Cu-$(ClO_4)_2$ in MeOH/THF in the presence of NEt_3 is facile and results in a clearly observed color change from light blue−green to deep blue−purple (see Figure S6 in the Supporting Information). Formation of the metal complex was further confirmed by UV−vis, multinuclear NMR, and high resolution MALDI-MS. In a similar fashion, we added first $Cu(ClO_4)_2$ and then NEt_3 to a block copolymer aggregate solution of PSTpyb-*b*-PS in methanol. At relatively high Cu(II) content, a light blue color similar to the one observed for the monomer complexation developed (see Figure S6 in the Supporting Information). SEM micrographs (Figure 5C,D) taken after the metal salt addition show evidence that the micelles link together which
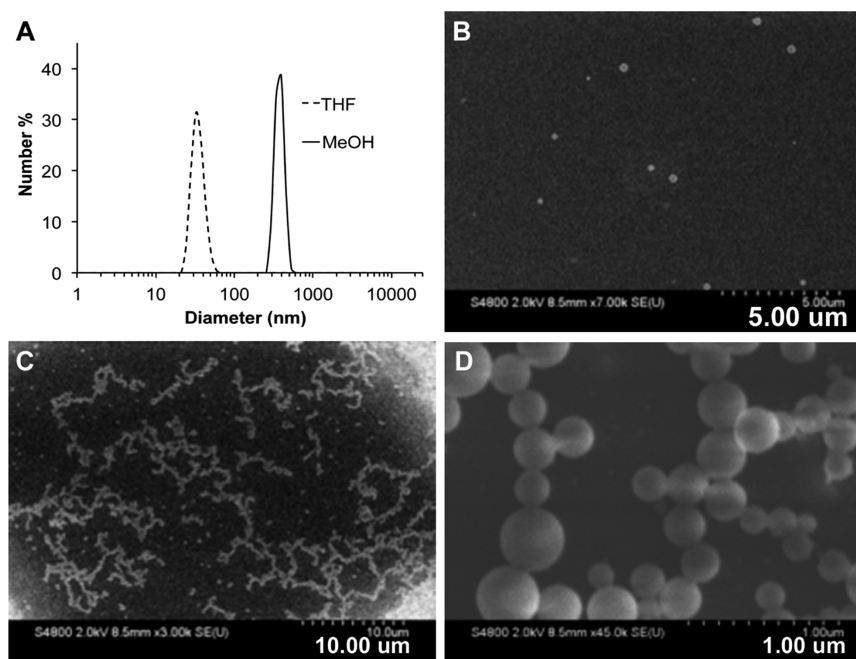
Figure 5. (A) Dynamic light scattering histograms of solutions of PSTpyb-*b*-PS after dialysis from CH_2Cl_2 to MeOH and THF, respectively. (B) SEM micrograph showing micelles of PSTpyb-*b*-PS formed upon dialysis from CH_2Cl_2 to MeOH. (C, D) SEM micrographs after addition of $Cu(ClO_4)_2$ to the micelle solution in MeOH.

indicates the formation of ML_2 complexes along the surfaces of the micelles. In contrast, the addition of $Cu(ClO_4)_2$ to the reverse micelles of PSTpyb-*b*-PS in THF did not generate corresponding chains of micelles according to SEM imaging.

In conclusion, we have established the synthesis of a new polymerizable scorpionate ligand based on tris(2-pyridyl)-borate. Utilizing nitroxide-mediated polymerization we successfully prepared homo- and block copolymers of this ligand. We also demonstrated that micellar structures or larger aggregates can be obtained using block-selective solvents. It is important to note that the properties of the anionic scorpionate-type ligands are very different from those of frequently employed terpyridines, resulting in vastly different properties of the corresponding polymeric materials. Work is currently underway to gain access to monodisperse micellar structures and to further explore the cross-linking of these micelles by complexation with redox-active metals. Also of potential interest is the reversible protonation of the polymers described herein, which could have implications on pH-dependent release properties and may prove useful for proton-conducting membrane development.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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