# Aqueous Cationic Polymerization of *p*-Methoxystyrene Using Hydrophilic Phenylphosphonic Acids

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## ABSTRACT

The use of phosphonic acids [$(HO)_2P(O)R$, R = Ph or Ph-*o,m,p*-$NO_2$] in conjunction with a water-tolerant Lewis acid, ytterbium trifluoromethanesulfonate [$Yb(OTf)_3$], induces the cationic polymerization of *p*-methoxystyrene (*p*MOS). The polymerization is performed by addition of *p*MOS to a suspension of either nitrophenylphosphonic acid ($NO_2PPA$) or phenylphosphonic acid (PPA) in an aqueous solution of $Yb(OTf)_3$ at 23°C. Higher [$NO_2PPA$]$_0$ yielded higher initial polymerization rates, but had no effect on ultimate monomer conversion. Compared to PPA, $NO_2PPA$ yielded higher polymerization rates and higher ultimate conversions; however, PPA resulted in more controlled molecular weights and lower molecular weight distribution (MWD). The number-average molecular weights of the polymers increased with conversion while MWD decreased. The polymerization rate was

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affected by the presence of polar or non-polar solvents. Increasing the polymerization temperature dramatically increased the polymerization rate.

## INTRODUCTION

Recent research reports have demonstrated that certain Lewis acids based upon rare earth lanthanide trifluoromethanesulfonates (triflates) are able to catalyze carbon–carbon bond-forming reactions in aqueous media. These reactions include Michael additions of $\beta$-ketoesters,[1] aldol reactions of silyl enol ethers with aldehydes,[2,3] allylation of aldehydes,[4] and Mannich-type,[5] and aza Diels–Alder reactions.[6] The lanthanide series containing compounds used in these reactions are considered strong Lewis acids because they possess strongly electron-withdrawing trifluoromethanesulfonate groups. The most commonly used Lewis acid in the aforementioned reactions is ytterbium trifluorometha-nesulfonate [Yb(OTf)$_3$].

Recently, the controlled cationic polymerization of p-methoxystyrene (pMOS) in aqueous media using Yb(OTf)$_3$ as the Lewis acid catalyst has been reported.[7] The reactions were conducted as suspension polymerizations at 30°C, in a solvent medium consisting of CCl$_4$/water (5/3 v/v), using an initiator with a structure similar to the monomer. The polymerizations proceeded in a controlled fashion, i.e., molecular weight increased linearly over time and molecular weight distributions (MWD) decreased with conversion; however, predetermined molecular weights were not achieved due to chain transfer reactions that occurred at high conversions. One major drawback to the polymerizations was the excessive reactions times required to reach high monomer conversion (98% conversion in 200 hr). This indicated an unusually slow polymerization rate for a cationic polymerization.

Attempts to increase the rate of polymerization of pMOS in aqueous media have been reported using surfactants[8] and sulfonic acid-based initiators.[9] Cationic surfactants based upon alkylammonium salts with long alkyl chains increased the rate of polymerization most effectively while cationic surfactants with short alkyl chains did not afford a stable emulsion because they were less surface active.[8] The time required to reach high conversions (>90%) was considerably less for this system than the suspension system (100 hr compared to 200 hr). It was further demonstrated that using water-soluble sulfonic acids dramatically decreased the polymerization time of the pMOS system to approximately 24 hr.[9] In this case, the initiating species was created in situ by the addition of the acid across the monomer double bond, which was reported to occur by diffusion of the sulfonic acid into the monomer phase. The polymers that were obtained using these reaction conditions increased in molecular weight with conversion and had relatively low polydispersities; however, extensive chain transfer occurred at high conversions.

In this article, we report the use of hydrophilic phosphonic acids to create novel initiating species in situ for the cationic polymerization of pMOS in a large volume of water using Yb(OTf)$_3$ as the Lewis acid. The polymerization rate and final polymer number average molecular weight ($M_n$) and MWD can be altered by changing either the polarity of the polymerization medium through the addition of polar or non-polar

cosolvents or by changing the temperature. These new initiators provide an alternate approach for polymerizing *p*MOS in an aqueous environment and are an economically attractive alternative to their sulfonic acid counterparts.

## EXPERIMENTAL

### Materials

4-Vinylanisole (*p*-methoxystyrene) (Aldrich, Milwaukee, WI) was distilled over $CaH_2$ under reduced pressure and stored at $-80°C$. Ytterbium trifluoromethanesulfonate [Yb(OTf)$_3$] was obtained as a hydrate (Aldrich, Milwaukee, WI) and used as received without further purification. Phenylphosphonic acid (PPA) (98%, Aldrich, Milwaukee, WI) and fuming nitric acid (Fisher, Pittsburgh, PA) were used as received. All other reagents were used as received unless specified.

### Measurements

Molecular weights and MWD of polymers were determined using a GPC system consisting of a Waters Alliance 2690 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector (MiniDAWN[TM], Wyatt Technology, Inc., Santa Barbara, CA), and an interferometric refractometer (Optilab DSP[TM], Wyatt Technology, Inc., Santa Barbara, CA), as previously described.[10] Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were 5 mg/mL in freshly distilled THF, and the injection volume was 100 μL. ^{1}H-NMR data were obtained using a Varian 300 (500 MHz) spectrometer, 5 mm O.D. tubes, $CDCl_3$ as solvent, and tetramethylsilane as the internal standard. Sample concentrations were 5% (w/v). The spectra were obtained using Galactic Grams v.5[®] software (Thermo Galactic, Salem, NH).

### Synthesis of Nitrophenylphosphonic Acid (Mixed Ortho, Meta, Para Isomers, NO₂PPA)

The NO$_2$PPA was prepared using a modification of a previously published procedure.[11] Phenylphosphonic acid (50.0 g, 0.316 mol) was slowly added over 15 min to stirred fuming nitric acid (290 mL). The resulting solution was stirred for an additional 1 hr and subsequently poured over ice (500 g). The solution was then transferred to a large round bottom flask and steam distilled until 1.5 L of distillate was collected. The residual solution left in the round bottom flask was vacuum stripped to remove $H_2O$, and the resulting solid was dried in a vacuum oven over concentrated $H_2SO_4$ (61.41 g, 96% yield, m.p. 138–140°C). The product was characterized by ^{1}H-NMR and FT-IR.

### General Polymerization Procedure

Into a small test tube, equipped with a magnetic stir bar and exposed to the atmosphere, were charged 1.0 mL of a 0.800 M solution of Yb(OTf)$_3$ in deionized water

and 0.15 mmol of an appropriate initiator. The reaction mixture was allowed to stir for 5 min; then 1.0 mL (7.52 mmol) $p$MOS was added. The molar concentrations, based upon the total reaction volume, were as follows: $p$MOS (3.76 M), initiator (0.075 M), and Yb(OTf)$_3$ (0.400 M). The target number average degree of polymerization ($X_n$) was 50 ($M_n = 6710$ g/mol). It should be noted that the above procedure was also modified to obtain polymers with target $X_n$ of 25 (3355 g/mol) by using 0.03 mmol (0.150 M) initiator. Polymerizations were quenched with excess toluene, acetone, and a H$_2$O/phosphoric acid solution (3 : 1 v/v). The organic layer was washed several times with the H$_2$O/PPA solution, filtered through a glass wool plug, and was subsequently precipitated into stirred methanol. Monomer conversion was determined via gravimetric analysis.

## RESULTS AND DISCUSSION

Hydrophilic phosphonic acids (PPA and NO$_2$PPA) were used to initiate the cationic polymerization of $p$MOS in water in conjunction with a water-tolerant Lewis acid, Yb(OTf)$_3$ (Fig. 1). The polymerizations were performed at 23°C in the presence of a large volume of water [1/1 aqueous/organic (v/v)] by first creating a suspension of the phosphonic acid in an aqueous solution of Yb(OTf)$_3$ followed by the addition of $p$MOS. As the polymerizations proceeded to high monomer conversions, polymer began to precipitate into the aqueous phase because the volume of the solvent (monomer phase) decreased. The polymerizations were quenched by dilution with an excess of toluene and a water/phosphoric acid solution. The water/phosphoric acid solution was used to remove an interphase present between the organic (toluene) and aqueous layers.

The polymerization rate was found to be dependent upon the nature and concentration of the phosphonic acid that was used. NO$_2$PPA resulted in a higher polymerization rate compared to the PPA-initiated system (Fig. 2). In addition, a slightly higher initial polymerization rate was observed for the higher initiator concentrations. The nitro group in NO$_2$PPA may increase its hydrophilicity, thus increasing its local concentration at the aqueous/organic interface. This is similar to the results observed in the aqueous cationic polymerization of $p$MOS initiated with $p$-substituted benzenesulfonic acids.[9]

For all polymerizations, the target $M_n$ was exceeded, indicating that molecular weight is not fully controlled by the monomer/initiator ratio (Table 1). In addition, the appearance of the GPC traces at low conversions suggests slow initiation possibly due to the heterogeneity of the system and the limited solubility of the phosphonic
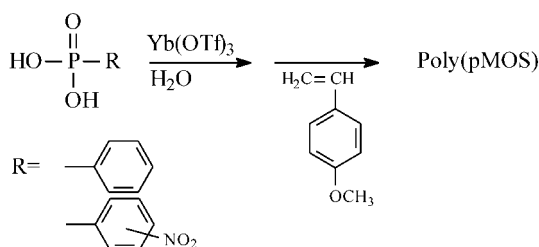


***Figure 1.*** Synthetic scheme for aqueous cationic polymerization of $p$MOS using PPA with Yb(OTf)$_3$.
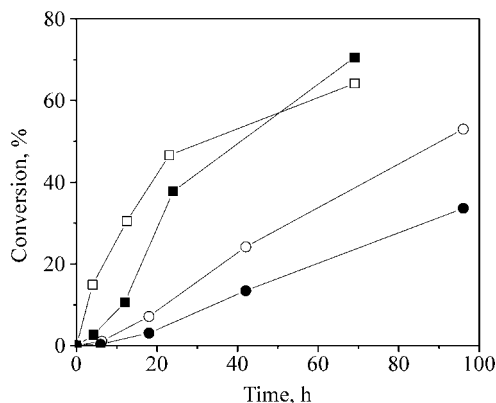
***Figure 2.*** Conversion–time plot for the polymerization of *p*MOS with $Yb(OTf)_3$ in $H_2O$ at 23°C initiated with $NO_2PPA$ or PPA. $[Yb(OTf)_3]_0 = 0.400\,M$, $[pMOS]_0 = 3.76\,M$, and $[NO_2PPA]_0 = 0.075$ (■) or $0.150\,M$ (□), or $[PPA]_0 = 0.075$ (●) or $0.150\,M$ (○). All concentrations calculated using total reaction volume; aqueous phase : organic phase $= 1/1$ (v/v).

acids in the aqueous and organic phases. The MWDs were relatively low ($M_w/M_n \sim 1.6$–$1.8$).

The structure of poly(*p*MOS) obtained using $NO_2PPA$ and PPA was examined using $^1$H-NMR spectroscopy (Fig. 3). The characteristic signals of poly(*p*MOS) were the same regardless of which phosphonic acid was used as initiator, i.e., aromatic protons (a),

***Table 1.*** Effect of various phosphonic acid initiators on polymerization of *p*MOS in aqueous media.[a]

| Initiator | $[Initiator]_0$ (mol/L) | Conversion $(\%)$[b] | Time (hr) | $M_n$ (g/mol) | PDI |
|---|---|---|---|---|---|
| $NO_2PPA$ | 0.075 | 3 | 4 | 7,130 | 1.7 |
| $NO_2PPA$ | 0.075 | 11 | 12 | 7,480 | 1.7 |
| $NO_2PPA$ | 0.075 | 38 | 24 | 9,780 | 1.7 |
| $NO_2PPA$ | 0.075 | 71 | 69 | 9,910 | 1.6 |
| $NO_2PPA$ | 0.150 | 15 | 4 | 9,510 | 1.8 |
| $NO_2PPA$ | 0.150 | 31 | 13 | 10,600 | 1.7 |
| $NO_2PPA$ | 0.150 | 47 | 23 | 10,600 | 1.7 |
| $NO_2PPA$ | 0.150 | 64 | 69 | 10,400 | 1.8 |
| PPA | 0.075 | 7 | 18 | 6,530 | 1.5 |
| PPA | 0.075 | 24 | 42 | 6,530 | 1.5 |
| PPA | 0.075 | 53 | 96 | 6,780 | 1.5 |
| PPA | 0.150 | 3 | 18 | 6,360 | 1.6 |
| PPA | 0.150 | 13 | 42 | 6,280 | 1.5 |
| PPA | 0.150 | 34 | 96 | 7,070 | 1.5 |

[a]$[Yb(OTf)_3]_0 = 0.400\,M$, $[pMOS]_0 = 3.76\,M$, and $[NO_2PPA]_0 = 0.075$ or $0.150\,M$, or $[PPA]_0 = 0.075$ or $0.150\,M$. All concentrations calculated using total reaction volume; aqueous phase: organic phase $= 1/1$ (v/v).
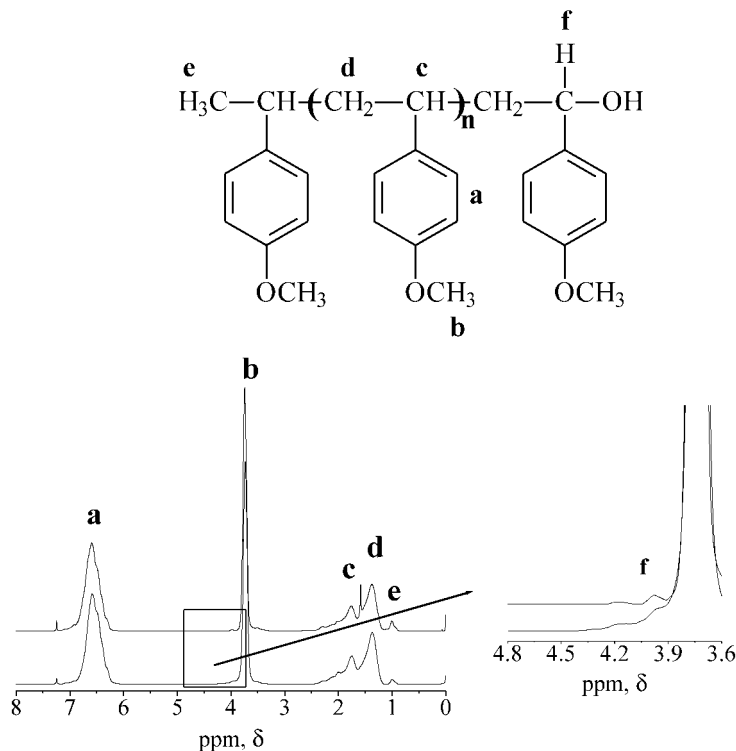[b]Determined by gravimetric analysis.

***Figure 3.*** $^1$H-NMR spectra of poly($p$MOS) initiated with (a) NO$_2$PPA ($M_n = 10{,}400$, $M_w/M_n = 1.8$) and (b) PPA ($M_n = 7060$, $M_w/M_n = 1.5$). [Yb(OTf)$_3$]$_0$ = 0.400 M, [$p$MOS]$_0$ = 3.75 M, [NO$_2$PPA]$_0$ = [PPA]$_0$ = 0.150 M.

methoxy groups (b), and main chain aliphatic protons (c and d). In addition, the resonance at 1.0 ppm (e), due to the methyl group at the head of the polymer chain, was observed, indicating that the polymer was initiated from the addition of a proton from NO$_2$PPA or PPA to the monomer. The resonance at 4.2 ppm (f) was attributed to the hydroxyl terminus of poly($p$MOS). Due to the large excess of water, the active cationic species may be terminated with water creating hydroxy-terminated polymer chains. This then implies that the aqueous cationic polymerization of $p$MOS proceeds via a dormant–active chain equilibrium in which Yb(OTf)$_3$ complexes with a hydroxyl end-group, resulting in reinitiation of the polymer chains. Reinitiation of hydroxy-terminated poly($p$MOS) chains has been previously reported using sulfonic acid based initiators in conjuction with Yb(OTf)$_3$.[9]

Table 2 lists the results of experiments in which either a polar (CH$_2$Cl$_2$) or a non-polar solvent (toluene) was added to the phosphonic acid-based polymerizations. As expected for a cationic polymerization, upon addition of CH$_2$Cl$_2$ the time to reach a specific monomer conversion decreased compared to a control system without solvent. Addition of toluene induced a slower polymerization compared to both the CH$_2$Cl$_2$ and control systems. It is also interesting to note that changing the aqueous : organic ratio affected the polymerizations. As the aqueous : organic ratio was decreased, the polymerizations

***Table 2.*** Cosolvent effects and aqueous : organic ratio effects on polymerization of _p_MOS in aqueous media.

| Cosolvent | Aq : Org[a] (v/v) | $[Yb(OTf)_3]_0$ (mol/L) | Conversion (%)[b] | Time (hr) | Temperature (°C) | $M_n$ (g/mol) | PDI |
|---|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | 1 : 1 | 0.400 | 8 | 5 | 23 | 9,970 | 1.8 |
| $CH_2Cl_2$ | 1 : 1 | 0.400 | 49 | 19 | 23 | 13,600 | 1.7 |
| $CH_2Cl_2$ | 1 : 1 | 0.400 | 85 | 27 | 23 | 17,900 | 1.5 |
| $CH_2Cl_2$ | 1 : 1 | 0.400 | 86 | 44 | 23 | 21,800 | 1.4 |
| $CH_2Cl_2$ | 2 : 3 | 0.320 | 7 | 4 | 23 | 11,300 | 2.1 |
| $CH_2Cl_2$ | 2 : 3 | 0.320 | 27 | 16 | 23 | 12,800 | 2.0 |
| $CH_2Cl_2$ | 2 : 3 | 0.320 | 51 | 40 | 23 | 13,200 | 2.0 |
| $CH_2Cl_2$ | 2 : 3 | 0.320 | 83 | 82 | 23 | 14,200 | 1.8 |
| Toluene | 1 : 1 | 0.400 | 44 | 25 | 23 | 2,710 | 3.8 |
| Toluene | 1 : 1 | 0.400 | 81 | 43 | 23 | 3,340 | 3.2 |
| Toluene | 1 : 1 | 0.400 | 91 | 65 | 23 | 9,670 | 1.8 |
| Toluene | 2 : 3 | 0.320 | 6 | 8 | 23 | 7,600 | 1.6 |
| Toluene | 2 : 3 | 0.320 | 16 | 24 | 23 | 7,480 | 1.6 |
| Toluene | 2 : 3 | 0.320 | 36 | 68 | 23 | 7,730 | 1.6 |
| None | 1 : 1 | 0.400 | 1 | 3 | 23 | 13,800 | 1.8 |
| None | 1 : 1 | 0.400 | 6 | 3 | 30 | 12,400 | 1.8 |
| None | 1 : 1 | 0.400 | 22 | 3 | 40 | 8,290 | 1.6 |
| None | 1 : 1 | 0.400 | 76 | 3 | 48 | 11,600 | 1.5 |
| None | 1 : 1 | 0.400 | 87 | 3 | 65 | 11,700 | 1.8 |

[a]Aqueous : organic ratio calculated based upon total reaction volume. 1 : 1 polymerizations = 1 mL _p_MOS + 0.5 mL cosolvent + 1.5 mL 0.800 M Yb(OTf)$_3$. 1 : 1.5 polymerizations = 1 mL pMOS + 0.5 mL cosolvent + 1.0 mL 0.800 M Yb(OTf)$_3$. [NO2PPA]$_0$ = 0.150 M.
[b]Determined by gravimetric analysis.

became slower because the overall concentration of catalyst $[Yb(OTf)_3]$ in the system decreased. However, the expected solvent effects were still present. The $M_n$ was higher than the target $M_n$ in almost all cases, with the exception of one of the toluene polymerizations. The presence of $CH_2Cl_2$ resulted in higher $M_n$ at a given conversion compared to the toluene or control systems. In general, the MWDs for all the polymerizations decreased with conversion, and most were in the range of 1.5–2.0.

The polymerization rate was found to be highly dependent upon temperature. Increasing the temperature from 23°C to 48°C increased monomer conversion dramatically; at the latter temperature conversion was >75% in just 3 hr (Fig. 4). Conversions higher than ~90% were not obtained, presumably because of the lack of solvent (monomer) at higher conversions. As the temperature was increased from 23°C to 65°C, the conversion after 3 hr increased from 1.8% to 87.4% (Table 2). The increase in temperature did not affect the $M_n$ or MWD dramatically.

The dramatic increase in the rate of polymerization with increasing temperature was surprising. For many cationic polymerizations, the energy of activation for polymerizations ($E_p$) is negative; however, monomer selection, initiator, coinitiator, and solvents can all affect both the sign and value of $E_p$. The $E_p$ for the $NO_2PPA$ polymerizations was estimated through the use of an Arrhenius plot using instantaneous
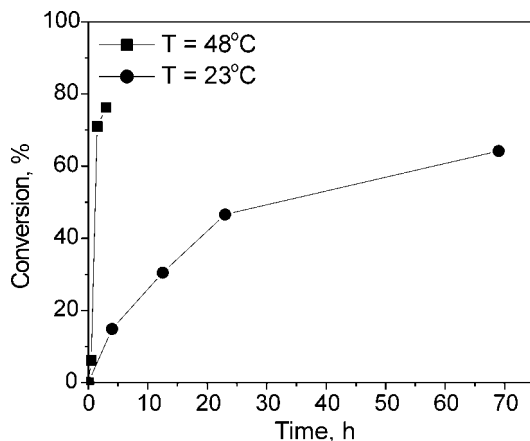
**Figure 4.** Conversion–time plot for the polymerization of $p$MOS with Yb(OTf)$_3$ in H$_2$O initiated with NO$_2$PPA at (■) 48 and (●) 23°C. [Yb(OTf)$_3$]$_0$ = 0.400 M, [$p$MOS]$_0$ = 3.76 M, and [NO$_2$PPA]$_0$ = 0.150 M.

rates of polymerization ($R_{pinst}$), calculated at low conversions ($<25\%$) as follows:

$$-\frac{d[M]}{dt} \cong -\frac{\Delta[M]}{\Delta t} = -\frac{[M]_x - [M]_0}{t_x - t_0} \cong \text{rate of polymerization}$$

The Arrhenius plot, shown in Fig. 5, revealed an apparent activation energy of 96 kJ/mol. The enhancement in the polymerization rate with increased temperature is probably due to higher catalytic activity of Yb(OTf)$_3$ caused by increased solubility in the monomer phase, enhancing the contact of the catalyst with the growing chains.
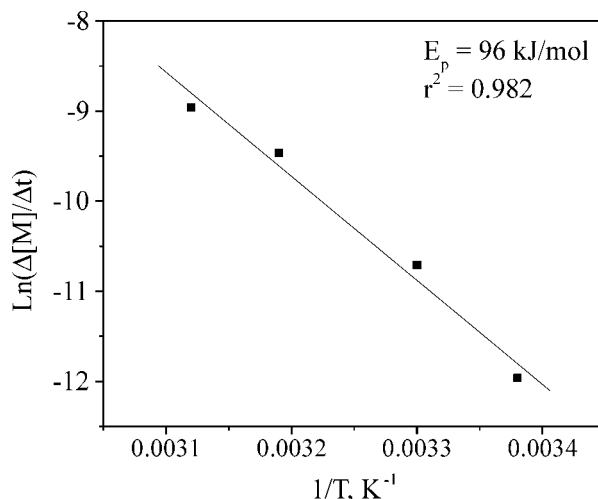


**Figure 5.** Arrhenius plot for the polymerization of $p$MOS in aqueous media using NO$_2$PPA as the initiator. [Yb(OTf)$_3$]$_0$ = 0.400 M, [$p$MOS]$_0$ = 3.76 M, and [NO$_2$PPA]$_0$ = 0.150 M.

## CONCLUSION

Various PPAs can be used to initiate *p*MOS in the presence of water in conjunction with the water tolerant Lewis acid, Yb(OTf)$_3$. Polymerizations run without additional solvents resulted in polymers with a moderately narrow MWD but poorly controlled $M_n$. Addition of a polar cosolvent induced faster polymerizations but resulted in polymers with broader MWD and much higher than target $M_n$. In contrast, addition of a non-polar solvent resulted in much slower polymerizations, which generally had narrower MWD and more controlled $M_n$. Increasing polymerization temperature yielded a significant increase in the rate of polymerization.

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