

Effect of Molecular Weight on the Rheological Properties of Atactic Poly(vinyl alcohol)/Dimethylsulfoxide/Water Solution

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ABSTRACT: This article describes the molecular weight effect of atactic poly(vinyl alcohol) (a-PVA) on the rheological properties of 7.5, 10.0, and 12.5 g/dL solutions of a-PVA with number-average degrees of polymerization (P_n) of 4000 and 1700 in dimethylsulfoxide/water mixture. a-PVA with a P_n of 1700 solutions exhibited almost Newtonian flow behavior, whereas high molecular weight a-PVA, with a P_n of 4000 solutions, exhibited shear-thinning behavior. On the plot of storage and loss moduli of a-PVA with a P_n of 1700 solutions, the dynamic storage modulus of a-PVA, with a P_n of 1700 solutions, was

smaller than the dynamic loss modulus over the frequency range of 10^{-1} to 10^2 rad/s. However, the dynamic storage modulus of a-PVA, with a P_n of 4000 solutions, was smaller than the dynamic loss modulus in the sol state and, in the postgel state, the dynamic storage modulus became larger than the dynamic loss modulus, indicating the evolution of viscoelastic solid properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 41–46, 2004

Key words: molecular weight; atactic poly(vinyl alcohol) (a-PVA); rheology; shear; modulus

INTRODUCTION

Poly(vinyl alcohol) (PVA) is generally prepared by the saponification of poly(vinyl ester) precursors such as poly(vinyl acetate) and poly(vinyl pivalate) because vinyl alcohol rearranges to give its tautomer, acetaldehyde, which cannot be polymerized.¹

PVA is a semicrystalline polymer whose molecular chain conformation in the crystal regions is very similar to that of polyethylene (PE), such as an all-*trans* structure. Thus, the crystal lattice modulus of PVA along the chain direction is estimated to be over 250 GPa,^{2,3} as high as that of PE. However, microhardness exists in the PVA crystalline phase, attributed to inter- and intramolecular hydrogen bondings between adjacent hydroxyl groups, which gives rise to the difference in the crystal structure of PE. Also, PVA is typically a water-soluble polymer, a good nontoxic material for human use, and a biodegradable polymer. It is used as a coating in textiles, a stabilizer in industrial fields, polarizing films, sizers, and adhesives for bio-

materials, drug-delivery systems, contact lenses, and nanomaterials, and its uses continue to expand.⁴

In particular, the molecular weight is a fundamental factor affecting physical properties of PVA.^{5–8} Generally, viscosity of aqueous PVA solutions is considered to be a function of molecular weight and concentration of PVA. Rheology is important in the formulation of polymeric materials, preparing them for the fabrication process. As a result, for materials such as fibers, films, and gels, it is a prerequisite to investigate the rheological properties of such materials. PVA solutions show various rheological behaviors with respect to temperature, degree of saponification (DS), molecular weight, stereoregularity, and so on.

Naito and coworkers^{9,10} studied the behavior of the aqueous solution viscosity of PVA at 1–10% concentration. From a detailed study, Naito concluded that each individual molecule is dispersed in water in the form of thread-filled spheres containing a large amount of water below the inflection point and that interaction (entanglement) occurs between these molecular spheres above the inflection point.

For this article, we investigated rheological behaviors of solutions with diverse polymer concentrations of atactic PVA (a-PVA) with different molecular weights in a dimethylsulfoxide (DMSO)/water mixture.

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TABLE I
Molecular Parameters of PVAs Used

| P_n | DS (%) | S-diad content (%) |
|-------|--------|--------------------|
| 1700 | 99.9 | 52.1 |
| 4000 | 99.9 | 52.4 |

EXPERIMENTAL

Materials

Vinyl acetate (VAc; Shin-Etsu Chemical Co., Shanghai, China) was washed with an aqueous solution of NaHSO_3 and water and dried with anhydrous CaCl_2 , followed by distillation in nitrogen atmosphere under reduced pressure. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN; Wako Pure Chemicals, Osaka, Japan) was recrystallized twice from absolute methanol before use. PVA, with a number-average molecular weight of 127,000 and degree of saponification of 88% (Aldrich Co., Milwaukee, WI), was used as a suspending agent. Other extrapure-grade reagents were used without further purification. Water used for all the procedures was deionized.

Preparation of PVA

For a-PVA with number-average degree of polymerization (P_n) of 1700, VAc was solution polymerized in methanol at 60°C with ADMVN as an initiator, followed by subsequent saponification. To synthesize high molecular weight a-PVA, having a P_n of 4000, VAc was suspension polymerized in water at 40°C with ADMVN as an initiator, followed by subsequent saponification. The molecular parameters of two PVAs are listed in Table I.

Characterization of PVA

The P_n of PVA was determined from the viscosities of the benzene solutions of the fully acetylated specimens. Syndiotactic diad (S-daid) content of PVA was determined from the components of the hydroxyl proton triple at 4.1–4.7 ppm, obtained by use of a ^1H -NMR spectrometer (Sun Unity 300; Varian Associates, Palo Alto, CA). The DS of PVA was determined by weight loss after saponification and by the ratio of *tert*-butyl and methylene proton peaks in the ^1H -NMR spectrum.

Preparation of PVA/DMSO/water solution

High molecular weight a-PVA with a P_n of 4000 was hard to completely dissolve in water at room temperature, so both a-PVA blends were dissolved in a mixture of DMSO and water (8/2, v/v) at 80°C for 2 h and maintained for 30 min to ensure homogenization.

Measurement of rheological properties of PVA/DMSO/water solution

The shear and dynamic rheological properties of solutions of PVAs in DMSO/water were measured at 30°C using a physical USD 200 rheometer, with a couette geometry having outer and an inner diameters of 23.50 and 22.75 mm, respectively, at maximum strain amplitude of 10%. The strain level was determined in the strain sweep test so that all measurements were carried out within the linear viscoelastic regime.

RESULTS AND DISCUSSION

The molecular weight is expected to influence the rheological properties of a-PVA because differences in molecular parameters may change the physical properties of polymer molecules in a solvent. In this study, we used DMSO as part of a cosolvent because it has very large dielectric permeability and can probably destroy the system of hydrogen bonds between PVA macromolecules.^{11–13} Figure 1 shows complex viscosity (η^*) of a-PVA solutions with different P_n 's of PVAs. It is worth mentioning that, over the range of frequencies examined, a-PVA with a P_n of 1700 solutions exhibited almost Newtonian flow behavior, whereas a-PVA with a P_n of 4000 solutions exhibited shear-thinning flow behavior. In addition, η^* of a-PVA with a P_n of 4000 solutions is generally much higher than that of a-PVA with a P_n of 1700 solutions. In a-PVA, with a P_n of 4000 solutions, as the polymer concentration is increased, the extent of shear thinning is increased. This may imply that solutions of a-PVA, with high molecular weight and high polymer concentration, develop molecular orientation more easily by shear. Unlike P_n of 1700 in Figure 1(a), this shear-thinning behavior is observed at high frequency for a P_n of 4000, as shown in Figure 1(b). This seems to originate from shear-induced phase separation in the case of high molecular weight. At high concentration the effect is compensated by shear thinning, so the phenomenon is more noticeable with low concentrations, which gives almost Newtonian flow behavior up to a frequency of 100 rad/s.

Shear viscosity (η_{sh}) of a-PVA solutions was also measured, and viscosity curves are shown in Figure 2. This figure also shows that a-PVA, with a P_n of 1700 solutions, gives rise to almost Newtonian flow behavior. On the other hand, a-PVA with a P_n of 4000 solutions shows a non-Newtonian flow region over the shear rate range observed. The non-Newtonian behavior might be explained by the fact that orientation of molecular segments by the flow field occurs. This orientation in turn promotes elasticity in the polymer solution. The orientation reduces the entropy of the system in a manner analogous to the reduction

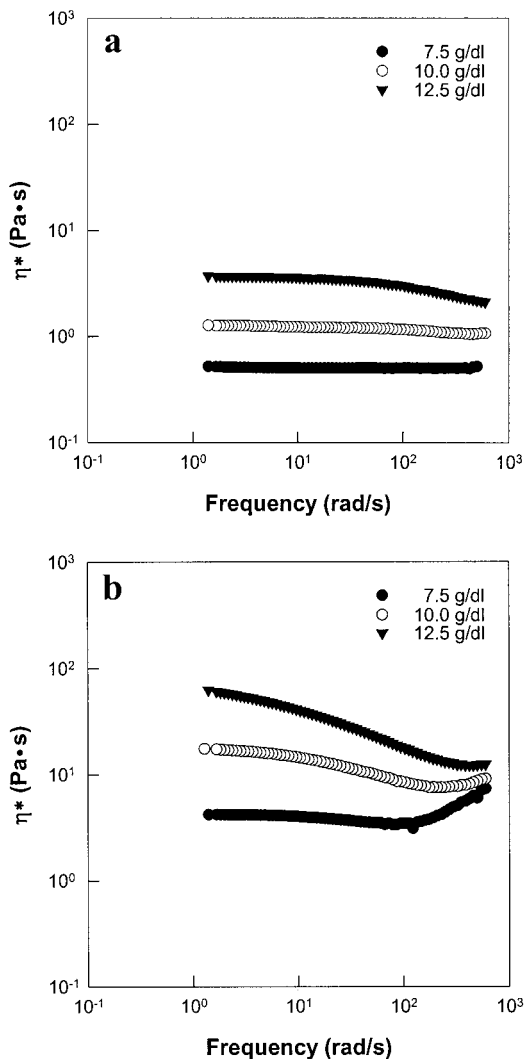


Figure 1 Complex viscosity of a-PVA with different P_n solutions in DMSO/water (8/2, v/v) at 30°C: P_n : (a) 1700; (b) 4000.

in entropy in the kinetic theory of rubber elasticity. In Figure 2(b) both shear-thinning and shear-thickening behavior are observed at high frequency. This is comparable with Figure 1(b), which deals with dynamic shear. If the concentration does not exceed 10.0 g/dL, dynamic shearing gives rise to shear thickening, whereas steady shearing leads to shear thinning. This is the result of time dependency of the rheological responses of PVA solutions in DMSO/water, particularly with high molecular weight. In the case of the dynamic test this solution is subjected to oscillatory shear, which results in molecular entanglement together with phase separation; consequently shear thickening occurs. At high concentrations, such as at 12.5 g/dL in Figure 2(b), an abrupt decrease in viscosity is attributed to strong physical gel formation at low temperature and at high shear rate.^{7,14,15}

Figure 3 shows the variation of storage modulus (G') and loss modulus (G'') of a-PVA solutions with

different P_n 's. This figure demonstrates that the phase of a-PVA with a P_n of 4000 solutions is heterogeneous rather than homogeneous. In a-PVA, with a P_n of 1700 solutions, G' was greater than G'' over the whole frequency range, implying that these solutions are homogeneous. In the case of a-PVA with a P_n of 4000, with increasing frequency, liquidlike viscoelasticity decreased and a solidlike property evolved that accompanied a crossover between G' and G'' . Such a crossover between G' and G'' is usually found in gelation systems. In solutions of a-PVA with a P_n of 4000, however, a noticeable point is that the crossover between G' and G'' occurs at the macroscopic sol state.

Figure 4 shows the loss tangent ($\tan \delta$), of a-PVA with different P_n solutions at 30°C, with frequency. In Figure 4(a), a value of $\tan \delta > 1$ over the whole frequency range indicates that the phase structures of a-PVA with P_n of 1700 solutions are almost homoge-

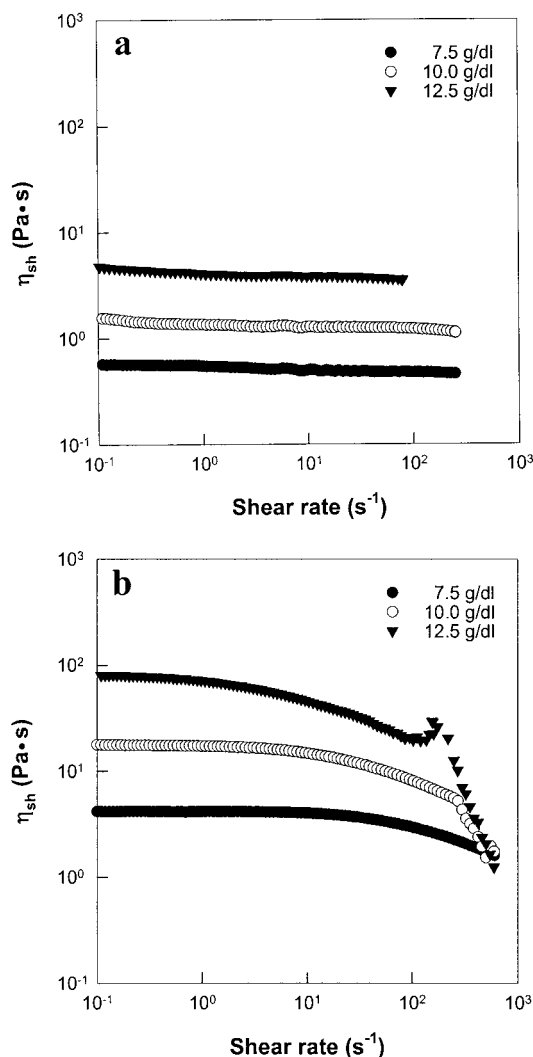


Figure 2 Shear viscosity of a-PVA with different P_n solutions in DMSO/water (8/2, v/v) at 30°C: P_n : (a) 1700; (b) 4000.

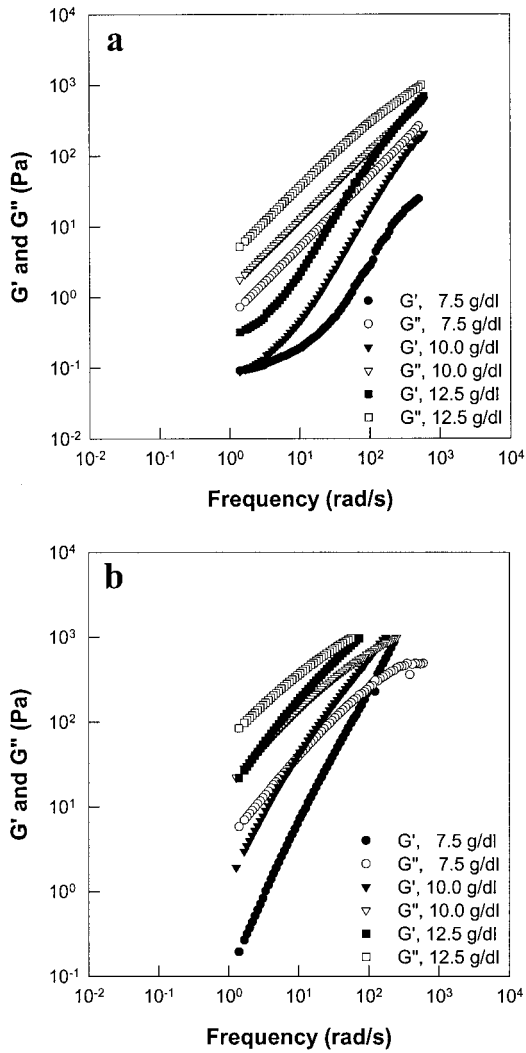


Figure 3 Storage and loss moduli of a-PVA with different P_n solutions in DMSO/water (8/2, v/v) at 30°C: P_n : (a) 1700; (b) 4000: filled symbols, storage; open symbols, loss.

neous. However, in a-PVA with a P_n of 4000 solutions, a value of $\tan \delta < 1$ in the high-frequency range implies that a solidlike property prevails over the system.

The yield stress of heterogeneous systems can be determined from the Casson plot, which is a plot of the square root of shear stress (τ) against the square root of shear rate ($\dot{\gamma}$) in steady shear flow. The yield stress (τ_0) is obtained from¹⁶

$$\tau^{1/2} = \tau_0^{1/2} + K\dot{\gamma}^{1/2} \quad (1)$$

Similarly, the intercept of the G'' axis (G''_0) on the plot of the square root of G'' against the square root of frequency (ω) may be regarded as a measure of yield stress in dynamic shear measurement as¹⁷

$$G''^{1/2} = G''_0^{1/2} + K'\omega^{1/2} \quad (2)$$

The square roots of G'' , of a-PVA with different P_n solutions at 30°C, are plotted against the square root of ω in Figure 5. In the case of a-PVA with a P_n of 1700, all the intercepts reduce to zero in the so-called Casson-type plots, irrespective of the polymer concentrations. This suggests that a-PVA with a P_n of 1700 forms little pseudostructure in the solutions. Solutions having high polymer concentration of a-PVA with a P_n of 4000 produces nonzero intercepts on the Casson-type plot, confirming the existence of yield stress of positive values. This suggests that some pseudostructure is present in solutions of a-PVA with a P_n of 4000. The yield stress substantially increases with polymer concentration, as may be observed in Figure 5.

Investigations of relaxation behavior of a-PVAs are useful in accounting for differences in the rheological properties of two polymers; that is, relaxation time may be much longer if some molecular order exists. For instance, a rigid-rod polymer exhibits a very long

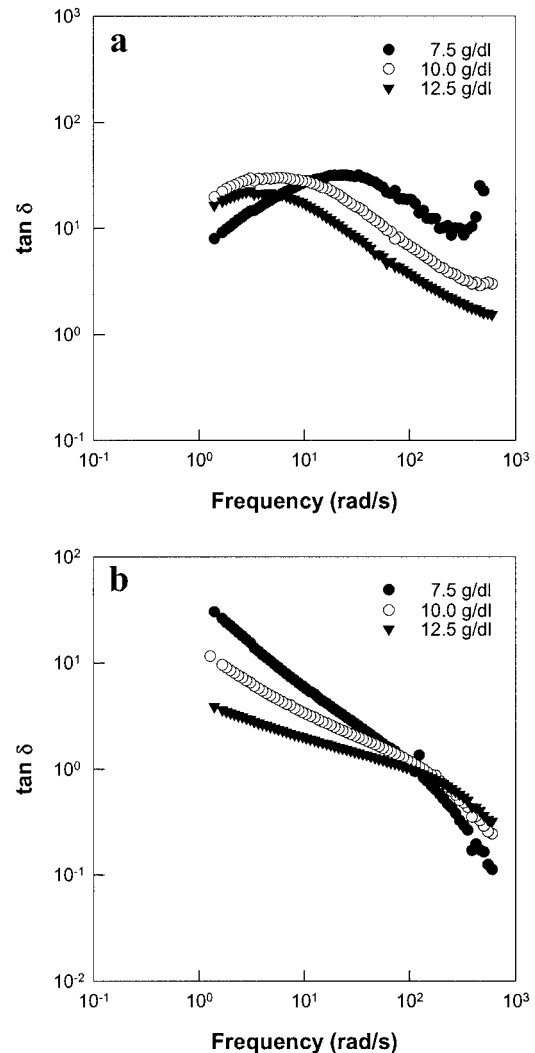


Figure 4 Loss tangent of a-PVA with different P_n solutions in DMSO/water (8/2, v/v) at 30°C: P_n : (a) 1700; (b) 4000.

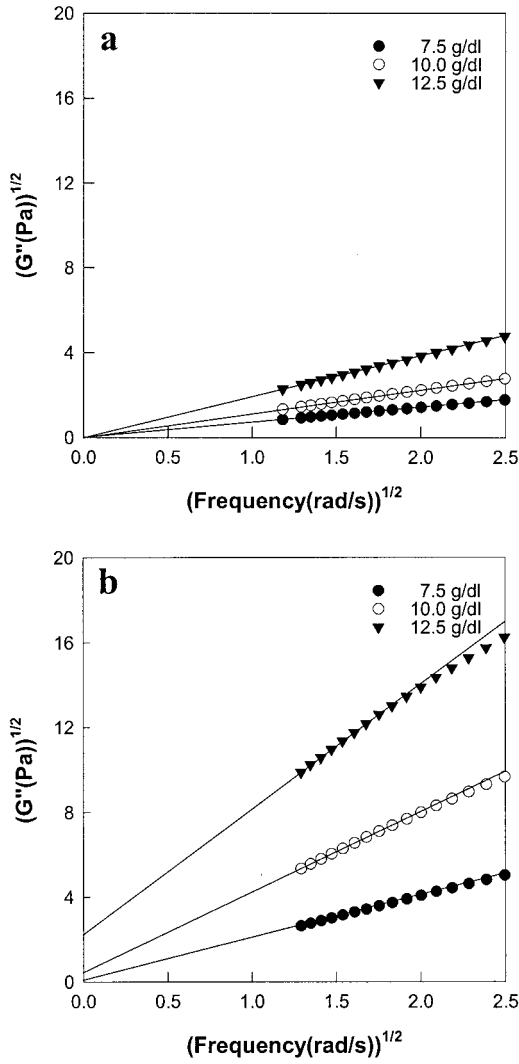


Figure 5 Square root of loss modulus of a-PVA with different P_n solutions in DMSO/water (8/2, v/v) at 30°C: P_n : (a) 1700; (b) 4000.

relaxation time when it forms an anisotropic phase. Similarly, the formation of a mesophase also leads to a long relaxation time. The relaxation time (λ) under dynamic shear may be calculated as¹⁸

$$J' = \frac{G'}{([\eta^*]\omega)^2} = \frac{\lambda}{[\eta']^2} \quad (3)$$

where J' and G' are compliance and storage modulus, respectively. Variations of relaxation times of a-PVA, with different P_n solutions at 30°C, with frequency are shown in Figure 6. a-PVA with a P_n of 4000 solutions exhibits a much longer relaxation time than that of a-PVA with a P_n of 1700 solutions. PVA, which consists of flexible chain polymer molecules, exhibits long relaxation times, particularly at lower frequencies. The slope of relaxation times, of a-PVA with a P_n of 1700 solutions, is decreased with frequency, whereas that of

a-PVA, with a P_n of 4000 solutions, is increased with frequency.

CONCLUSIONS

Through investigation of the effect of molecular weight on the rheological properties of a-PVA solutions, we may conclude the following: in a-PVA solutions in DMSO/water, the molecular weight of PVA played a significant role in determining rheological properties. a-PVA, with a P_n of 1700 solutions, produced an isotropic phase only over the frequency range. On the other hand, a-PVA with a P_n of 4000 solutions showed rheological responses typical of a heterogeneous systems. It is expected that these results can be used to establish conditions of gel spinning using a-PVA with a P_n of 4000. In the near future, we will report on the molecular weight effect of PVA

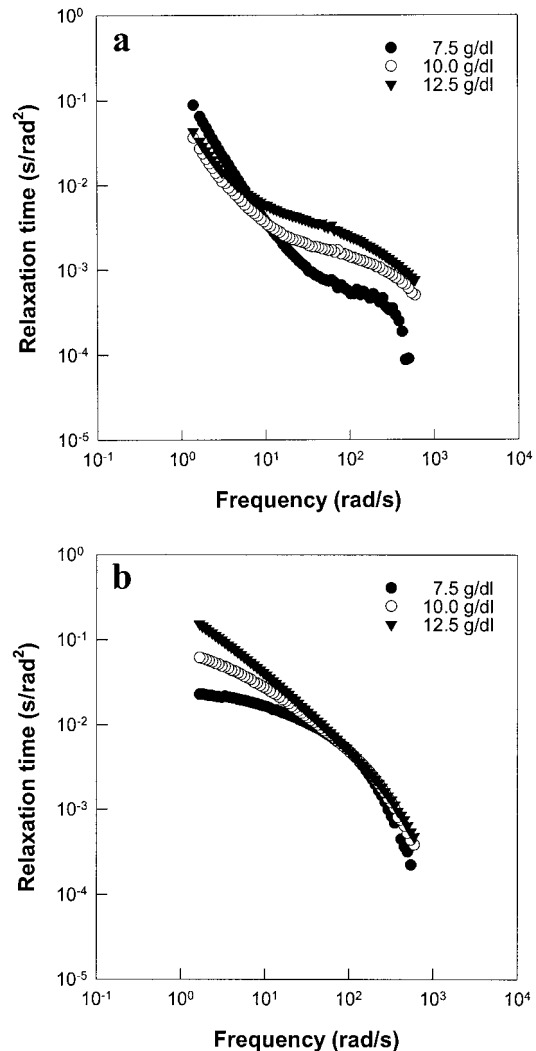


Figure 6 Variation in relaxation time of a-PVA with different P_n solutions in DMSO/water (8/2, v/v) at 30°C: P_n : (a) 1700; (b) 4000.

on the rheological properties of syndiotactic PVA solutions.

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