Facile tailoring of thermal transition temperatures of epoxy shape memory polymers

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ABSTRACT

A critical parameter for a shape memory polymer (SMP) lies in its shape memory transition temperature. For an amorphous SMP polymer, it is highly desirable to develop methods to tailor its T_g, which corresponds to its shape memory transition temperature. Starting with an amine cured aromatic epoxy system, epoxy polymers were synthesized by either reducing the crosslink density or introducing flexible aliphatic epoxy chains. The thermal and thermomechanical properties of these epoxy polymers were characterized by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). All the crosslinked epoxy polymers with T_g's above room temperature were found to possess shape memory properties. Overall, our approach represents a facile method to precisely tune the T_g of epoxy SMP polymers ranging from room temperature to 89 °C.

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1. Introduction

Shape memory polymers (SMP) [1,2] represent polymers that are capable of memorizing temporary shapes and recovering their permanent shapes upon external stimulation [1–5], most typically thermal activation. In contrast to shape memory alloys, SMP possess many advantages including excellent processability, light weight, and great flexibility in terms of material design [1,2,6,7]. Indeed, SMP have shown great promises for a wide range of applications due to the above characteristics [1,2,6–13]. For a polymer to possess shape memory properties, it has to have a permanent network and a reversible phase [1,2]. Here, the word "permanent" refers to its function in defining and memorizing the permanent shape, which can be achieved via chemical crosslinking or physical crosslinking (e.g. chain entanglement and crystallization). The fixing of temporary shapes, on the other hand, is due to the reversible phase, which corresponds to either a glass transition or a melting transition. When a reversible thermal phase transition is utilized to fix temporary shapes, the corresponding temperature is typically called the shape memory transition temperature. Since most polymers possess at least one reversible thermal transition, they can be converted into SMP by introducing a permanent network (e.g. chemical crosslinking). The ample opportunities to create and tailor the shape memory properties of SMP through molecular design are exemplified by the variety of SMP discovered

[1–14] and the wide range of T_g's (from −30 to +70 °C) obtainable with polyurethane SMP [15–17].

Owing to their superior mechanical properties, ease of processing, and excellent chemical resistance, epoxy based polymers have been widely used as structure, coating, and adhesive materials in many demanding applications [18]. The use of epoxy polymers as functional materials, however, remains rather rare. Specifically for the shape memory effect of epoxy polymers, only sporadic examples of epoxy SMP have been mentioned in the literature [19–22]. While the success of utilizing an SMP for a certain application depends on the ability to tailor its shape memory transition temperature (e.g. T_g for an amorphous polymer), such a material design flexibility has not been demonstrated for epoxy SMP. In this paper, we demonstrate methods to precisely tune the T_g's of epoxy SMP. The flexibility and simplicity of the chemistry involved represent a great benefit in terms of material accessibility to the SMP community.

2. Experimental section

2.1. Materials

The diglycidyl ether of bisphenol A epoxy monomer (EPON 826) and the curing agent poly(propylene glycol)bis(2-aminopropyl) ether (Jeffamine D230) were available from Hexion and Huntsman, respectively. Neopentyl glycol diglycidyl ether (NGDE) was manufactured by TCI America. Decylamine was purchased from Aldrich. All chemicals were used as-received.

2.2. Epoxy polymer synthesis

The detailed formulations of the epoxy SMP are summarized in Table 1. EPON 826 was weighed into a glass bottle and melted by heating in an oven preset at 70 °C. After melting EPON 826, weighed Jeffamine D230, and NGDE (or decylamine) were introduced into the bottle, which was then shaken vigorously by hand for about 10 s to mix the components. Next, the mixture was poured into an aluminum pan. The epoxy samples were thermally cured at 100 °C for 1.5 h and postcured at 130 °C for 1 h. Upon the completion of the cure, the epoxy samples were demolded and cut into rectangular shapes for DMA and shape recovery testing.

2.3. Characterization

The differential scanning calorimetry (DSC) measurements were made under nitrogen using a DSC Q1000 (TA instruments) at a heating rate of 10 °C min^{-1}. The T_g values were obtained as the inflection temperatures in the DSC curves. The dynamic mechanical analysis (DMA) experiments were conducted in a tensile mode using a DMA Q800 (TA instruments). Samples with thickness of 0.7–0.8 mm were used. All runs were performed in a "multi-frequency, strain" mode at 1 Hz, 0.2% strain, and a heating rate of 3 °C/min.

2.4. Evaluation of the shape memory properties

Sample **NGDE2** (listed in Table 1), with an original rectangular shape ($1 \times 3 \times 50$ mm), was immersed in a 70 °C water bath for 6 s. It was deformed manually into a temporary shape immediately after it was taken out of the hot water bath. Fixing was allowed by quickly dipping the sample in a cold water bath (20 °C) while maintaining the deformation load. For shape recovery, the sample with the fixed temporary shape was immersed back in the same hot water bath. The photos of different shapes at various stages of the shape memory cycles are shown in Fig. 8.

Quantitative shape memory properties were evaluated using DMA in a tensile and force controlled mode. The heating and cooling rates were both 5 °C/min. The shape fixity (R_f) and shape recovery (R_f) were calculated using:

$$R_f = \varepsilon_d / \varepsilon_{dload} \text{ and } R_r = (\varepsilon_d - \varepsilon_{rec}) / \varepsilon_d,$$

where ε_{dload} and ε_d, represent the instantaneous strain upon loading and the fixed strain after cooling and load removal, and ε_{rec} is the recovered strain.

3. Results and discussion

The chemical structures of the reactants used in our epoxy formulation are shown in Fig. 1. The base epoxy polymer (**REF** in Table 1) consists of a rigid aromatic diepoxide (EPON 826) and an
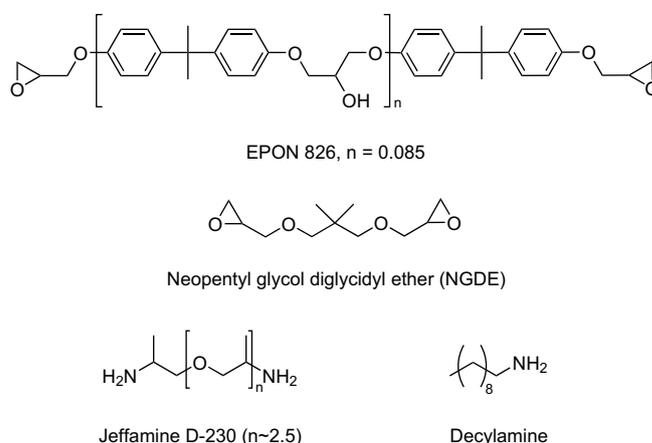
Table 1
Compositions, shape fixity, and shape recovery of the epoxy samples.

Samples	EPON 826 (mol)	D230 (mol)	DA (mol)	NGDE (mol)	M_c	R_f (%)	R_r (%)
REF	0.02	0.01	0	–	475	91.3	99.1
DA1	0.02	0.0075	0.005	–	647	95.2	99.2
DA2	0.02	0.005	0.01	–	992	94.2	99.8
DA3	0.02	0.0025	0.015	–	2026	102.3	98.2
DA4	0.02	0	0.02	–	∞	–	–
NGDE1	0.015	0.01	–	0.005	439	92.3	99.2
NGDE2	0.01	0.01	–	0.01	403	96.4	99.7
NGDE3	0.005	0.01	–	0.015	367	96.8	99.3
NGDE4	0	0.01	–	0.02	331	–	–

EPON 826, n = 0.085

Neopentyl glycol diglycidyl ether (NGDE)

Jeffamine D-230 (n~2.5)   Decylamine

Fig. 1. Chemical structures of the epoxy components.

aliphatic diamine crosslinker (Jeffamine D230, abbreviated as D230 hereafter). To tailor the T_g's of the epoxy system, two approaches were taken: (1) reducing the crosslink density by substituting the diamine curing agent with a monoamine such as decylamine (DA); (2) introducing chain flexibility by replacing the EPON 826 with a flexible aliphatic diepoxide NGDE. Based on these two approaches, two series of epoxy polymers were synthesized: DA series (**DA1** through **DA4**) and NGDE series (**NGDE1** through **NGDE4**). The molar compositions for all epoxy synthesized are summarized in Table 1. The average molecular weights between crosslink points (M_c) of the epoxy samples (listed in Table 1), were calculated using Eq. (1) for the NGDE series and Eq. (2) for the DA series.

$$M_c = \frac{n_{EPON} \cdot M_{EPON} + n_{NGDE} \cdot M_{NGDE} + n_{D230} \cdot M_{D230}}{n_{D230}} \quad (1)$$

$$M_c = \frac{n_{EPON} \cdot M_{EPON} + n_{DA} \cdot M_{DA} + n_{D230} \cdot M_{D230}}{n_{D230}} \quad (2)$$

where n and M represent the molarity and molar mass of the corresponding component in the epoxy formulations.

In the DA series, starting from the **REF** epoxy sample, the fraction of the crosslinker (D230) is systematically reduced, while the total amounts of epoxy functionality and active hydrogen functionality on the amines are maintained equal. The reduction in the crosslinker led to the decrease in crosslinking density, as reflected in the increase of M_c in Table 1. Among these samples, **DA4** contains no crosslinker and is not expected to possess shape memory properties – it was used here as a reference.

The DSC curves of the cured DA series samples are shown in Fig. 2. All samples showed distinctive glass transition temperatures ranging from 30 to 89 °C. The samples were further characterized by DMA and the curves are shown in Fig. 3. All the samples show relatively constant storage moduli in their respective glassy and rubbery regions and the difference between the glassy modulus and rubbery modulus for each individual sample ranges from 2 to 3 orders of magnitude. A closer examination of Fig. 3 reveals that the reduction in the crosslink density (increase in M_c) leads to the reduction in the rubbery modulus for the DA series. This observation is consistent with the theory of rubber elasticity stating that the rubbery modulus of a thermoset system is proportional to its crosslink density. The T_g values obtained from the DSC and DMA (tan δ) are summarized in Fig. 4. In this figure linear relationships between the T_g's and the mole percentage of amine from the crosslinker ($n_{NH_2-Jeffamine}$) are observed, indicating that any T_g in this entire temperature range could be obtained.
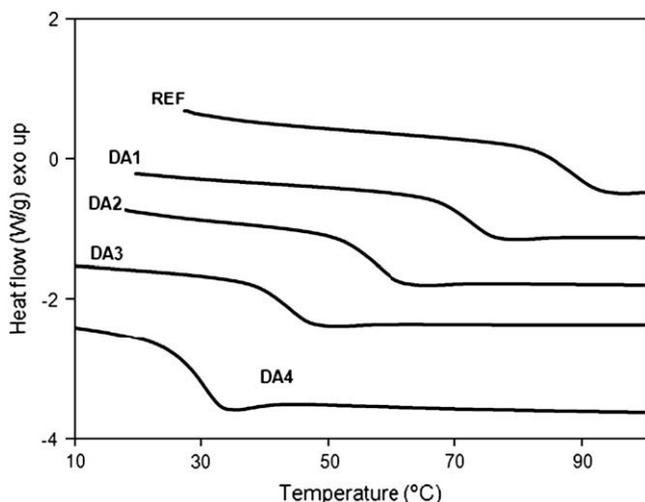
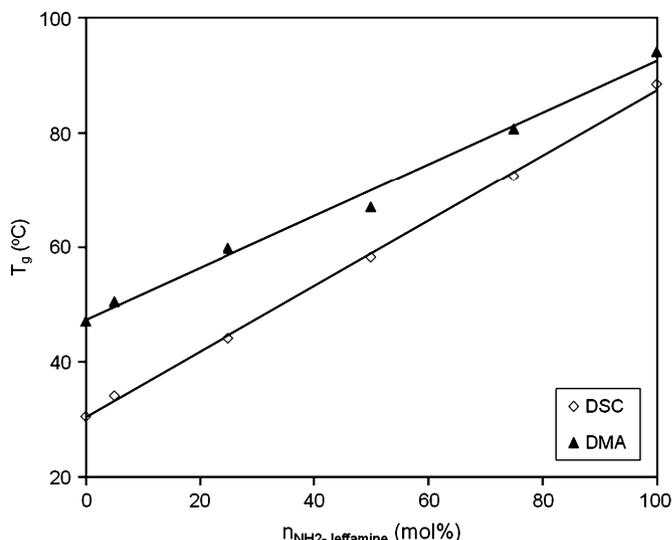Fig. 2. DSC curves for the DA epoxy series.

Fig. 4. Glass transition temperatures (T_g's) of the DA epoxy series.

In the NGDE series, the aromatic diepoxide (EPON 826) was systematically substituted with the more flexible aliphatic diepoxide (NGDE). The DSC curves for the NGDE polymer series (Fig. 5) show that all the samples possess sharp and distinctive glass transitions and that the introduction of NGDE leads to epoxy polymers with lower T_g's ranging from 88 to 6 °C. The samples, except **NGDE4** for which the T_g is too low for use as an SMP, were further evaluated using DMA and the curves are shown in Fig. 6. Similar to the DA series, all the samples in the NGDE series show relatively constant glassy moduli that are 2–3 orders of magnitude higher than their corresponding rubbery moduli. The T_g's obtained from the DSC and DMA (tan δ) are plotted in Fig. 7, against the mole percentage of NGDE (n_{NGDE}). Fig. 7 shows that T_g decreases linearly with increasing n_{NGDE}, indicating again that any T_g in the entire temperature range of 6–88 °C could be obtained.

Figs. 2–7 suggest that replacing D230 by DA in the DA polymer series and substituting EPON 826 with NGDE in the NGDE series appear to have a similar effect on their thermal and thermomechanical behaviors. We note, however, that the underlying molecular principles of the two approaches are quite different. In the NGDE series, substituting EPON 826 with NGDE leads to an increase in the crosslink density (reflected in the M_c values in Table 1) since NGDE has an epoxy equivalent weight of 108, which is lower than that of EPON 826 with an epoxy equivalent weight of

178. In principle, increasing the crosslink density alone would increase the material rigidity. However, replacing the rigid aromatic epoxide with the flexible aliphatic epoxide increases the chain flexibility of the material, thereby reducing its T_g. The results, shown in Figs. 5–7, suggest that the impact of increasing the crosslink density by introducing NGDE is more than compensated for by the increase in the overall chain flexibility, resulting in a net reduction in T_g and rubbery modulus.

Among all the epoxy polymers listed in Table 1, **DA4** is not crosslinked and the T_g of **NGDE4** is lower than room temperature, neither is suitable for use as an SMP above room temperature. All the other epoxy polymers in Table 1 show typical shape memory properties, with shape fixity above 90% and shape recovery around 100% (Table 1). Interestingly, it appears that the shape fixity for the DA series including the **REF** seems to increase as more and more DA was present in the formulation. A similar trend was observed for the NGDE series (including **REF**), i.e., the shape fixity increases with the addition of NGDE. The difference in shape fixities for all the epoxy samples can be correlated to the difference in glassy modulus and rubbery modulus for each individual sample
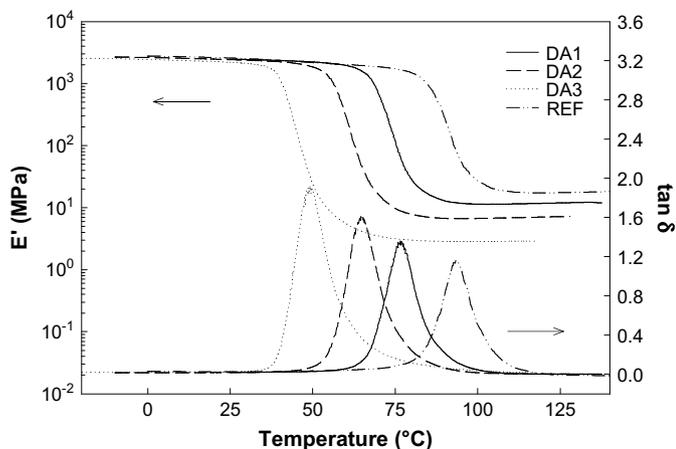

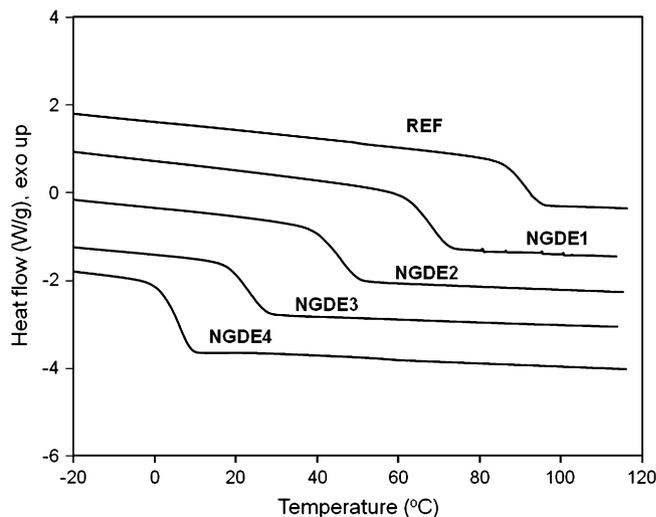Fig. 3. DMA curves for the DA epoxy series.
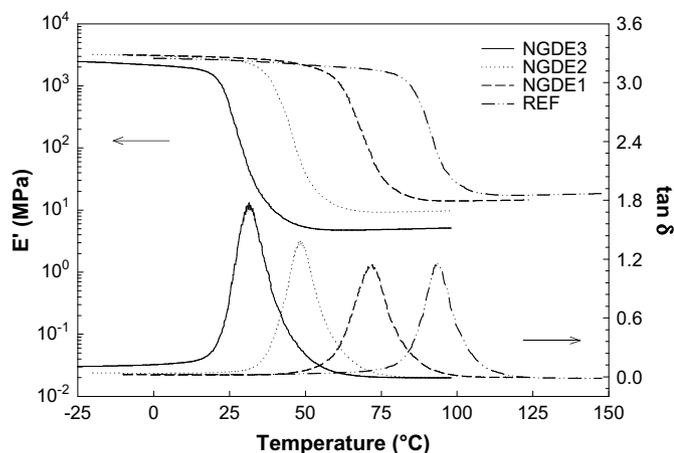

Fig. 5. DSC curves for the epoxy NGDE series.

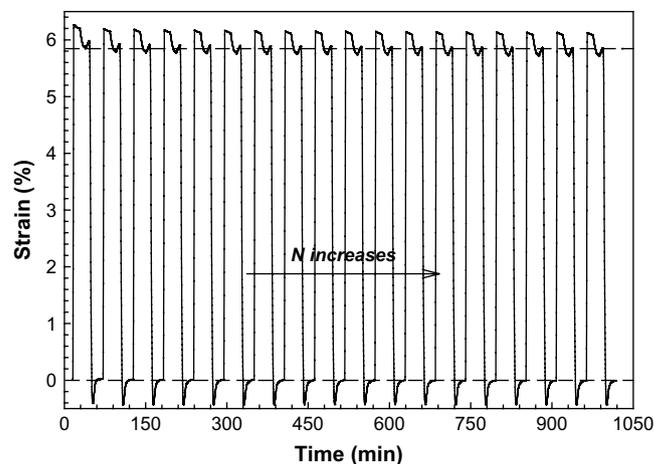Fig. 6. DMA curves for the epoxy NGDE series.

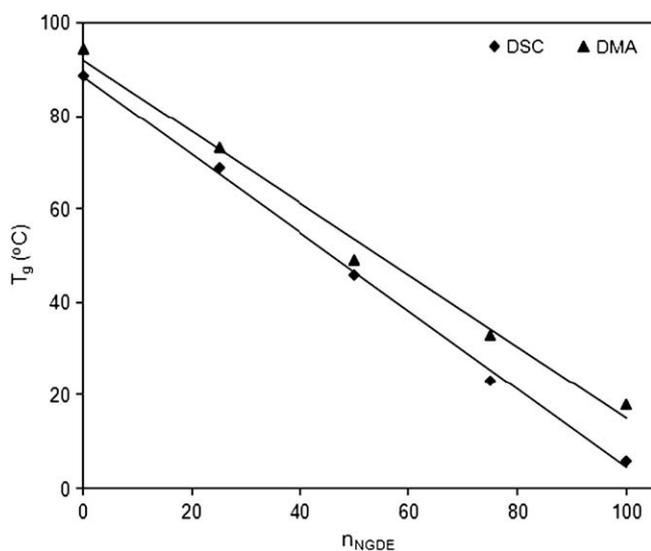Fig. 9. Consecutive shape memory cycles for **NGDE2**.

Fig. 7. Glass transition temperature (T_g's) of the epoxy NGDE series.

(Figs. 3 and 6). The glassy modulus for sample **REF** (with lowest shape fixity) is only 2 orders magnitude higher than its rubbery modulus. By introducing either DA or NGDE in the epoxy polymers, the difference between glassy modulus and rubbery modulus (still within 3 orders of magnitude) is widened (Figs. 3 and 6), which may be responsible for the increase in shape fixity.

Besides its impact on shape fixity, the difference in rubbery modulus for the various epoxy samples (Figs. 3 and 6) suggests that

the recovery stress of this type of SMP can be tuned, in addition to the shape memory transition temperature. Additionally, the glass transitions for all the epoxy polymers (both DA and NGDE series) occur within a relative narrow temperature range. The breath of the glass transition, as defined by the full width at half maximum (FWHM) of the tan δ peaks, falls into a temperature range of $12.5 \pm 1.0\,^{\circ}$C for all samples. The narrow glass transitions of our epoxy polymers are the result of the structural homogeneity of the cured polymers due to the well-defined chain length of the epoxy reactants and the low viscosities of the precured mixtures. The narrowness of the transition translates into the temperature sensitivity of a material's mechanical properties around T_g. Practically, this means that the shape recovery and shape fixing of an SMP with a narrower glass transition could be triggered at temperatures closer to its T_g. It further implies that a full shape memory cycle can occur within a narrower temperature range and the shape memory cycle time can be reduced.

The shape memory properties of a representative sample, **NGDE2**, are visualized in Fig. 8. Starting from the original (permanent) rectangular shapes (see Fig. 8a), **NGDE2** can be deformed into different shapes through twisting and bending. Upon cooling under load, these deformed temporary shapes (see Fig. 8b) were fixed. Subsequent immersion in a 70 °C water bath allowed complete recovery of the original rectangular shapes (see Fig. 8c) in about 6 s. The recovered shapes were indistinguishable from the original shapes, confirming the excellent shape fixity and recovery. To investigate the cycling capability, **NGDE2** was subjected to consecutive shape memory cycles. As illustrated in Fig. 9, no noticeable changes (deformation strain, shape fixity, and shape recovery) occurred after 18 cycles. We believe that the excellent
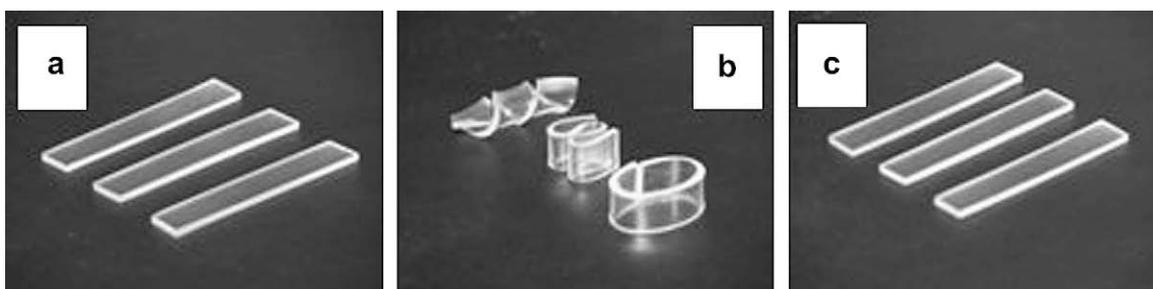

Fig. 8. Visual demonstration of shape memory properties for **NGDE2** (a: original/permanent shapes, b: fixed temporary shapes, c: recovered shapes).

cycling capability is due to the excellent thermal stability of epoxy polymers and its chemical crosslink nature.

4. Conclusion

The glass transition temperatures of our epoxy polymers can be tuned by varying the crosslink density or chain flexibility of the systems. All the crosslinked epoxy samples showed SMP characteristics, including easily tailored thermal transition temperatures ranging up to 89 °C as dictated by their T_g, sharp transition temperatures and excellent shape fixity and recovery. The flexibility and simplicity of the chemistry involved in the synthesis of the SMP represent a benefit in terms of material accessibility to the SMP community. The general approaches of tuning shape memory properties of polymers can be potentially applied to other polymer systems.

Acknowledgement

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