Polymer Bulletin 44, 353–360 (2000)

Polymer Bulletin

Enthalpy relaxation in glassy polymers

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Received: 5 December 1999/Revised version: 28 February 2000/Accepted: 2 March 2000

Summary

Constitutive equations are derived for enthalpy recovery in amorphous glassy polymers. The model is based on the concept of cooperative relaxation which treats a polymer as an ensemble of flow units rearranging at random times. The rate of rearrangement is determined by the Eyring theory of thermally activated processes. Fair agreement is demonstrated between results of numerical simulation and experimental data for polycarbonate, poly(ether imide), poly(methyl methacrylate), polystyrene and a glycerol glass.

Introduction

The paper is concerned with enthalpy relaxation in amorphous glassy polymers after thermal treatment. This subject has attracted substantial attention in the past decade because differential scanning calorimetry provides a convenient procedure for studying equilibration processes in disordered media (1-4). The latter is of essential importance for applications, since structural recovery is accompanied by changes in static and dynamic elastic moduli, yield stress, elongation to break, fracture toughness, fatigue failure and impact strength (5). The significance of enthalpy relaxation for polymer engineering is explained by its role as an indicator of transition from ductile to brittle modes of failure (6-8).

Enthalpy recovery is conventionally observed in a one-step thermal test, when a specimen equilibrated at some temperature T_0 above the glass transition temperature T_g is quenched to a temperature $T < T_g$ and is preserved at the annealing temperature,

$$T(t) = T_0 \quad (t \le 0), \qquad T(t) = T \quad (t > 0). \tag{1}$$

Experiments evidence that the specific enthalpy per unit mass H decreases with time and approaches its equilibrium value $H_{eq}(T)$.

Physical aging is traditionally described by two phenomenological models. The first is based on the hypothesis that the rate of approaching equilibrium is proportional to some measure of departure from the equilibrium state (3,9,-11). This assumption seems rather plausible, but constitutive equations with a single thermokinetic structure fail to predict observations in tests with non-monotonic thermal programs (10,12), whereas multiparameter (10,12) and multiorder (13) relations, where free volume and fictive temperature are split into several fragments with different rates of equilibration, have no physical meaning (14).

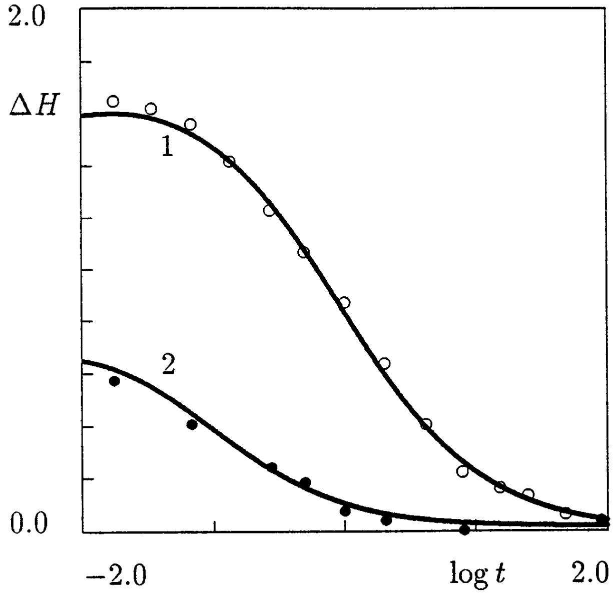

Figure 1: The excess enthalpy ΔH J/g versus time t h for polycarbonate ($T_g = 142.5$ °C) annealed at $T = 135$ (curve 1) and $T = 140$ °C (curve 2). Circles: experimental data (11). Solid lines: predictions of the model with $k_B T N = 1.0$ J/g. Curve 1: $L^0_{\rm eq} = 2.3$ 1/h, $\bar{w}(0) = 0.43$, $\bar{w}_{\rm eq}(T) = 0.09$; curve 2: $L^0_{\rm eq} = 22.0$ 1/h, $\bar{w}(0) = 0.4$, $\bar{w}_{\rm eq}(T) = 0.2$

The other model presumes that enthalpy evolution is governed by the stretched exponential (Kohlrausch-Williams-Watts) law (1,4,15). Despite some attempts to "deduce" the KWW function from molecular concepts (16-19), the constitutive equations remain merely phenomenological, because they provide no way to predict observations in one test (e.g., calorimetric, dielectric, dilatometric, mechanical, etc.) using data in another experiment. The applicability of the stretched exponential function was questioned in several studies where this law was replaced by an algebraic time dependence (20).

The objective of this note is to derive constitutive equations that adequately describe enthalpy relaxation and may be applied to predict the response of glassy polymers in other tests. Enthalpy recovery in polymers at an arbitrary thermal program $T = T(t)$ is studied by using the theory of cooperative relaxation (21) in a version of the trap concept (22,23). A similar approach was previously employed for the analysis of thermo-mechanical response in soft glasses (24) and amorphous polymers (25).

Rearrangement of a flow unit

The time-dependent response of polymers is conventionally treated as rearrangement of long chains in a temporary network. For glassy polymers, this process requires cooperative dynamics of chain molecules, when scores of neighboring strands change their position simultaneously (21). An amorphous glassy polymer is modeled as an ensemble of cells (cooperatively rearranging regions or flow units) which are thought of as globules consisting of long chains, short chains and free volume clusters (24).

In accordance with the transition-state theory (26), we assume that some liquid-like (reference) state exists on the energy landscape, where cells change their configurations. The position of an arbitrary flow unit trapped in a cage with respect to the reference state is characterized by the energy w of its potential well. For definiteness, we set $w = 0$ for the reference state and $w > 0$ for relaxing regions.

Rearrangement of cells is treated as a sequence of random hops of flow units driven by thermal fluctuations (23). This process is characterized by its rate (the number of

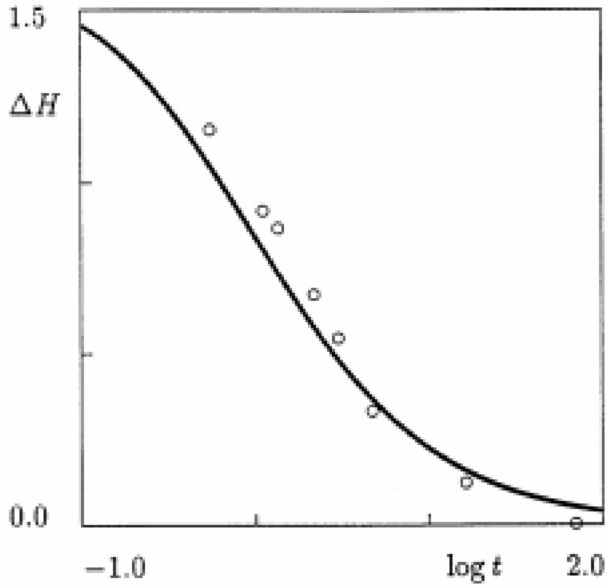

Figure 2: The excess enthalpy ΔH J/g versus time t h for polystyrene ($T_g = 103.5$ °C) annealed at $T = 93$ °C. Circles: experimental data (34). Solid line: prediction of the model with $k_B T N = 1.0$ J/g, $L^0_{\mathrm{eq}} = 2.0$ 1/h, $\bar{w}(0) = 0.4$ and $\bar{w}_{\mathrm{eq}}(T) = 0.09$

hops per unit time) and intensity (the probability for a rearranging region to reach the excess energy *w* over the bottom level of its potential well). Denote by $q(t, w, m)$ the current probability for a cell with energy *w* to hop *m* times per unit time, and by $\pi(w)$ the probability to reach (in an arbitrary hop) the energy level that exceeds the bottom level of the potential well by *w*. Referring to (23), we set $\pi(w) = A \exp(-Aw)$, where *A* is a material constant, and determine the probability for a cell with potential energy *w* to reach the reference state in a hop

$$\Pi(w) = \int_w^\infty \pi(\omega) d\omega = \exp(-Aw). \tag{2}$$

The probability for a cell to make *m* hops per unit time reads

$$q(t, m, w) = b(t, w)\vartheta^m \qquad (m = 1, 2, \ldots), \tag{3}$$

where $\vartheta \in (0, 1)$ is a material parameter and $b(t, w)$ is a prescribed function. For mutually independent hops, *Eqs. 2* and *3* together with the formula for conditional probability imply the probability for a cell with potential energy *w* to reach the reference state per unit time

$$L(t, w) = \sum_{m=1}^{\infty} q(t, w, m)\Pi(w)[1 - \Pi(w)]^{m-1} = \frac{\vartheta b(t, w) \exp(-Aw)}{1 - \vartheta[1 - \exp(-Aw)]}.$$

The average number of hops per unit time is given by

$$\Gamma(t, w) = \sum_{m=1}^{\infty} m q(t, w, m) = \frac{b(t, w)\vartheta}{(1 - \vartheta)^2}.$$

Combining these equalities, we arrive at the formula

$$L(t, w) = \frac{(1 - \vartheta)^2 \Gamma(t, w) \exp(-Aw)}{1 - \vartheta[1 - \exp(-Aw)]}. \tag{4}$$

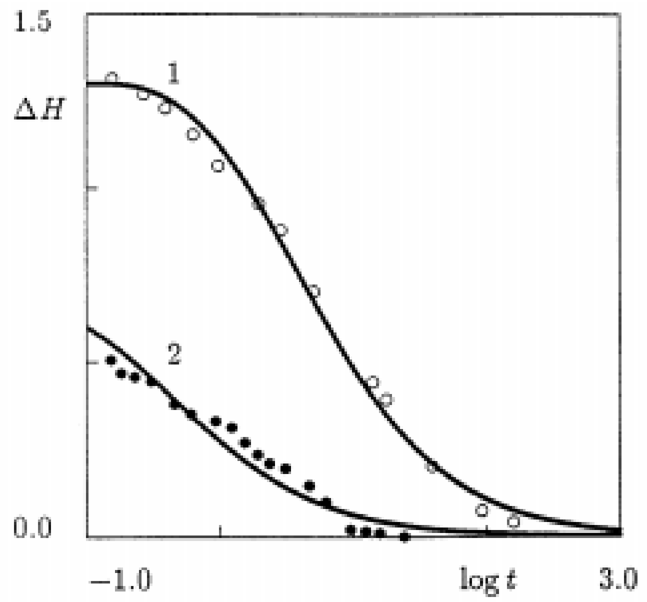

Figure 3: The excess enthalpy ΔH J/g versus time t h for poly(methyl methacrylate) ($T_g = 121.8$ °C) annealed at $T = 102$ (curve 1) and $T = 114.5$ °C (curve 2). Circles: experimental data (1). Solid lines: predictions of the model with $k_B T N = 1.14$ J/g and $\bar{w}(0) = 0.4$. Curve 1: $L^0_{\mathrm{eq}} = 0.5$ 1/h, $\bar{w}_{\mathrm{eq}}(T) = 0.13$; curve 2: $L^0_{\mathrm{eq}} = 5.0$ 1/h, $\bar{w}_{\mathrm{eq}}(T) = 0.22$

For $\vartheta << 1$. *Eq. 4* coincides with the Eyring formula (27) for the rate of thermally activated processes

$$L(t, w) = \Gamma_0(t) \exp(-Aw), \tag{5}$$

provided the rate of hops is independent of the depth of potential well, $\Gamma(t, w) = \Gamma_0(t)$.

The kinetic equation

Any rearrangement event is modeled as a hop of a flow unit from its quasi-equilibrium state on the energy landscape to a liquid-like state, where the unit "forgets" its previous configuration, followed by landing from the reference state either to the previous or to a new quasi-equilibrium state (22). Since the duration of a hop (several picoseconds) is small compared to the characteristic time of relaxation in the α-region, we treat hops as instantaneous. The main hypothesis is that in the overwhelming majority of hops, relaxing regions come back into their previous states (which models the viscoelastic response), but in a small amount of events, their energies change, and flow units land in new quasi-equilibrium states (which models structural relaxation in disordered media). This allows discrepancies between characteristic rates of structural recovery and mechanical response to be explained by the difference between the frequencies of "usual" (hops returning to previous states) and "rare" (hops landing in new states) events, in contrast with other approaches, where different physical mechanisms are used for structural and mechanical relaxation (28).

The number of cells (per unit mass) with potential energy lying within the interval $[w, w + dw]$ that hop to the reference state per unit time reads $NL(t, w)p(t, w)dw$, where N is the number density of cells (per unit mass) and $p(t, w)$ is the distribution function of cells with potential energy w.

The first assumption is that the number of flow units changing their energy per unit time is proportional to the excess of the current number of rearranging regions with a given energy w over their equilibrium number at the current temperature $T(t)$. This means that cells with $p(t, w) < p_{\mathrm{eq}}(T(t), w)$, where $p_{\mathrm{eq}}(T, w)$ is the equilibrium probability density of flow units with potential energy w at temperature T, come back to their quasi-equilibrium states after hops, whereas the number of cells (in unit mass per unit time) with $p(t, w) \geq p_{eq}(T(t), w)$ landing in new states is given by $dQ_-(t, w) = \chi\ N\ L(t, w)p(t, w)[p(t, w) - p_{eq}(T(t), w)], w)]dw$, where χ is a material parameter. The total number of rearranging regions (per unit mass) changing their potential energy per unit time reads

$$Q_-(t) = \chi N \int_0^\infty L(t, w)p(t, w)[p(t, w) - p_{\rm eq}(T(t), w)]\mathcal{H}\Big(p(t, w) - p_{\rm eq}(T(t), w)\Big)dw,$$

where H is the Heaviside function. The other hypothesis is that cells changing their states are redistributed proportionally to the difference between the equilibrium number and the current number of flow units with appropriate potential energies. This means that only the population of cells with $p(t, w) < p_{eq}(T(t), w)$ increases, and the number of regions (per unit mass) acquiring (per unit time) the energy in the interval $[w, w + dw]$ reads $dQ_+(t, w) = cQ_-(t)[p_{eq}(T)(t), w) - p(t, w)]dw$, where c is a material parameter. The total number of cells changing their energy per unit time is given by

$$Q_+(t) = cQ_-(t) \int_0^\infty [p_{\rm eq}(T(t), w) - p(t, w)]\mathcal{H}\Big(p_{\rm eq}(T(t), w) - p(t, w)\Big)dw,$$

where the constant c is found from the balance law $Q_-(t) = Q_+(t)$. These formulas result in the nonlinear integro-differential equation

$$\begin{aligned}\frac{\partial p}{\partial t}(t, w) \quad = \quad & -L^0(t, w)p(t, w)[p(t, w) - p_{\rm eq}(T(t), w)]\mathcal{H}\Big(p(t, w) - p_{\rm eq}(T(t), w)\Big) \\ & + \int_0^\infty L^0(t, u)p(t, u)[p(t, u) - p_{\rm eq}(T(t), u)]\mathcal{H}\Big(p(t, u) - p_{\rm eq}(T(t), u)\Big)du \\ & \times \frac{[p_{\rm eq}(T(t), w) - p(t, w)]\mathcal{H}\Big(p_{\rm eq}(T(t), w) - p(t, w)\Big)}{\int_0^\infty [p_{\rm eq}(T(t), u) - p(t, u)]\mathcal{H}\Big(p_{\rm eq}(T(t), u) - p(t, u)\Big)du},\end{aligned} \tag{6}$$

where $L^0 = \chi L$ is the rate of nonrelapsing hops (when a cell lands in a new state). Equation *6* generalizes "the energy master equation" (22,29,30). To derive this relation, two assumptions were used similar to those in the Kovacs model (10). The difference between the two approaches is that Kovacs' hypotheses are formulated for various kinds of free volume clusters (that have no physical meaning), whereas our postulates are applied to the probability density of traps with various potential energies.

Comparison with experimental data

The configurational entropy per rearranging region (that characterizes the level of disorder in an ensemble of cells) is given by (31)

$$s(t) = -k_B \int_0^\infty p(t, w) \ln p(t, w) dw, \tag{7}$$

where k_B is Boltzmann's constant. The Adam-Gibbs equation (21) reads

$$\Gamma_0(t) = \Gamma_{\rm eq}(T(t)) \exp\Big[-\frac{\Delta\mu\, s_*}{RT(t)}\Big(\frac{1}{s(t)} - \frac{1}{s_{\rm eq}(T(t))}\Big)\Big], \tag{8}$$

where $\Gamma_{eq}(T)$ is the equilibrium average rate of hops, $s_{eq}(T)$ is the equilibrium configurational entropy of a cell at temperature T, $\Delta\mu$ is the free-energy barrier hindering rearrangement. R is the gas constant, $s_* = k_B \ln n$ is the critical entropy, and n is the

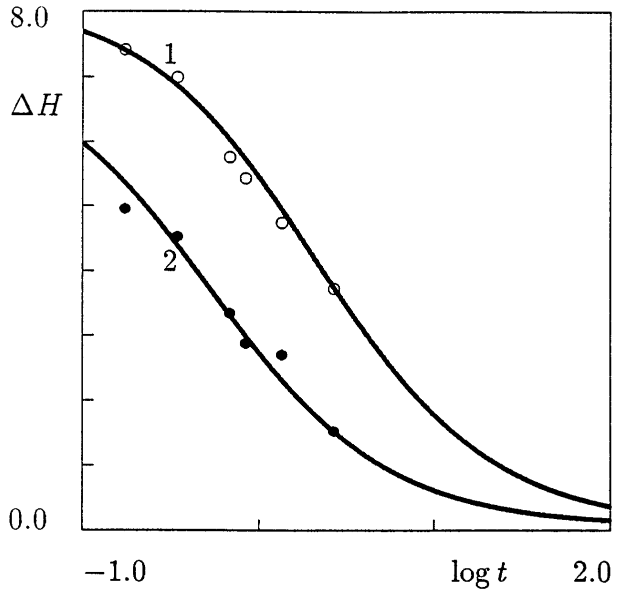

Figure 4: The excess enthalpy ΔH J/g versus time t h for a glycerol glass ($T_g = -84$ °C) annealed at $T = -110$ (curve 1) and $T = -105$ °C (curve 2). Circles: experimental data (35). Solid lines: predictions of the model with $k_B T N = 3.0$ J/g and $\bar{w}(0) = 0.47$. Curve 1: $L^0_{\text{eq}} = 1.0$ 1/h, $\bar{w}_{\text{eq}}(T) = 0.03$; curve 2: $L^0_{\text{eq}} = 4.2$ 1/h, $\bar{w}_{\text{eq}}(T) = 0.04$

smallest number of strands permitting rearrangement. Formula *8* was employed (in another context) to describe enthalpy relaxation in polymeric glasses in (32). Given material parameters χ, $\Delta\mu$, s_* and functions $\Gamma_{\text{eq}}(T)$ and $p_{\text{eq}}(T, w)$, *Eq. 6* with coefficients *7* and *8* determines the current probability density $p(t, w)$ of flow units with potential energy w. Subtracting the equilibrium configurational entropy $s_{\text{eq}}(T(t))$ at temperature $T(t)$ from the current configurational entropy $s(t)$, we determine the excess entropy per cell Δs and the specific excess entropy per unit mass $\Delta S = N\Delta s$. The specific excess enthalpy $\Delta H = H(t) - H_{\text{eq}}(T(t))$ is expressed in terms of the specific excess entropy ΔS by means of the conventional formula $\partial\Delta H/\partial\Delta S = T$. For isothermal annealing, this equation is explicitly integrated,

$$\Delta H(t) = k_B T N \int_0^\infty \Big[p_{\text{eq}}(T, w) \ln p_{\text{eq}}(T, w) - p(t, w) \ln p(t, w)\Big] dw. \tag{9}$$

We accept the Rayleigh formula for the equilibrium probability density of flow units

$$p_{\text{eq}}(T, w) = \frac{\pi w}{2\bar{w}^2_{\text{eq}}(T)} \exp\Big[-\frac{\pi w}{4\bar{w}^2_{\text{eq}}(T)}\Big], \tag{10}$$

where $\bar{w}_{\text{eq}}(T)$ is the average energy of cell at temperature T. It is assumed that at rapid heating (cooling), the distribution function preserves its shape, whereas the average energy of rearranging regions changes. For thermal test *1*, this means that function *10* with some $\bar{w}(0)$ may serve as an initial condition for *Eq. 6*.

Enthalpy relaxation in an amorphous polymer is determined by 6 material parameters: A. $\Delta\mu$. N, L^0_{eq} $\chi\Gamma_{\text{eq}}(T)$, $\bar{w}(0)$ and $\bar{w}_{\text{eq}}(T)$. The quantity A characterizing the scale for potential energy w may be chosen arbitrarily; for convenience of numerical simulation, we set $A = 0.1$ and treat w as a dimensionaless quantity. To reduce the number of adjustable constants, we suppose that $\Delta\mu \ln n/(RT) = 0.1$. For $n = 2$ (21) and tests at ambient temperature, this implies that $\Delta\mu = 357.64$ J/mol. Comparing

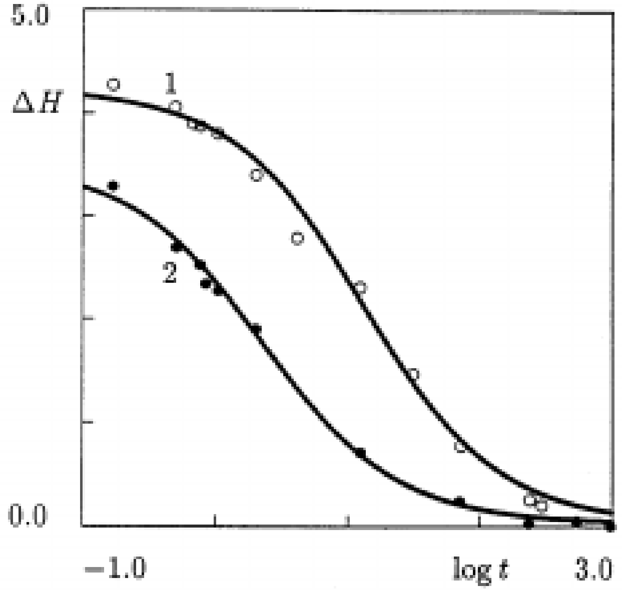

Figure 5: The excess enthalpy ΔH J/g versus time t h for poly(ether imide) ($T_g = 215$ °C) annealed at $T = 195$ (curve 1) and $T = 200$ °C (curve 2). Circles: experimental data (36). Solid lines: predictions of the model with $k_B T N = 1.5$ J/g and $\bar{w}(0) = 0.47$. Curve 1: $L^0_{\mathrm{eq}} = 0.16$ 1/h, $\bar{w}_{\mathrm{eq}}(T) = 0.028$; curve 2: $L^0_{\mathrm{eq}} = 1.0$ 1/h, $\bar{w}_{\mathrm{eq}}(T) = 0.045$

this value with appropriate activation energies for creep in a number of polymers [Table 3 in (33)], we find that the activation energy for structural recovery is about 4% of that for mechanical relaxation (in qualitative agreement with experimental data on the effect of temperature on the characteristic times for physical aging and stress relaxation). Other parameters are found by fitting experimental data for polycarbonate, polystyrene, poly(methyl methacrylate), a glycerol glass, and poly(ether imide). For detailed descriptions of the experimental procedures, we refer to (1,11,34-36). Figures 1 to 3 show that the value of $k_B TN$ is about unity. For polycarbonate, this implies that $N = 1.46 \times 10^{27}$ m^{-3}, which is in good agreement with observations for polyethylene (37) which result in $N = 0.73 \times 10^{27}$ m^{-3} (the difference by twice may be explained by the high level of crystallinity in polyethylene: the concept of traps reflects only the response in an amorphous phase of a semi-crystalline polymer). Figures 1 to 3 and 5 provide similar magnitudes of the excess enthalpy for amorphous and semi-crystalline polymers: the quantity ΔH in Figure 5 weakly exceeds that depicted in Figures 1 to 3, but it is in agreement with other data for polystyrene (38)]. Figure 4 demonstrates higher values of ΔH for the supercooled molecular liquid than for amorphous polymers. An increase in the excess enthalpy of glycerol compared to conventional amorphous polymers is in agreement with experimental data obtained by dielectric spectroscopy (39) and neutron scatering (40,41) and may be explained by the severe effect of vibrational modes on structural relaxation (40,41).

Concluding remarks

A model has been derived for enthalpy recovery in amorphous glassy polymers after thermal treatment. The constitutive relations are based on the theory of cooperative relaxation in a version of the concept of traps. The model adequately predicts enthalpy recovery at isothermal annealing in amorphous [polycarbonate, poly(methyl methacrylate), polystyrene, a glycerol glass] and semi-crystalline [poly(ether imide)] polymers.

Acknowledgement: Financial support by the Israeli Ministry of Science through grants 9641-1-96 and 1202-1-98 is gratefully acknowledged.

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