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Rheological study of some photo-response stimuli azo-polysiloxanes

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Polymers with azo groups in the main or side chain have aroused a great interest due to the possibility of conformational modification under UV irradiation. This property can be exploited in the field of data storage, drugs controlled release, in holographic technique, etc. In the present study we have synthesized and investigated a series of compounds with azo groups, namely: poly (styrene-*ran*-cloromethylstyrene) graft on a cyclic polysiloxane. More of than, some linear azo-polysiloxanes were modified too, with thymine groups. It was also tested the possibility to emphasize by means of rheological measurements the conformational modification of these compounds under UV irradiation. For the investigated samples, a sharp variation of the viscoelastic parameters (the elastic modulus, the loss modulus, the complex viscosity and the loss tangent) was observed. This variation occurs over several decades (more than four orders in magnitude). This behaviour can be associated with the conformational changes induced by *trans/cis* isomerization given by the azobenzenic groups. An association of polymer chains due to the changes of the azo-groups dipole-moment on the macromolecular chain can also occur.

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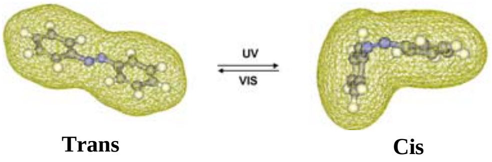
1. Introduction

In the last period, polymers with azo groups in the main or side chain have received attention, due to the possibility of the conformational modification controlled by the UV irradiation. This property can be exploited in the field of information storage (for the future generation of optical computers), drugs control release, in holographic technique, etc. In the present study it was tested the possibility of transforming some polysiloxanes through the connection of some azobenzene units in the side chain using a SN2 substitution taking place in solution, in a temperature range of 80-90°C. The reactive groups are the chloro-benzyl (on the polymeric chain) and phenolat respectively (in azobenzenic structures). The aromatic sequences are not fully rigid, the connection of the first aromatic nucleus to azo groups being made through an ethyl flexible group. It is expected that partial mobility of the aromatic sequences to facilitate the *trans/cis* isomerization of the azobenzenic groups. During isomerization the polymeric chains are changing their shape, adopting new configuration responsible for the birefringence and dichroism.



The isomerization effect in some azo-polymeric systems through the viscoelastic properties of their solutions in a non-polar solvent, before and after UV irradiation was investigated.

2. Experimental

We have synthesized and characterized from the chemical structure point of view, linear and cyclic polysiloxanes, with chloro-benzyl groups in the side chain. The presence of the chloro-benzyl groups is essential for the subsequent modification of polysiloxanes due to connection in the side chain of different types of azobenzenic groups, respectively of nucleobases. In the same time, the presence of chloro-benzyl groups will permit using this polysiloxanes as macro-initiators for the synthesis of polymers with complex architectures which can be later modified with azobenzene. For the present study the following compounds were synthesized:

- a copolymer (styrene-chloromethylstyrene) graft on a cyclic polysiloxane backbone, modified with azo units, denoted **sample 1**;
- a linear polysiloxane with azo groups (75%) and thymine (25%), denoted **sample 2**;
- a linear polysiloxane with azo groups (50%) and thymine (50%), denoted **sample 3**;

For the **sample 1** we have prepared solutions in toluene with different concentrations (1,5; 3; and 6 %), and for **sample 2** and **sample 3** a 3% in toluene solution was used. All samples were kept for one day in the dark and filtered before beginning the experiments. The maintaining of samples in the dark is necessary to obtain a maximum amount of *trans* conformations, due to the fact that natural UV radiation can induce (according to chemical structure of the azo group and the intensity of light) a certain quantity of the *cis* isomer. The samples irradiation has preceded the rheological tests made in the absence of light.

The synthesized polymers had different architectures and chemical structures, one of the objectives of the present study being to observe the influence of chain architecture over the rheological behaviour.

Thus, the **sample 1** is a graft polymer obtained by ATRP reaction (Fig. 1), having a cyclic polysiloxane backbone and the side chain being formed by a (styrene-chloromethylstyrene) copolymer.

The presence of chloro-benzyl groups in the side chain has permitted chain connection of azobenzenic units by a Williamson substitution reaction (Fig. 2).

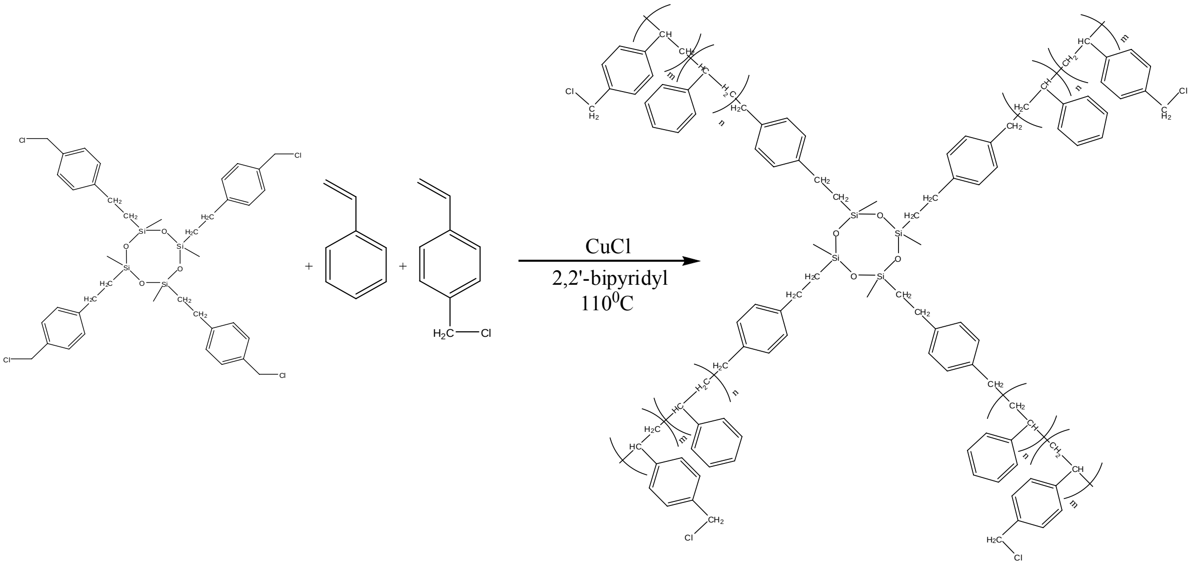


Fig. 1. ATRP reaction for obtaining (styrene – chloromethylstyrene) copolymer graft on cyclic polysiloxane.

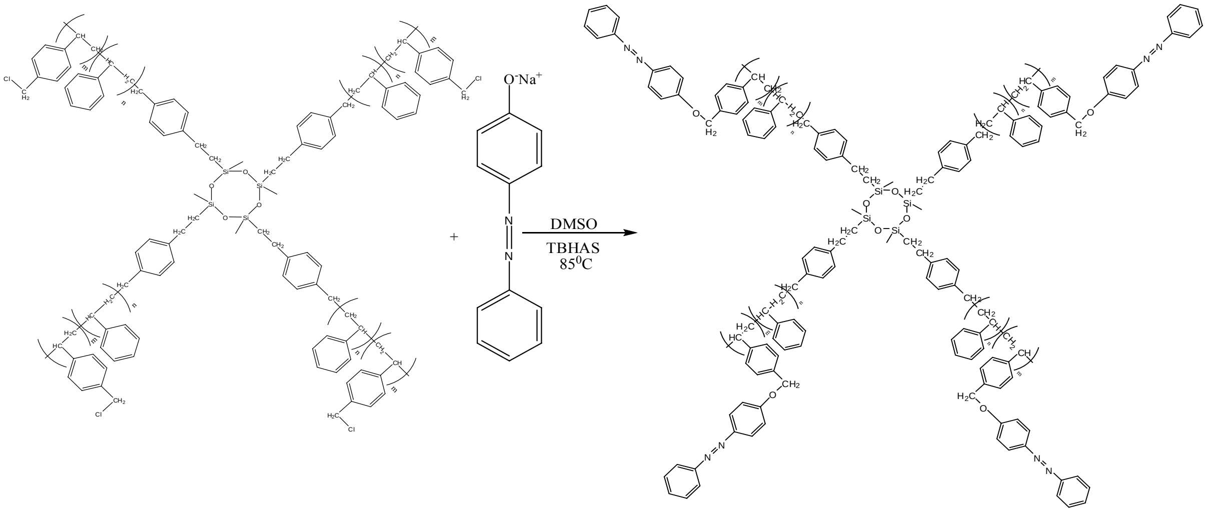


Fig. 2. Williamson substitution reaction for connecting azobenzene units in the side chain.

The rheological measurements were performed at 20 °C using a CVO Rheometer with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by Peltier effect. Prior to rheological measurements, suitable shear amplitude was determined by measuring the shear stress dependence of moduli to ensure the linearity of dynamic viscoelasticity. For all samples it was observed that the linear domain is in the range of 0.1 to 3 Pa (Figs. 3a, 3b) A shear stress of 1Pa was selected for the frequency sweep tests, and this corresponds to a deformation of approx. 1%.

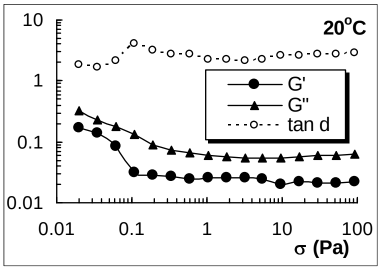


Fig. 3a. Amplitude sweep for 6% sample 1 in toluene (non-irradiated) at 20 °C.

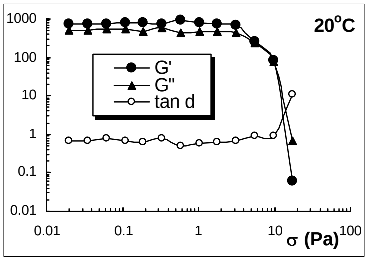


Fig. 3b. Amplitude sweep for 3% sample 2 in toluene (non-irradiated) at 20°C.

3. Results and discussions

1. Rheological behaviour of cyclic polysiloxane grafted with poly (styrene-ran-cloromethylstyrene)

The oscillatory tests involve the application of a sinusoidal stress (or strain) to the upper plate of the rheometer. The resulting strain (or stress) can be resolved into components that are in phase with the input (elastic response) and π/2 out of phase with the input (viscous response). From these data a complex modulus, G*, is determined as a function of frequency:

$$G^*(\omega) = G'(\omega) + iG''(\omega) \qquad (1)$$

where G'(ω) (storage or elastic modulus) and G" (ω) (loss or viscous modulus) give information on energy storage and energy dissipation during the flow, respectively. For a perfectly elastic solid, G" = 0 and according to eq. (1) G*(ω) = G'(ω). For a Newtonian fluid, G'(ω) = 0 and η = G"/ω, where ω is the oscillation frequency.

Figs. 4-6 give the evolution of the viscoelastic parameters G' and G" as well as the complex viscosity, η* for **sample 1** in toluene at different copolymer concentrations. The experimental investigations were performed at 20 °C for non-irradiated samples as comparative with samples submitted to irradiation for 15 minutes, considering σ = 1 Pa and ω = 10 rad/s. Excepting the non-irradiated 3% **sample 1**, after a period of time depending on the copolymer concentration, a sharp increase of viscoelastic parameters can be observed, the variation occurring over several decades (more than four orders in magnitude). This change of the properties can be associated with a *tans-cis* isomerization due to azobenzene groups.

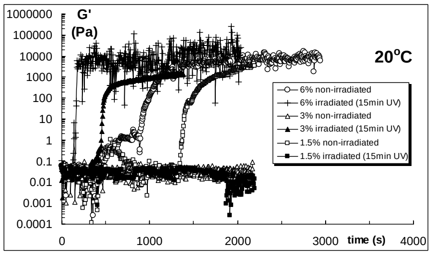


Fig. 4. The evolution of the elastic modulus as a function of time for different concentrations of sample 1 solutions in toluene, samples non-irradiated as compared with samples UV irradiated 15 minutes (20 °C).

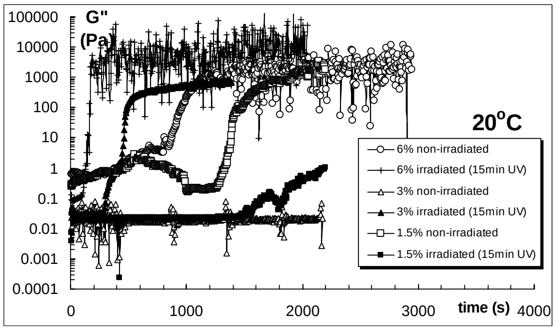


Fig. 5. The evolution of the viscous modulus as a function of time for different concentrations of sample 1 solutions in toluene, samples non-irradiated as compared with samples UV irradiated 15 minutes (20 °C).

The effect of the photo-isomerization of azo-benzene groups from the *trans* configuration (stable from the energetic point of view) in a *cis* one (metastable) can induce the following changes:

- severe modification of the conformation of the macromolecular chains, with direct consequences on the sizes of macromolecule (the radius of gyration);
- important changes of the dipole moment corresponding to azobenzene group, from a value of 0.1 for the *trans* configuration to 3.5 D corresponding to *cis* configuration. The dipole-moment changes can also induce conformational changes of polymer chains such as a strong increase of intramolecular interactions or an increase of association capacity due to the intensification of intermolecular interactions.

Table 1 collects the isomerization times for the **sample 1** solutions. One observes that the response of the copolymer is influenced by its concentration in solution and by the presence or absence of the irradiation. At low polymer concentrations (1.5%), for the system submitted to irradiations, a slow increase of the response time can be observed (from 1350 s to 1600 s), whereas for high concentrations (6%) the effect is opposite, the response time decreases from 900 s to 140 s after the sample irradiation. For the non-irradiated 3% **sample 1** solution in toluene it was not observed any isomerization, but for the same sample submitted to UV irradiation, the response of the material is registered after 250 s for a period of 200 s, when an increase of G', G" and η* over 4 decades is observed. The loss tangent presents a maximum in the transition interval and remains nearly constant ($\tan\delta = 1$) before and after the transition (Fig. 7).

Table 1. The time of isomerization (in seconds) for different concentrations of the ***sample 1*** *in toluene at 20°C, at σ = 1 Pa and ω = 10 rad/s.*

Copolymer concentration (% wt.)	Non-irradiated sample	UV Irradiated Sample (15 minutes)
1.5	1350	1600
3	-	250-400
6	900	140

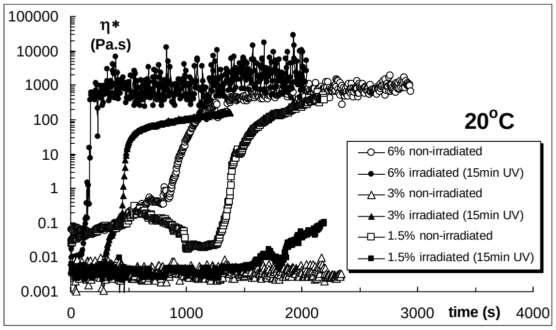


Fig. 6. The evolution of the complex viscosity as a function of time for different concentrations of sample 1 solutions in toluene, samples non-irradiated as compared with samples UV irradiated 15 minutes (20°C).

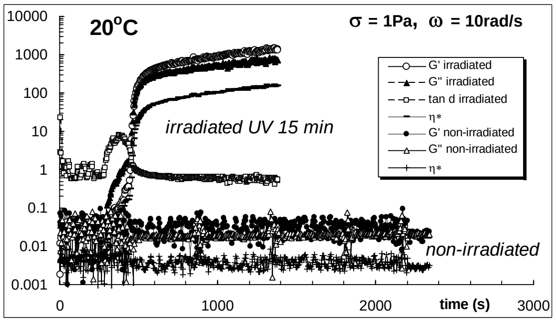


Fig. 7. The evolution of viscoelastic parameters as a function of time for 3% concentration of sample 1 in toluene, non-irradiated sample comparatively with UV irradiated sample 15 minutes (20 °C).

For solutions with low polymer concentrations, the UV irradiation determines an early apparition of the transition phenomenon (a sharp variation of the dynamic parameters) as compared with the same samples without irradiation. This suggests the fact that a UV radiation determines a supplementary mobility of the macromolecular segments and, as a consequence, the transitions occur easier.

The transition phenomenon is very complex and sensitive to polymer concentration, UV exposure and external stress. Fig. 8 presents the variation of the viscoelastic parameters G', G", tanδ and η* for 6% **sample 1** solution in toluene in a frequency sweep test, by decreasing the frequencies from 40 rad/s to 0.2 rad/s. Around a frequency of ω=0.5 rad/s, the sharp variation of viscoelastic parameters can be observed, this variation occurring in an interval of 1000s-1400s from the beginning of the experiment. At this frequency, G'=G" and, considering valid the Maxwell model [12], the relaxation time (θ) is calculated as θ = 1/ω = 2 s.

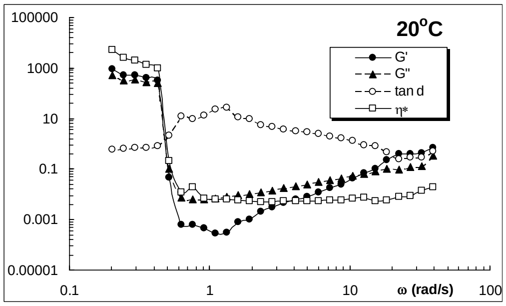


Fig. 8. The variation of G', G", tanδ and η as a function of oscillation frequency for the sample 1 in toluene at 20°C. The tests were carried out with fresh sample from high to low values of oscillation frequency.*

2. *Rheological behaviour of polysiloxanes with azo groups and thymine in their structure*

For this study, two polymers with azobenzene and thymine as pendant groups were selected: **sample 2** - a polysiloxane with 75% azo-groups and 25% thymine and **sample 3** - a polysiloxane with 50% azo-groups and 50% thymine.

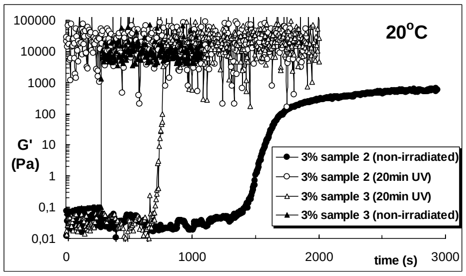


*Fig. 9. The evolution of the elastic modulus for 3% solutions of **sample 2** and **sample 3** in toluene, non-irradiated and UV irradiated (20 minutes) samples at 20 °C.*

Figs. 9-11 present the evolution of the viscoelastic parameters as a function of time for 3% solutions of **sample 2** and **sample 3** in toluene at 20°C. Thymine can form itself H bonding and determining the formation of associated structures.

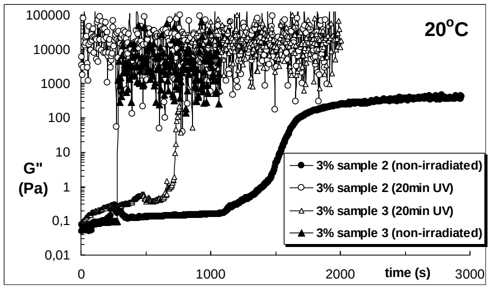


Fig. 10. The evolution of the viscous modulus for 3% solutions of samples 2 and sample 3 in toluene, non-irradiated and UV irradiated (20 minutes) samples at 20 °C.

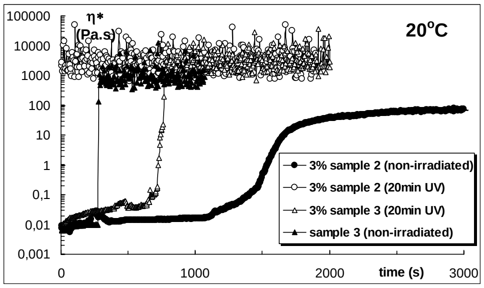


Fig. 11. The evolution of the complex viscosity for 3% solutions of sample 2 and sample 3 in toluene, non-irradiated and UV irradiated (20 minutes) samples at 20 °C.

For the non-irradiated **sample 2**, the change of the rheological parameters occurs after 1100 s, whereas for the irradiated sample this transformation has occurred before the rheological measurement, probably during UV exposure. For the non-irradiated **sample 3**, the variation of the parameters is observed after 275 s, and the irradiated sample show a transformation after 700s.

The behaviour of the two non-irradiated **samples 2** and **3** is different, for lower thymine content the response appears after a longer period of time (Figs. 12 and 13).

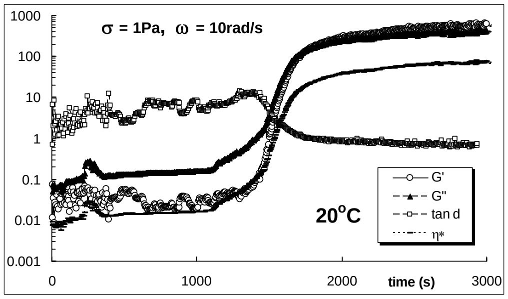


Fig. 12. Variation in time of the viscoelastic parameters for the non-irradiated sample 2 (3% in toluene) at 20 °C.

This can be explained by considering a competition of specific interaction between the pendant groups (the solvent being non-polar, it has no influence on the polar interactions).

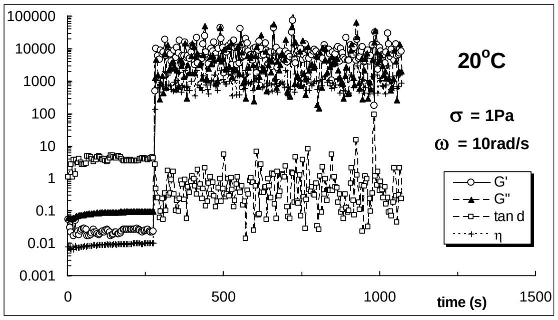


Fig. 13. The evolution of G', G", tanδ si η parameters as a function of time for the sample 3 in toluene (3%, without irradiation) at 20 °C.*

After the isomerization, the chains remain in the *cis* state, as it is shown in Figure 12. For the **sample 3**, after isomerization, the rheological parameters show some fluctuations around an equilibrium value, suggesting the occurrence of some continuous conformational changes under the shear conditions (the continuous formation and destruction of the physical bondings which are able to form supramolecular structures).

In a frequency sweep test realized after following the time dependence illustrated in Fig. 11 and using the same sample, one observes that the viscoelastic parameters are in the same range of high values (Fig. 14).

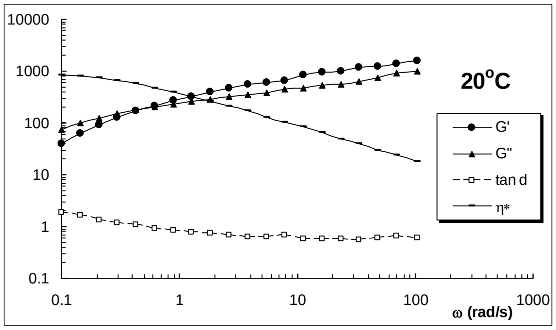


Fig. 14. G', G", tanδ and η vs. ω for 3% solution of sample 2 in toluene at 20 °C. The test was realized after the time test shown in Fig. 12.*

After the isomerization, the polymers conserve their *cis* state, even in the conditions of high shear stresses.

4. Conclusions

In the present study, a series of polymers with azo groups were synthesized, i.e.: poly (styrene-*ran*-chloromethylstyrene) graft on cyclic polysiloxane and azo-polysiloxanes with thymine groups. It was tested the possibility to evidence the *cis-trans* transitions by following the evolution of the viscoelastic parameters for solutions in toluene. The behaviour of samples submitted to UV irradiation was investigated in comparison with the non-irradiated samples.

After a period of time, depending on the polymer concentration, it was observed a sharp variation of the rheological parameters such as: the elastic (G') or the viscous (G") moduli, the complex viscosity (η*), the variation of these parameters covering more than four decades. These changes of the viscoelastic parameters can be associated with the configuration changes induced by the *trans-cis* isomerization undergone by the azobenzene groups. In the solutions of a non-polar solvent, some association phenomena can occur due to the modification of the dipole-moment characteristic to the azo-groups in *trans* and *cis* states, respectively.

For polysiloxanes with azo-groups and thymine, the dynamic behaviour can be explained as the result of a competition of specific interactions of different pendant groups which are in the system. In the presence of the thymine, the behaviour is influenced by the tendency to form some associations due to the hydrogen bonding. In the presence of a shear field, continuous conformational changes can occur due to the dynamic formation/destruction of the supramolecular structures.

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