The Crosslinking of Ethylene-Vinyl Acetate with Organometaluc Compounds

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ABSTRACT

Organometallic compounds such as aluminum trialkyl (AlR_3) and lithium alkyl react nonradically with ethylene–vinyl acetate copolymers (EVA) to yield very high crosslinking rates. The mechanism is characterized by simultaneous reactions: addition, reduction, and enolization accompanied with ethene and ethane elimination. The crosslinking reaction is exclusively due to enolization and subsequent dimerization. Systems containing anisole, ether, or quinoline together with $AlEt_3$ were investigated. It is shown that only free AlR_3 is able to crosslink EVA. The reaction mechanisms were proved experimentally. The process allows the production of polymers exhibiting improved mechanical properties. The polar groups formed during the reaction, and the metal content, improve the ability of the modified polymers to combine with polar polymers. This leads to an increase in adhesiveness to inorganic surfaces compared to radically crosslinked EVA.

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INTRODUCTION

The free radical crosslinking of polyethylene, ethylene copolymers with vinyl acetate (EVA) [1–7], and their crosslinking by means of grafted alkoxysilanes [8] is well known.

In 1971 [9] we published data on the crosslinking of EVA with aluminum alcoholates and demonstrated that the reaction mechanism is a transesterification with the formation of aluminum polyalcoholate and acetic acid ester:

$$PO-\underset{\underset{O}{\|}}{C}-CH_3 \;+\; Al(OR)_3 \;\xrightarrow{\;\;1\;\;}\; PO-Al(OR)_2 \;+\; CH_3-\underset{\underset{O}{\|}}{C}-OR$$

$$PO-\underset{\underset{O}{\|}}{C}-CH_3 \;+\; PO-Al(OR)_2 \;\xrightarrow{\;\;2\;\;}\; (PO)_2AlOR \;+\; CH_3-\underset{\underset{O}{\|}}{C}-OR$$

$$PO-\underset{\underset{O}{\|}}{C}-CH_3 \;+\; (PO)_2AlOR_3 \;\xrightarrow{\;\;3\;\;}\; (PO)_3Al \;+\; CH_3-\underset{\underset{O}{\|}}{C}-OR$$
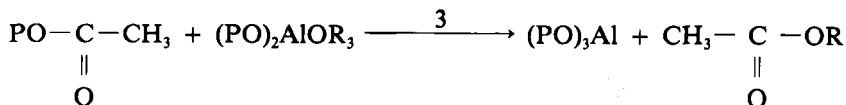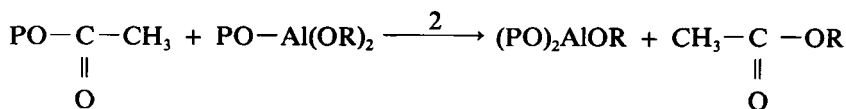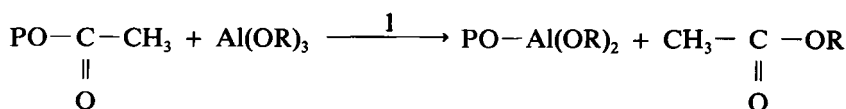
Furthermore, we investigated the crosslinking of EVA with sodium alcoholates [10]. We demonstrated that in the polymer melt two reactions take place side by side: a crosslinking reaction with the formation of $C-C$ bonds and alcoholysis with the formation of vinyl alcohol moieties. The covalent crosslinking bonds are produced by an incomplete Claisen ester condensation.

During the last few years we have investigated the crosslinking of dissolved or molten EVA with organometallic compounds. The rate of reaction is so high that its determination is not possible. In the melt, a homogeneous distribution of the metal alkyls could not be achieved due to the formation of highly crosslinked components. Also, in solution, even below 0°C, gel formation was reached after a few seconds. These facts led us to become particularly interested in the mechanism of this reaction through searching for possibilities to reduce the reaction rate.

Baba [11, 12], Cianelli and coworkers [13], and Pasynkiewicz and Sli-

wa [14, 15] found, upon investigating the reaction mechanism of alumi-
num alkyls with carbonyl compounds, that the reactions between AlEt$_3$
and aldehydes or ketones follow an analogous mechanism. They demon-
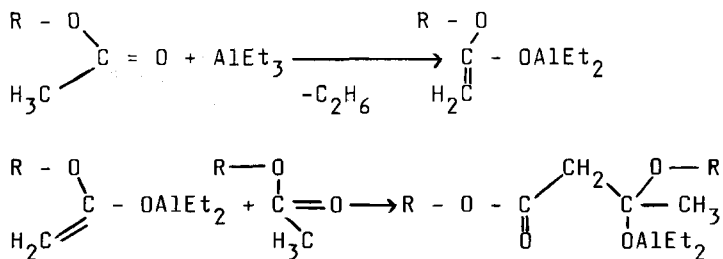strated with ketones that side by side addition, reduction, and enolizing
reactions occur. The product formed by enolization can react with a
second ketone molecule under dimerization.

As shown by Amemiya and coworkers [16], AlEt$_3$ reacts with simple
esters by addition and reduction whereas the part of reaction products
preponderates:

$$R - O \diagdown C = O + AlEt_3 \left\{ \begin{array}{l} \xrightarrow{\text{addition}} \quad R - O \diagdown \diagup OAlEt_2 \\ \qquad\qquad\qquad H_3C \diagup C \diagdown C_2H_5 \\ \\ \xrightarrow[-C_2H_4]{\text{reduction}} \quad R - O \diagdown \diagup OAlEt_2 \\ \qquad\qquad\qquad H3C \diagup C \diagdown H \end{array} \right.$$
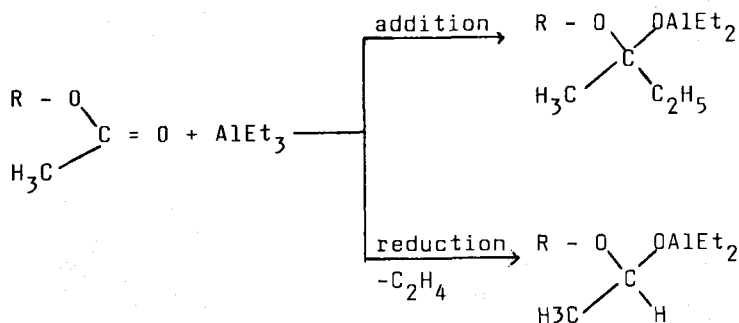
In comparison, esters with steric hindrance nearly exclusively give ad-
dition products. Enolization reactions and subsequent dimerization, as
shown by the following equations, could not be found.

$$R - O \diagdown C = O + AlEt_3 \xrightarrow[-C_2H_6]{} \quad R - O \diagup C - OAlEt_2$$
$$H_3C \diagup \qquad\qquad\qquad H_2C$$

$$R - O \diagdown C - OAlEt_2 + C = O \longrightarrow R - O - C \diagup CH_2 \diagdown C \diagup O - R$$
$$H_2C \diagup \qquad H_3C \qquad\qquad\qquad O \qquad OAlEt_2 \qquad CH_3$$

We have investigated the crosslinking of EVA with metal alkyls (e.g.,
AlR$_3$ and LiR) and observed very high crosslinking rates. We tested the
course of the reaction with the low-molecular model compound acetic
acid pentyl-3-ester.

EXPERIMENTAL CONDITIONS

The crosslinking studies were performed in solutions of EVA or acetic acid pentyl-3-ester in toluene. Copolymers of ethylene and vinyl acetate were produced by the high-pressure process, with an vinyl acetate content of 34.7 wt% and MFI (190°C/21.2 N) of 130 dg/min.

Synthesis of Model Compound

(a) Pentanol-3 by Reduction of Diethyl Ketone. Catalytic hydrogenation of the ketone is possible by means of Raney nickel in a 1-L shaker autoclave at 150°C and a hydrogen pressure of 10 MPa [7]. The alcohol was purified by fractionation distillation employing a 1-m Vigreux column.

(b) Acetic Acid Pentyl-3-ester. Pentanol-3 was reacted with acetyl chloride [8]. The raw product was pre-dried over calcium hydride for several days. After decantation and the addition of another portion of calcium hydride, the mixture was refluxed for 1 h. A 1-m packed column ("Braunschweiger Wendeln") was used for fractionation. The fraction obtained between 132 and 134°C was the desired product ($n_D^{20} = 1.966$; purity 99% as determined by gas chromatography).

AlEt$_3$ was distilled *in vacuo* and used with a purity of 99%. The mechanistic studies of the crosslinking reaction were performed with solutions of AlEt$_3$ in dry *n*-heptane (30 wt% AlEt$_3$).

INVESTIGATIONS ON THE MECHANISM OF THE CROSSLINKING REACTION

1. Accomplishment of the Reactions

Special Schlenk apparatuses [17, 18] were used for the reactions. After repeated purging of the apparatus with dry argon, 0.1 mol of the model substance or 100 g of an EVA copolymer solution (toluene, 25 wt%), respectively, were put into the reaction vessel (multinecked flask with reflux condenser) and kept at a constant temperature of 308 K. By means of a syringe, 0.088 mol AlEt$_3$, dissolved in dry *n*-heptane, was added dropwise. The reaction products obtained are volatile and were collected in a gas collection tube.

2. Analysis of the Gaseous Reaction Products

The gas mixtures obtained were analyzed by means of gas chromatography. A gas chromatograph, type GCHF 18/3 (from Giede, Berlin, GDR, with a heat-conduction cell as detector), was used. A column of 1 m length was filled with Poropax-Q, and hydrogen with a flow of 3 L/h (chart speed, 3600 mm/h) was used as the carrier gas. For comparison purposes, the pure components were injected and the products identified.

3. Working-up of the Reaction Mixtures

The reaction mixtures in question were cooled by petroleum ether/dry ice mixtures. Subsequently, distilled water was added dropwise. The gas mixture obtained was analytically studied as described in Paragraph 2.

After termination of the reaction, an amount of concentrated hydrochloric acid just sufficient to dissolve the generated aluminum hydroxide was added. The organic phase was made neutral by the use of distilled water, dried with magnesium sulfate, and fractionally distilled.

4. Gas-Chromatographic Determination of the Hydrolysis Products

The substance mixtures of the single fractions were identified by comparison injections of the pure components. The gas chromatograph mentioned above, with a column of 3 m length and filled with neopentyl glycolsuccinate, was used under the conditions previously described.

VISCOMETRIC PURSUIT OF THE CROSSLINKING REACTION OF EVA WITH AlEt$_3$/ELECTRON DONOR COMPLEXES

20 mL samples of a copolymer solution containing 15 wt% of the EVA copolymer mentioned earlier were put into an ampule made oxygen-free by repeated purging with dry argon. Subsequently, the ampule was kept at the reaction temperature in an oil thermostat. 2 mL of the respective complex solutions in n-heptane, containing a constant amount of 5×10^3 mol pure AlEt$_3$, was injected.

Reaction termination was possible by rapidly cooling the ampules and keeping them at a constant temperature of 20°C for 10 min. The viscosity

of the respective reaction mixtures was measured by means of a Ubbe-
lohde viscometer (capillary size 2) at 20°C.

RESULTS AND DISCUSSION OF THE MECHANISM

In the EVA reaction in a toluene solution with $AlEt_3$, only ethane
could be identified as a volatile product independent of the reaction
temperature (243 to 413 K). Gel formation was observed in each case.
This result points to an enolization reaction following dimerization, but it
does not exclude crosslinking by an addition reaction.

After reacting the polymer solution with lithium-*n*-butyl, gel forma-
tion was observed and the volatile reaction product was found to be *n*-
butane. In this case, crosslinking is only possible by an enolization reac-
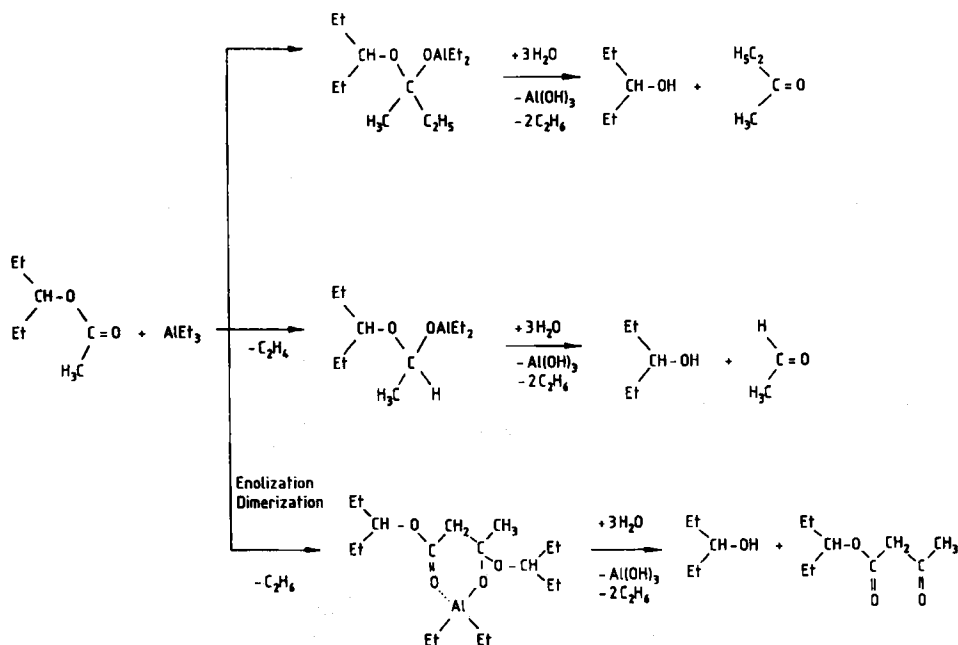tion following dimerization.

In the reaction of the model substance pentyl-3-acetate with $AlEt_3$,
volatile reaction products of a different composition were obtained de-
pending on the reaction temperature (Table 1).

The results show an increase in reduction with increasing temperature,
but in every case it dominates the enolization. Information about the
addition reaction could be obtained by treating the liquid reaction prod-
ucts with water and analyzing the final products.

All three reaction possibilities should be considered (Scheme 1). Gas-
chromatographic analysis of the hydrolysis products yielded much pen-
tanol-3 (besides the model substance itself), small amounts of methyl
ethyl ketone, and only traces of acetaldehyde. In all instances the amount
of pentanol-3 was much larger than the sum of methyl ethyl ketone and
acetaldehyde. Furthermore, a high-boiling yellowish residue was ob-
tained, and it consisted of a multiplicity of different condensation prod-

TABLE 1.

Reaction temperature, °C	Ethane, %	Ethylene, %
140	85	15
120	90	10
30	100	—
0	100	—
− 20	100	—

SCHEME 1.

ucts. The isolation of single components of sufficient purity from this mixture was not possible. The results also showed that the enolization reaction, followed by dimerization, predominates when using pentyl-3-acetate, while the addition and reduction reactions play only a subordinate role.

By comparing the results obtained in the reaction of EVA or pentyl-3-acetate with AlEt$_3$, the mechanism of the crosslinking reaction shown in Scheme 1 is postulated, in agreement with the literature: The first compound to be formed is the well-known charge-transfer complex. In consideration of the electronic distribution, the boundary structure is suggested. The following reaction is the enolizing step in a cyclization mechanism leading to the formation of a six-membered ring with separation of ethane and formation of a C=C double bond. The keto–enol equilibrium is illustrated. The dimerization reaction is introduced by coordination of the carbonyl group of a second polymer molecule to the Al atom. The electron transfers proceed via a cyclic transition state, resulting in the formation of a crosslinking site.
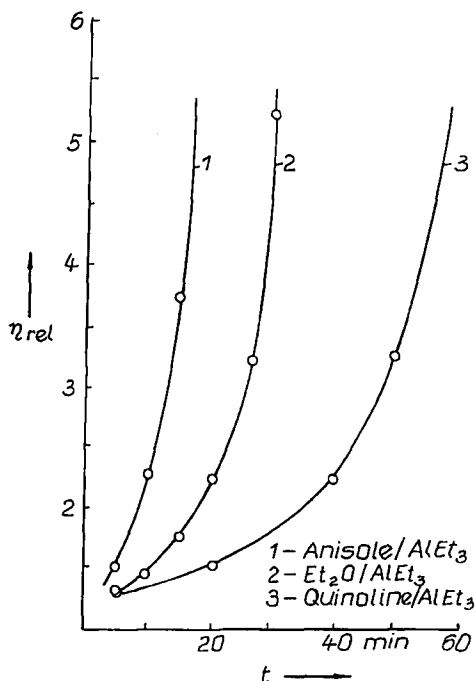
FIG. 1. Change in the dependence of the relative viscosity on the reaction time. Mole ratio of donor: $AlEt_3$ = 1:1. $c^0_{polymer}$ = 5.1 wt% (corresponding to 0.2 mol polymer-bound vinyl acetate per liter solution). $c^0_{complex}$ = 0.176 mol/L. Solvent: Toluene. Reaction temperature: 358 K.

The high reaction rate of metal alkyls with EVA is a practical problem because the crosslinking is essentially faster than the homogeneous distribution of the metal alkyl in the melt or solution. For this reason, products with a high gel content are obtained in every instance. Moreover, metal alkyls are very sensitive to air and water, and consequently their practical use involves large expense.

We therefore investigated the possibility that charge-transfer complexes of $AlEt_3$ (with electron donors being essentially more stable to air and water) also act as a crosslinking agent, and the possibility of influencing the reaction rate in this way.

We have investigated the reactions of EVA with the complexes of $AlEt_3$ and ethers or quinoline by measuring the increase of the relative viscosity

TABLE 2. Dependence on Time for Reaching the Gel
Point on the Formation Enthalpy of Complexes
of AlEt₃ with Electron Donors at a Reaction
Temperature of 358 K

Electron donor	ΔH, kcal/mol	Time, min
Anisole	− 12.3	25
Diethylether	− 21.0	45
Quinoline	− 29.9	75

as a function of time, in toluene as solvent, at a reaction temperature of
358 K. Figure 1 illustrates the experimental results. The crosslinking rates
correlate with the reaction enthalpies (ΔH) of the complex formation
between electron donors and AlEt₃ as measured by Troeber [19] (Table 2).
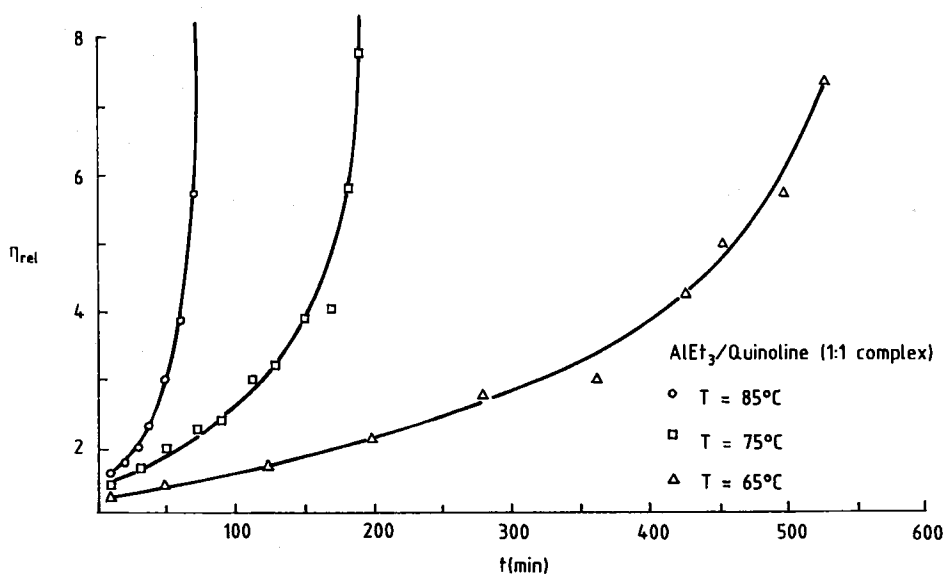As expected, the reaction rate decreases with increasing complexing

FIG. 2. Change in the dependence of the relative viscosity on the reaction
temperature and the reaction time. $c^0_{polymer}$ = 5.1 wt%. $c^0_{complex}$ = 0.176 mol/L.
Solvent: Toluene.

strength of the electron donors, i.e., it decreases from anisole to quinoline.

The temperature dependence of the relative viscosity η_{rel} for crosslinking EVA with the complex of $AlEt_3$ and quinoline is demonstrated in Fig. 2.

With increasing reaction temperature, the rate of the crosslinking reaction also increases. Referring to publications of Tüdös and coworkers [20], we determined the reaction order and rate constants for the reaction of EVA with the 1:1 complex Et_2O/quinoline, and calculated the overall activation energy of the crosslinking reaction (Fig. 3): $E_A = 57$ kcal/mol.

Figure 4 illustrates the crosslinking rate of EVA with quinoline/$AlEt_3$ as a function of the reaction time with different ratios of quinoline to $AlEt_3$. The reaction rate decreases with increasing quinoline content. At a mole ratio of 3:1, no further reaction was observed at 358 K. The results show that the complex itself is not able to effect a crosslinking. Only the $AlEt_3$, present in free form, in the complex formation equilibrium is able to crosslink. This corresponds with the reaction mechanism discussed above.
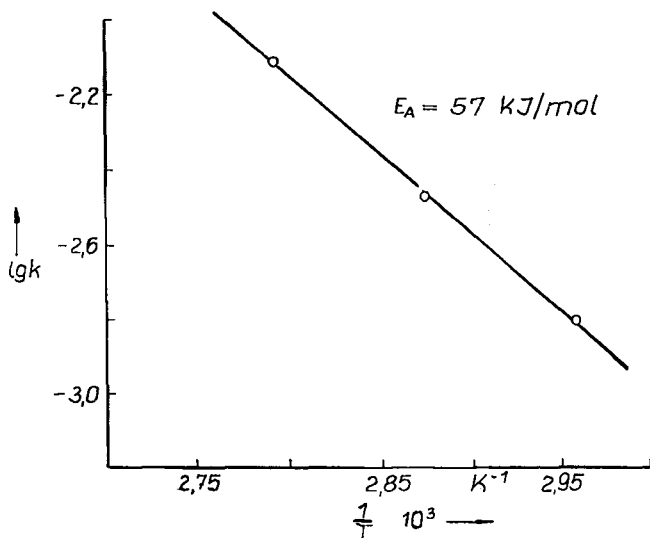
FIG. 3. Determination of the overall activation energy of the crosslinking reaction for the system EVA–$AlEt_3$/quinoline (1:1 complex) in toluene.
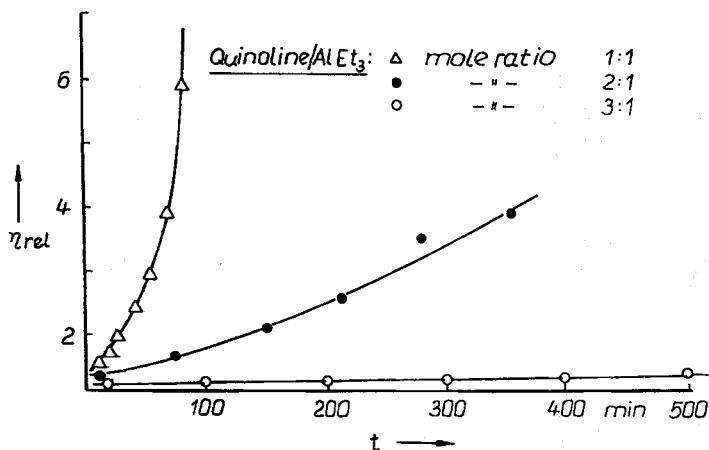
FIG. 4. Change in the dependence of the relative viscosity on the quinoline/AlEt₃ mole ratio and the reaction time. $c^0_{polymer} = 5.1$ wt%. $c^0_{AlEt_3} = 0.176$ mol/L. Solvent: Toluene. Reaction temperature: 358 K.

The modification of EVA by metal alkyls is an interesting variant of crosslinking. In particular, the high but fluctuating complex formation crosslinking rates of AlEt₃ open new ways for surface treatment. Thus, it is possible to improve the flowability of granulates made from high-percentage EVA types, to increase the surface hardness of half-stuffs, and to decrease the blocking of sheets made of EVA having a high VAc content.

CONCLUSION

Metal alkyls, e.g., AlEt₃ and Li-n-butyl, react with EVA by crosslinking. The mechanism of the reaction is due to an enolization reaction followed by dimerization. The crosslinking with pure metal alkyls is so fast that little interest exists for such a reaction. It is possible by the use of AlEt₃ complexes with electron donors to influence the rate of the crosslinking reaction, depending on the complex strength. It was demonstrated that only the AlEt₃ is free of equilibrium effects in crosslinking when complexes of AlEt₃ are used.

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