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### The Crosslinking of Ethylene-Vinyl Acetate Copolymers with Sodium Alcoholates

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## THE CROSSLINKING OF ETHYLENE-VINYL ACETATE COPOLYMERS WITH SODIUM ALCOHOLATES

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### ABSTRACT

When reacting ethylene-vinyl acetate copolymers (EVA) with sodium alcoholates in alcohol, the alcoholysis of EVA is accompanied by crosslinking reactions. Crosslinking can be detected by the increase in torque in a plastograph. This paper reports on investigations on the mechanism of the crosslinking reaction. Both crosslinking via C—C bonds and formation of a thermally reversible network via polymer alcoholate structures can be found. If an ethylene-vinyl alcohol copolymer is obtained by complete saponification of EVA, however, only thermally reversible crosslinking can be demonstrated. This leads to the conclusion that irreversible crosslinking is established through a reaction of the acetate side chains. The reaction products of the low-molecular weight model substances, pentanol-3-acetate and sodium isopropylate in isopropanol, are analyzed by means of gas chromatography. These results suggest a partial Claisen condensation as a mechanism of the irreversible crosslinking process.

## INTRODUCTION

The continuation of our studies on crosslinking of ethylene-vinyl acetate (EVA) copolymers with aluminum alcoholates [1] and aluminum alkyls [2] led to investigations on the mechanism of the crosslinking reaction. Thus, we investigated reactions of EVA copolymers with sodium alcoholates.

During the last few years, Lambla and coworkers [3, 4] studied sodium-alcoholate-catalyzed alcoholysis of EVA copolymers in the extruder. They proved that the crosslinking reaction accompanying the alcoholysis can be repressed almost entirely when alcohols with a length of more than  $C_{10}$  are used. On the contrary, we were interested in generating products with a defined degree of crosslinking, and of alcoholysis using low-molecular weight alcohols with a chain length of  $C_1$  to  $C_4$ . Low molecular weight alcohols are less expensive and can readily be removed from the melt mixture. Examinations of the reaction mechanism were necessary, since existing theories on crosslinking and its effects are unsatisfactory.

## EXPERIMENTAL

The mechanism of the crosslinking reaction was studied in a polymer melt (Brabender Plasticorder) or with low-molecular weight model compounds in solution (ampules). Different EVA copolymers produced by the high-pressure process with a vinyl acetate content of 6 to 32 wt% were investigated. Pentanol-3-acetate was used as the small molecule model.

### Synthesis of Pentanol-3-acetate [5]

(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. The alcohol was purified by fractionated distillation using a 1-m Vigreux column.

(b) *Acetic Acid Pentyl-3-ester (pentanol-3-acetate).* Pentanol-(3) was reacted with acetyl chloride. The raw product was predried over calcium hydride for several days. After decantation and 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%, determined by gas chromatography).

For comparison purposes, a completely saponified EVA copolymerizate (starting content of vinyl acetate: 32 wt%) was used.

The alcohol-containing sodium alcoholates used or their corresponding alcohol solutions were prepared by direct reaction of sodium with the corresponding alcohol. Alcohol-free sodium alcoholate was created by reacting a sodium dispersion in dry xylene with the stoichiometric amount of alcohol and subsequent separation of the xylene by distillation *in vacuo*.

### Investigations in the Brabender Plasticorder

The reactions were performed in a Brabender roller kneader type W 50 with 30 rpm. In each experiment the kneader was fed with 40 g of the corresponding copolymerizate. The sodium alcoholates were added either as a solid, paste, or an alcohol solution when a constant torque had been achieved. The experiment was finished when a constant final torque was reached, or if the load decreased after the torque maximum had been achieved. The melt flow index (MFI) of the final products was determined according to TGL 25244 (or ASTM D 1238).

### Reactions in Solution

Pentanol-3-acetate (5 mL) was reacted for 5 h under inert gas at boiling temperature in ampules with 8 mL of a mixture of sodium isopropylate/isopropanol (38.8 wt% isopropylate). After reaction mixture hydrolysis, the dried organic phase was analyzed by means of gas chromatography.

A gas chromatograph, type GCHF 18/3 from Giede, Berlin, GDR, with a heat-conduction cell as a detector was used. The column (3-m length) was filled with neopentyl glycolsuccinate, and hydrogen with a flow of 3 L/h (chart speed: 3600/h) served as the carrier gas.

## RESULTS AND DISCUSSION

Reaction of EVA copolymers with alcohol-containing sodium alcoholates in the melt is always accompanied by a crosslinking reaction. This is expressed by an increase in torque (Fig. 1) and a decrease of the

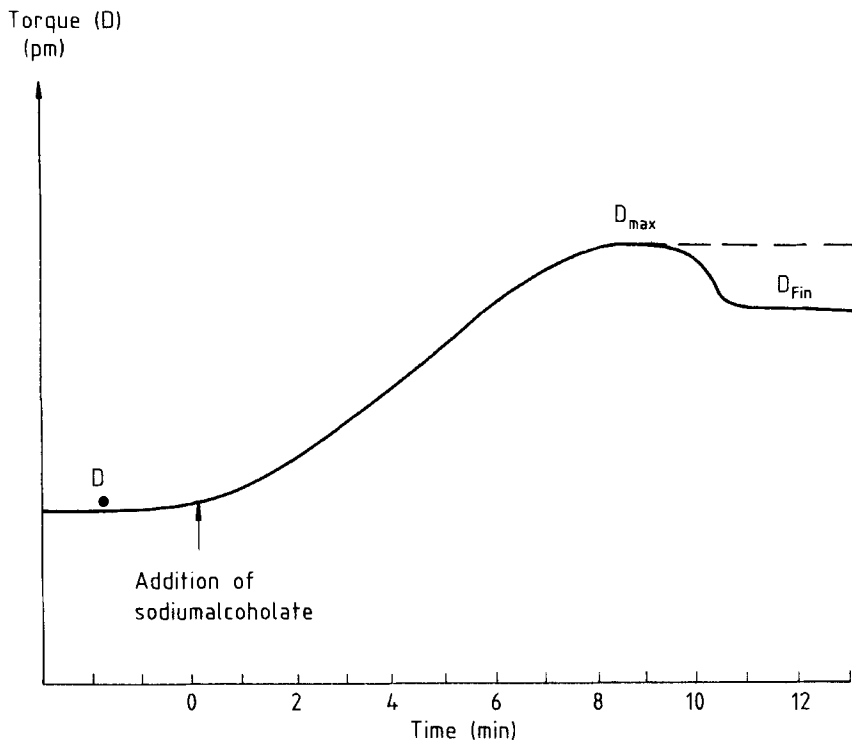


FIG. 1. Typical curve for the reaction of EVA copolymers with sodium alcoholates in the Brabender Plasticorder. pm = pound meter.

MFI correlated with it. The correlation between the concentration of the crosslinking agent and the MFI of the final product is represented in Fig. 2 for the system sodium *t*-butylate/*t*-butanol. The reaction rate can be increased, as was expected, by raising the sodium alcoholate concentration and/or the reaction temperature.

The reaction rate can also be influenced by variation of the alcohol that corresponds to the sodium alcoholate. Table 1 illustrates the influence of the alcoholate residue.

Increases in torque ( $\Delta D$ ) are found from methylate to *t*-butylate. The increase in  $\Delta D$  after 3 minutes reaction time,  $D_{3 \text{ min}}$ , is compared to the maximum torque attained  $D_{\text{max}}$ . The torque, which is an expression for the power consumption of the melt mixture, is inversely proportional to the MFI of the EVA copolymer.

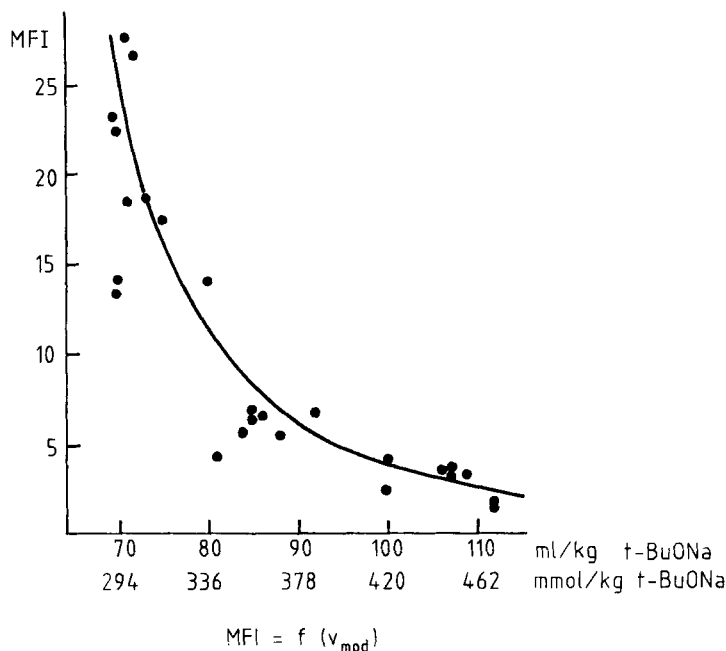


FIG. 2. Dependence of the crosslinkage state of EVA copolymer (32 wt% VAc), expressed by MFI values, on the amount of alcoholate added. Kneader case temperature: 120°C.

TABLE 1. Reaction of an EVA Copolymer (vinyl acetate content: 32 wt%) with Different Sodium Alcoholates: Increase in Torque after a Reaction Time of 3 min ( $\Delta D_{3 \text{ min}}$ ) and Maximum Torque ( $\Delta D_{\text{max}}$ ). Kneader Case Temperature: 120°C. Alcoholate Concentration:  $8.33 \times 10^{-3}$  mol/40 g copolymer

Alcoholate	$\Delta D_{3 \text{ min}},$ $N \times m$	$\Delta D_{\text{max}},$ $N \times m$	MFI = $i_{190},$ g/min
Methylate	2.26	5.59	1.86
Ethylate	8.43	11.87	1.12
Isopropylate	13.44	15.99	0.64
<i>n</i> -Butylate	20.11	29.43	0.03
<i>t</i> -Butylate	29.92	29.92	Infusible

The reactivity of the sodium alcoholates depends mainly on the basicity of the corresponding alcoholate anion. However, this influence is modified by steric effects and the different solution behaviors of the alcoholates when worked into the polymer melt.

The free alcohol content in the corresponding sodium alcoholate is of particular importance for the course of the reaction. It may decisively influence not only the rate of crosslinking but also the properties of the final products.

Figure 3 illustrates the influence of the alcohol content on the crosslinking rate by using the sodium methylate/methanol system as an example. The crosslinking agent was dosed in the solid state.

The torque reached within a reaction time of 12 minutes ( $\Delta D_{\text{Fin}}$ ) increases with rising alcohol content of the sodium methylate. Simultaneously, the rising alcohol content decreases the time needed to reach  $\Delta D_{\text{max}}$ . Hence, the rate is found to increase with rising free alcohol concentrations.

The free alcohol acts as a solvent and diluting agent, and thus promotes a homogeneous working-in of the crosslinking agent into the plastic melt. Application of alcohol-free sodium alcoholate or sodium alcoholates with a free alcohol content that does not allow complete dissolution causes the rate of the working-in process to be smaller than the one of crosslinking. Consequently, inclusions of sodium alcoholates are formed. The inclusions consist of sodium alcoholate particles surrounded by highly crosslinked copolymerizate. This effect reduces the degree of conversion and formation of a nonuniform network.

When using EVA copolymerizates with different vinyl acetate contents, the crosslinking rate increases with increasing vinyl acetate content. This dependence and influence of the basicity of the alcoholate anion on the course of crosslinking give important information concerning the reaction mechanism.

To explain the crosslinking mechanism of EVA copolymers with sodium alcoholates, a completely saponified EVA, i.e., the corresponding EVAL copolymer, was reacted, for comparison, under the same conditions. The MFIs at 190°C ( $i_{190}$ ) and the maximum torques ( $\Delta D_{\text{max}}$ ) in the Brabender Plasticorder were compared to determine their dependence on reaction temperature.

The experiments were performed with an EVA copolymer with a vinyl acetate content of 32 wt%, and the corresponding ethylene-vinyl alcohol (EVAL) copolymer formed by complete saponification. As a crosslinking agent, sodium methylate in methanol (33 wt% free methanol) was

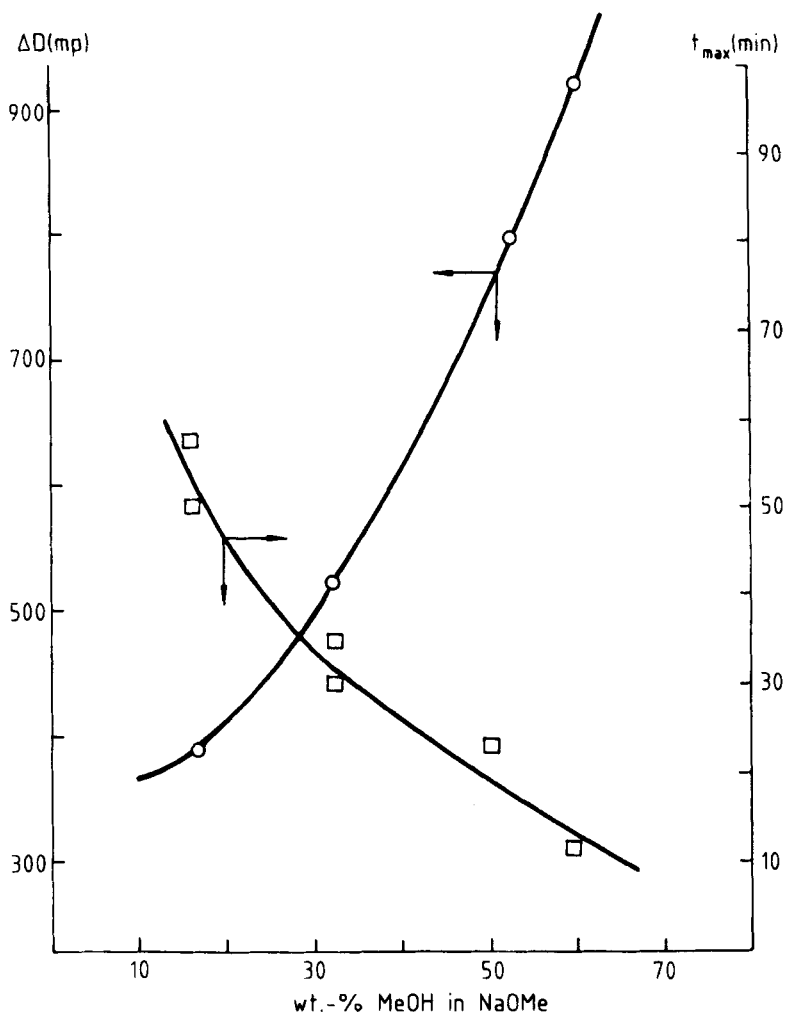


FIG. 3. Dependence of torque and time before reaching the maximum of EVA crosslinking (32 wt% VAc) on the alcohol content of sodium methylate.  $C_{NaOMe} = 1.5$  wt% (related to pure alcoholate). Kneader case temperature:  $120^{\circ}\text{C}$ .  $\Delta D$  at  $t = 12$  min ( $\Delta D_{Fin}$ ). pm = pound meter.



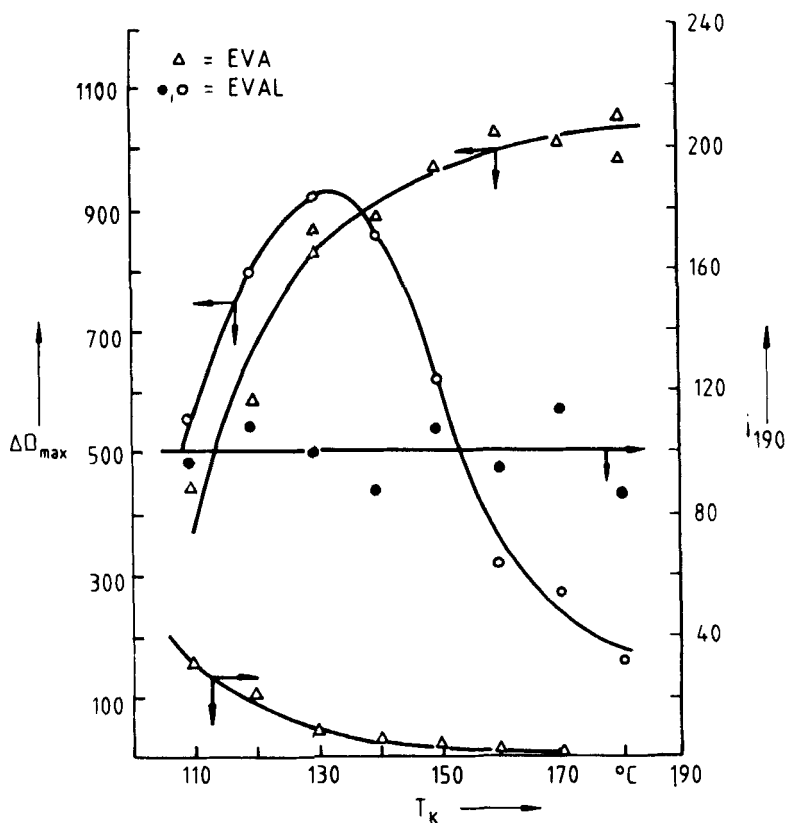


FIG. 4. Dependence of  $\Delta D_{\max}$  and the MFI on the reaction temperature in the reactions of EVA (32 wt% VAc) ( $\Delta$ ) and of the EVAL ( $\circ$ ,  $\bullet$ ) produced from it by complete saponification with sodium methylate.

used in an amount that was 1.5% of the free sodium methylate. The results are presented in Fig. 4.

While the MFIs of the reaction products of the EVA copolymer decrease with increasing kneader case temperature ( $T_k$ ), the values obtained for the reaction products of EVAL remain constant within the error limits. This indicates that irreversible crosslinking is brought about via the formation of C—C— bonds when EVA copolymers are used. The course of the torque/reaction temperature curve for the crosslinking reaction of the EVA copolymers supports this assumption. Taking into consideration the temperature dependence of  $\Delta D_{\max}$  in the reaction of

Eval with sodium methylate in methanol, the torque increase at the beginning of the reaction is due to the formation of polymer alcohol structures, and the torque decreases again above 130°C.

Obviously, the initially crosslinked structures are decomposed above 130°C. If the melt is cooled again, the torque increases slowly at first, and at 130°C it exhibits a sudden increase.

Further cooling causes a steady rise of the torque; the ascent can be described by an exponential function. If the polymer melt is heated anew, the torque-temperature plot again shows unsteadiness at 130°C. These experiments clearly demonstrate the thermal reversibility of the crosslinked products formed in the reaction of EVAL copolymers with sodium alcoholate. Comparison of this thermally reversible crosslinking reaction with that of known ionomers proves there is a thermal stability limit of the modified EVAL copolymers about 40 to 50°C lower. This allows us to conclude that alcoholate-modified EVAL copolymers are generated by the formation of thermally reversible polymer alcoholate structures with an ionogenic character.

Therefore, the decomposition temperature of the reversible part of crosslinking depends on the concentration of polymer alcoholate bonds. Figure 5 presents a comparison between the shear loss modulus of EVAL obtained from an EVA copolymer containing 23 wt% vinyl acetate and the product of the reaction of the same EVAL with sodium isopropylate. It shows a distinct shift of the  $\alpha$ -maximum from 8 to 25°C, and a shift of the  $\beta$ -maximum from -44 to -39°C. The shear storage modulus shown in Fig. 6 provides evidence that, in this case, the difference between the curves for both samples diminishes with increasing temperature, and above 100°C the curves are identical. The thermoreversible alcoholate bonds are decomposed in this temperature range. For us, the question was whether thermally reversible alcoholate structures are present in the EVA copolymer irreversibly crosslinked with alcoholates. When studying the temperature dependence of the MFI of EVA copolymerizates crosslinked with sodium methylate (synthesized under the reaction conditions mentioned in Fig. 4) and the solution viscosity of these products in paraffinic oil, our measurements showed inconsistencies in the range near 130°C which allowed us to reach conclusions concerning the presence of thermally reversible crosslinked structures.

Thus, two reactions can be found to run simultaneously when EVA copolymers are reacted with alcohol-containing sodium alcoholates in the corresponding alcohol: irreversible crosslinking and alcoholysis.

In order to find an explanation for the reaction mechanism of the irreversible crosslinking process, the reaction of the low-molecular

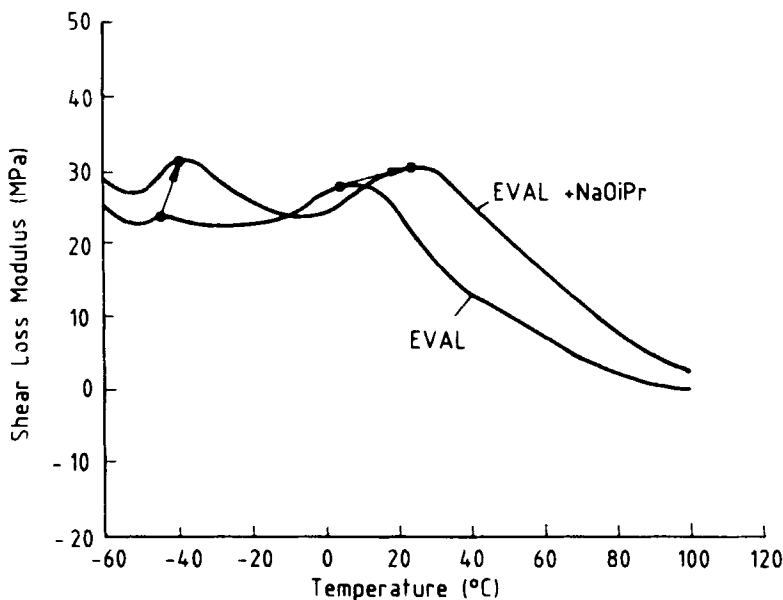


FIG. 5. Comparison between the shear loss modulus of EVAL and the reaction product of the same EVAL with sodium isopropylate EVAL from EVA (23 wt% VAc).

weight model substance for EVA, pentanol-3-acetate, with alcohol-containing sodium alcoholates was investigated. The model substance was reacted with sodium isopropylate in isopropanol, and the reaction mixture was subsequently hydrolyzed with water. Gas chromatographic analysis served to identify the cleavage products: isopropanol, pentanol-(3), acetic acid isopropyl ester, and a mixture of high-boiling reaction products. Free acetic acid was not detected. More pentanol-(3) than acetic acid isopropyl ester was found in all experiments, i.e., alcoholysis (transesterification) must be accompanied by another reaction that consumes pentanol-3-acetate and produces pentanol-(3). Traces of pentanol-(3) acetoacetic ester were detected.

The irreversible crosslinking reaction is described by a Claisen ester condensation mechanism (Scheme 1). First an ester enolate (4a, 4b) and a low-molecular weight alcohol (AOH) are formed (3). The polarization of the carbonyl group is intensified by coordination of a further carbonyl group of the same or a second EVA copolymer molecule to the sodium

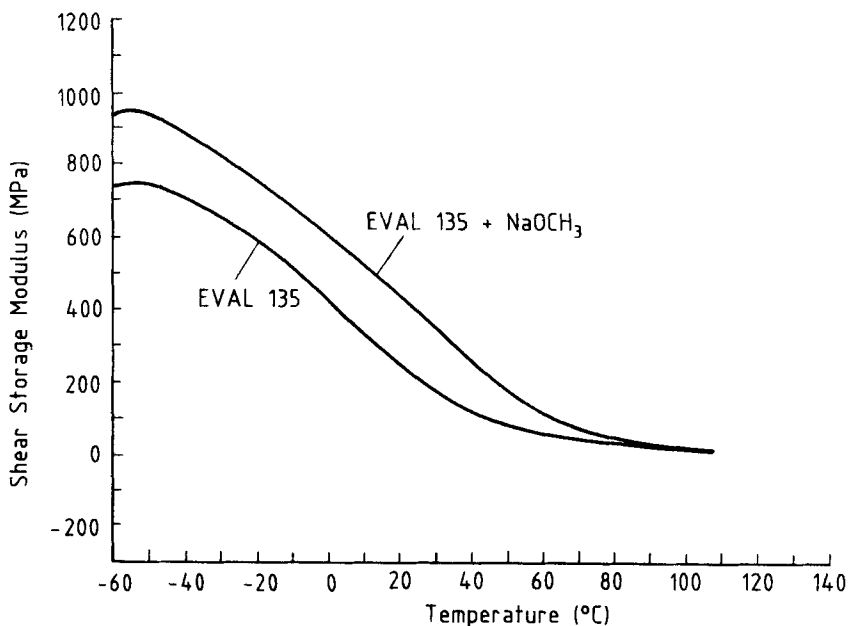


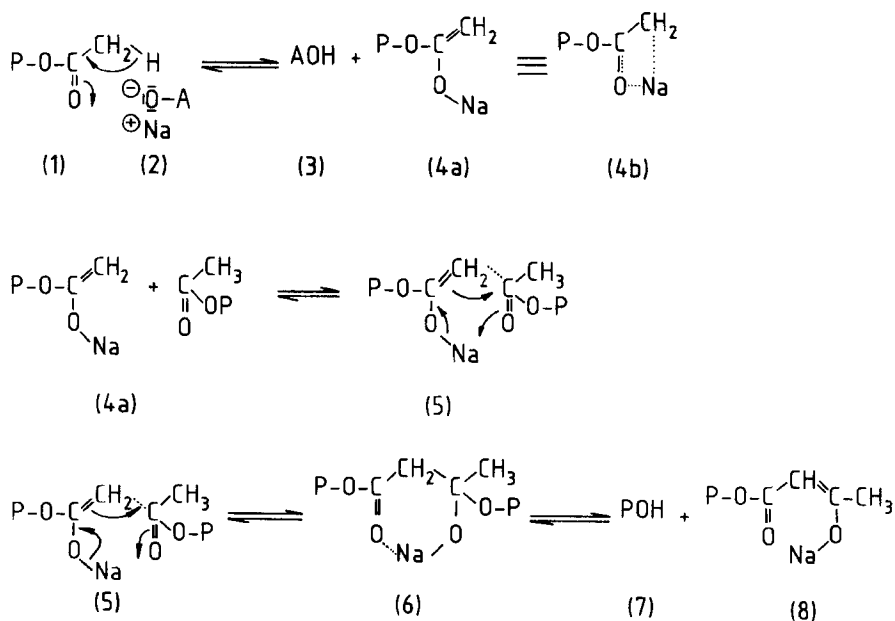
FIG. 6. Comparison between the shear storage modulus of EVAL and of the reaction product of the same EVAL with sodium methyleate. EVAL as in Fig. 5.

cation. The other electron transitions run via a cyclic complex (5); a conjugated unsaturated system (8) is formed by splitting off a POH molecule (7). The energy of the complex is relatively low.

Since crosslinking of EVA copolymers is found, the analogous polymer reaction must quickly occur in the melt and the POH (7) produced is not removed from the reaction mixture, preferential formation of the reaction product is concluded (6). This mechanism is also supported by the increase in the crosslinking rate with increasing vinyl acetate content of the copolymer. In addition, the highest crosslinking rates are obtained for the sodium *t*-butylate/*t*-butanol system.

## CONCLUSION

When EVA copolymers are reacted with NaOR in the corresponding alcohol, two reactions compete in the polymer melt: 1) a crosslinking reaction with the formation of C—C bonds, and 2) alcoholysis with the



A = isopropyl; P = pentyl-3-

SCHEME 1.

formation of EVAL units. In a subsequent reaction, the OH groups formed can be converted to alcoholate groups.

Comparisons of the reactions of EVA copolymers, EVAL copolymers, and pentanol-3-acetate as a model substance lead us to the following crosslinking reaction mechanism:

1. Incomplete Claisen ester condensation gives rise to covalent crosslinking bonds. The rate of this crosslinking reaction depends on the vinyl acetate content of the EVA copolymer used, on the concentration and basicity of the sodium alcoholate used, on the free alcohol content of the respective sodium alcoholate, and on the reaction temperature.
2. In addition to covalent crosslinking bonds, thermally reversible crosslinking has also been found. They are due to the existence of polymer alcoholate structures.

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