

The Conversion of Ethylene-Vinyl Acetate Copolymers with Aluminum Alcoholates

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Synopsis

If ethylene-vinyl acetate copolymers are converted with aluminum alcoholates, cross-linked products will form. This reaction was studied on the basis of the viscosity variation and the amount of acetic acid ester formed. The constants of the reaction velocity for the conversion with various aluminum alcoholates were determined and a reaction mechanism is discussed.

INTRODUCTION

The hardening of high polymeric materials becomes more and more important at the present moment. It is one of the methods to obtain new properties for plastic materials. We took ethylene-vinyl acetate copolymers (EVAC) and examined the well-known method of radically initiated crosslinking with and without activators by re-alcoholization with aluminum alcoholates. The re-alcoholization reaction is often applied in organic chemistry for the production of difficult accessible alcoholates. In this case the equilibrium reaction follows a velocity law of second order.¹⁻³ The kinetics of such reactions have not been investigated on polymeric esters. At present, only a few patents are known which deal with the crosslinking of various polymers with alcoholates of multivalent metals.⁴⁻⁷ It was the object of our work for this reason to investigate the re-alcoholization of aluminum alcoholates $\text{Al}(\text{OR})_3$ with ECAV. The reaction rate within the temperature range of 100° to 135°C at concentrations of 0.022 to 0.7 mole/l. $\text{Al}(\text{OR})_3$ with 0.186 mole/l. EVAC* in xylene, referred to vinyl acetate, was proved by changes in viscosity during the reaction.

EXPERIMENTAL

A Höppler viscometer was used to determine the changes in viscosity. The falling ball time, plotted against the reaction time, resulted in curves which at first show a gradual, but later a steep, increase in viscosity due to increasing gel formation.

* EVAC with 34% vinyl acetate, melt flow index, $\dot{v}_{2.16} = 140$ g/10 min at 190°C, $\rho = 0.949$ g/cm³, inherent viscosity = 500 cm³/g.

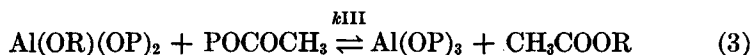
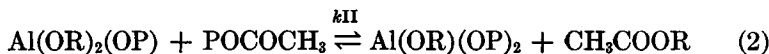
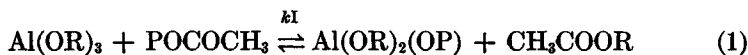
The reaction time from the beginning of the reaction until reaching a ball falling time of 55 sec (in a fall tube with a diameter of 15.9 mm and a glass ball with a diameter of 15.6 mm and a specific weight of $\rho = 2.423 \text{ g/cm}^3$) is defined as the gel time.

The reaction rate was also measured in parallel to this by determining the very volatile acetic acid ester.

The conversion was carried out in an Erlenmeyer flask, and the non-converted and newly formed aluminum alcoholate was destroyed after certain intervals of time by adding water. The volatile acetic acid ester was subsequently azeotropically distilled off with isopropanol and determined by saponification with KOH.

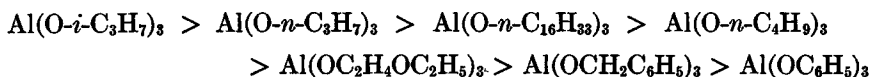
RESULTS AND DISCUSSION

The re-alcoholization of aluminum alcoholates, Al(OR)_3 , with EVAC extends over several reaction stages:



where P = polymers.

The first stage of the reaction does not increase the viscosity, while the second and third stages, i.e., the conversion of the second or third alcoholate, group, will lead to crosslinking and thus to an increase in viscosity. The first reaction stage is included, however, in the determination of the formed ester. Investigations showed that the velocity of the re-alcoholization in the stage



is reduced in the case of the elementary aluminum alcoholates Al(OR)_3 . This can be observed from the gelling periods and the velocities of the ester formation reaction. It is supposed that these relations are caused by the different electrophilic character of the residual alcoholates.

The gelling periods are for this reason plotted in Figure 1 against the Taft σ^* -values of the polarizability of the alcohol on which the alcoholate is based. Figure 1 and Table I show that the gelling periods increase with increasing σ^* -values whereby the $\text{Al(OC}_6\text{H}_5)_3$, which has the highest σ^* -value of this group, does not effect any increase of viscosity in the melt, even at temperatures of 200°C . An exception in this case is $\text{Al(O-}t\text{-C}_4\text{H}_9)_3$, which, in accordance with Table I should display the shortest period of gelling but does not enter any reaction with the polymers. The reason for this may be steric which is indicated by the influences of the *t*-butyl group

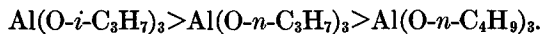
TABLE I
Dependency on Gelling Time (G) of Various Aluminum Alcoholates $\text{Al}(\text{OR})_3$ from
Polarizability at 120°C

R	G , min	σ^* ROH ^a
<i>t</i> -Butyl	No reaction	-0.3
Isopropyl	7	-0.19
Propyl	10	-0.115
Butyl	17	-0.13
Ethoxyethyl	177	
Benzyl	412	+0.22
Phenyl	No reaction	+0.6

^a Values from Taft.¹¹

in $\text{Al}(\text{O}-t\text{-C}_4\text{H}_9)_3$, which is present as the dimer,⁸ whereas the aluminum alcoholates are otherwise present as trimeric and tetrameric compounds. The polarity of the polymer alcohol residue has also to be taken into account when considering the polar influences.

The reaction velocity of the acetic acid ester formed corresponds with the velocity law of second order (Fig. 2). The reaction velocity constants decrease in the case of elementary alcoholates $\text{Al}(\text{OR})_3$ and in correspondence with the results obtained with the viscosity investigations in the order of



This indicates that the re-alcoholization velocity of alcoholates $\text{Al}(\text{OR})_3$ with EVAC decreases with increasing electrophilic character of the alcohol groups of the aluminum alcoholate. The first step for the conversion of aluminum alcoholate with EVAC is as follows (Fig. 4, eq. (1)):

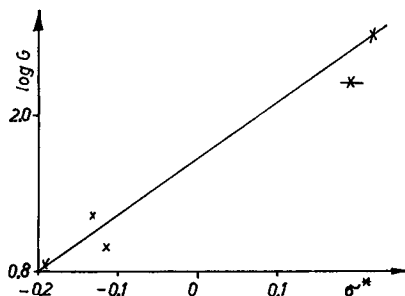


Fig. 1. Log gelling time versus Taft's σ^* -values of alcohols on which the alcoholates shown in Table I are based.

An aluminum alcoholate is added to the carboxyl oxygen of the polymer, and simultaneously the carboxyl group is polarized. The more electronegative the aluminum due to the electrophilic character of the alcoholate group, the easier should be the run of the reaction. This stage cannot be rate determining, since this is not the case here. The reaction rates also

decrease as the electronegativity of the aluminum is lowered by a higher electrophilic alcoholate group and gradual replacement of the isopropylate groups in $\text{Al}(\text{O}-i\text{-C}_2\text{H}_7)_3$.

The above illustrated dependence is thus confirmed again. The increase in viscosity within the duration of the reaction with gradual replacement of isopropylate groups by ethoxyethylate groups at 110°C is illustrated in Figure 3. The curves show that the increase in viscosity is clearly slowed down within the replacement of the isopropylate groups at the aluminum by ethoxyethylate groups. The gas-chromatographic analysis of the formed acetic acid esters proved also that predominantly formation of the ester of the less electrophilic isopropanol occurred.

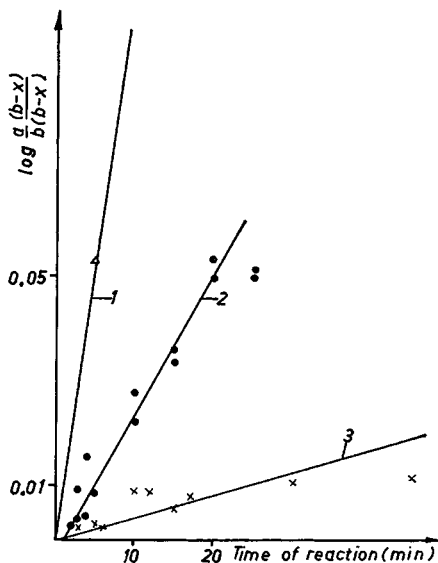


Fig. 2. Dependence on the gelling periods of various $\text{Al}(\text{OR})_3$ from polarizability at 120°C . $\text{EVAC} = 0.186$ mole/l.; $\text{Al}(\text{OR})_3 = 0.3$ mole/l. 1 = $\text{Al}(\text{O}-i\text{-C}_2\text{H}_7)_3$; 2 = $\text{Al}(\text{O}-n\text{-C}_3\text{H}_7)_3$; 3 = $\text{Al}(\text{O}-n\text{-C}_4\text{H}_9)_3$.

If the first stage of reaction is not the determining factor of the reaction rate, then it stands to reason that the rearrangement has to be the velocity-determining stage. Possibilities (2a) and (2b) in Figure 4 apply in this case, which differ inasmuch as on the one hand the positively polarized carboxyl carbon coordinates with an alcoholate group of the added aluminum alcoholate under simultaneous addition of the polymer residue to the aluminum and, on the other hand, that this addition is effected by a second aluminum alcoholate, (2b). The reaction stage (2b) is more probable, since the reaction is in this case of second order. If this reaction stage is velocity determining, then it agrees with the changed electronegative behavior of the aluminum on the basis of the different electrophilic character of the alcohol groups.

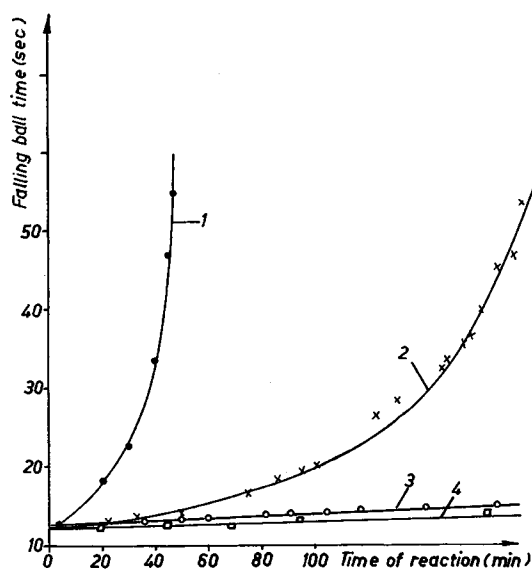


Fig. 3. Dependence on viscosity increase due to duration of reaction during conversion of 0.044 mole/l. alcoholates with 0.186 mole/l. EVAC at 110°C in xylene. 1 = Al(O-*i*-C₃H₇)₃; 2 = Al(O-*i*-C₃H₇)₂OCH₂CH₂OCH₂CH₃; 3 = Al(O-*i*-C₃H₇)(OCH₂CH₂OCH₂CH₃)₂; 4 = Al(OCH₂CH₂OCH₂CH₃)₃.

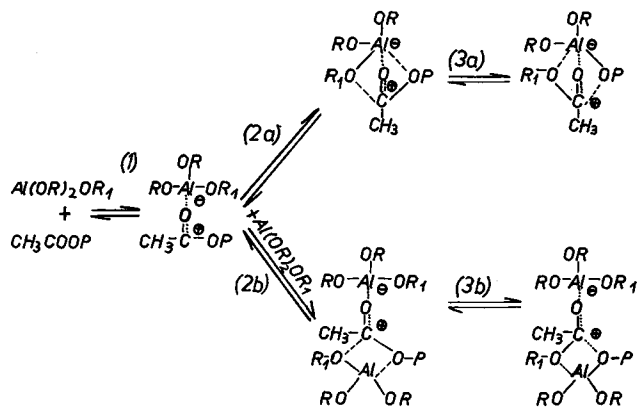


Fig. 4.

In the subsequent third stage, exchange of the alcoholate groups occurs, whereby the less electrophilic polymer alcohol is bound to the more electrophilic aluminum. The anomaly at Al(O-*t*-C₄H₉)₃ can be explained by the steric effect or by the fact that the *t*-butyl alcohol is less electrophilic than the polymer alcohol, assuming that its electrophilic character is that of a secondary alcohol. The less electrophilic *t*-butyl alcohol would have to be replaced by the more electrophilic polymer alcohol, which is not to be expected, however.

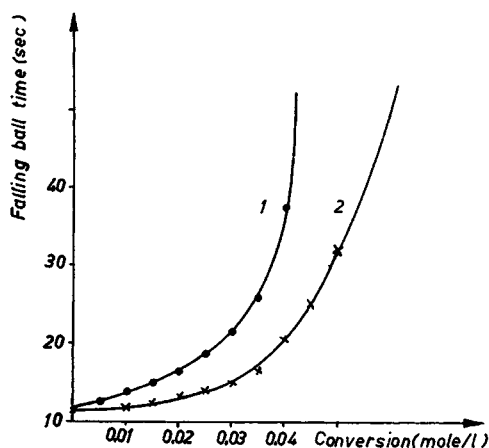


Fig. 5. Dependence on the falling ball time from the conversion at 0.3 mole $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3$ at 120°C in xylene. 1 = $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_2(\text{OC}_6\text{H}_5)$; 2 = $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3$.

Of special interest is once again the question if either all three alcohol groups are participating in the re-alcoholization reaction or the reaction is only proceeding up to the second alcoholate group.

As has been mentioned already, various partial steps of crosslinking were covered by the two methods used in tracing the increase of viscosity and determining the ester formed in the reaction. Since the third reaction stage should influence the increase of viscosity more than the conversion, the increase in viscosity in the conversion with alcoholates having only two reactive alcoholate groups should be, on the other hand, slower than in the case of three reactive alcoholate groups, if the reaction of the third alcoholate group is important. Conversion viscosity observations have for this reason been employed with regard to $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3$ and $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_2(\text{OC}_6\text{H}_5)$ (Fig. 5). No significant differences were observed.

It follows that the reaction of the third alcoholate group is not or only little important for crosslinking and has no influence on the increase of viscosity. (Owing to the steric conditions resulting from the reaction of the aluminum alcoholate with the polymer, this can also not be expected, as the probability that the third alcoholate group will react with an additional polymer is much less than the probability that it reacts with an acetate group of the polymer which has already been attached to the aluminum. On the other hand, it could be proved that in the reaction of $\text{Al}(\text{O}-i\text{-Pr})_3$ with EVAC with 34% of vinyl acetate, a maximum of 56% of the alcoholate groups will be converted.¹³

If one compares the reaction rates of mixed alcoholates $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_2(\text{OR})$, i.e., of such alcoholates in which the isopropylate group has been replaced by a different alcohol group, we will find, as shown in Table II, that the constant of the reaction velocity is decreasing in the order *i*-propylate > benzylate > ethoxy ethylate > phenolate. It is remarkable in this case that the $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_2(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)$ is not placed in front of

TABLE II
Dependence of Reaction Velocities of Various $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_2\text{OR}$ with 0.186m EVAC
at 125°C in Xylene on σ^* -Values and Relative Acidities

ROH	Alcoholate, mole/l.	k_2 , mole/sec	σ^* ^a	Rel. acidity ^b
Isopropanol	0.233	3.84×10^{-3}	-0.19	0.076
Benzyl alcohol	0.7	3.36×10^{-4}	+0.22	2.1
Ethoxyethanol	0.7	1.58×10^{-4}	<+0.22 ^c	12.0
Phenol	0.7	5.06×10^{-4}	+0.60	

^a From Taft.¹¹

^b From Hine and Hine.¹²

^c Value is derived from the values of compounds having one CH_2 group less.

$\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_2$ ($\text{OCH}_2\text{C}_6\text{H}_5$), although $\text{Al}(\text{OCH}_2\text{C}_6\text{H}_5)_3$ reacts more slowly with the polymers than $\text{Al}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$. A comparison of the Taft σ^* values of the polarizability with the relative acidities of various alcohols shows that both these alcohols are also exchanged here against one another. The acidity of the alcohols on which the alcoholates are based influences apparently the electronegativity of the aluminum, while the polarizability of the reacting alcoholate group determines its reaction velocity. The influence of the polarizability of the reacting groups is predominant in accordance with the values of the gelling periods of the elementary alcoholates $\text{Al}(\text{OR})_3$.

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Received March 17, 1970

Revised August 25, 1970