Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Study of the Alcoholysis of Ethylene-Vinyl Acetate Copolymers with Butanol-1 in the Extrusion Process

A. Hesse[a]; M. Rätzsch[a]
[a] Department of Research and Development, PCD Polymere Gesellschaft m.b.H., Linz, Austria

To cite this Article Hesse, A. and Rätzsch, M.(1994) 'Study of the Alcoholysis of Ethylene-Vinyl Acetate Copolymers with Butanol-1 in the Extrusion Process', Journal of Macromolecular Science, Part A, 31: 10, 1425 — 1445
To link to this Article: DOI: 10.1080/10601329409350101
URL: http://dx.doi.org/10.1080/10601329409350101

J.M.S.—PURE APPL. CHEM., A31(10), pp. 1425–1445 (1994)

STUDY OF THE ALCOHOLYSIS OF ETHYLENE–VINYL ACETATE COPOLYMERS WITH BUTANOL-1 IN THE EXTRUSION PROCESS

A. HESSE and M. RÄTZSCH

Department of Research and Development
PCD Polymere Gesellschaft m.b.H.
St.-Peter-Strasse 25, A-4021 Linz, Austria

ABSTRACT

We studied the alcoholysis of different ethylene–vinyl acetate products with octanol (OcOH) and butanol (BuOH). Sodium methanolate was used as a very powerful catalyst for this reaction. The experiments were carried out in a twin screw extruder with a specially designed reaction zone. The influence of catalyst quantity on conversion yield was investigated for different levels of added alcohol. Both the EVA/BuOH and EVA/OcOH systems showed a similar reaction behavior. Increasing the catalyst concentration accelerated transesterification so much that the equilibrium state could be achieved during the residence time in the extruder. Equilibrium conversions were determined from the starting molar ratio ROH/VA over a broad range, and the equilibrium constants of alcoholysis were calculated: K(EVA/BuOH) = 2.35 and K(EVA/OcOH) = 2.18. We tried to evaluate the experimental data kinetically by using an integrated rate equation derived from the general reaction scheme, including the catalyst concentration. The equation provides a homogeneous reaction system. In the case of EVA/BuOH, a good accommodation of the model curves was reached with the rate constants $k_1 = 20.2$ and $k_{-1} = 8.0\ \mathrm{L^2 \cdot mol^{-2} \cdot min^{-1}}$. It is possible to produce defined modification products with desired compositions over a large range by alcoholysis of EVA with BuOH during extrusion.

INTRODUCTION

The production of polyvinyl alcohol and ethylene-vinyl alcohol copolymers (EVAL) is technically important because of their material properties and their barrier property toward oxygen.

Vinyl alcohol, $CH_2{=}CH{-}OH$, is the simplest unsaturated alcohol. It does not exist as a monomer; only in its energy poor, tautomeric shape as the acetaldehyde:

For this reason a direct synthesis of vinyl alcohol polymers by polymerization is not possible. Therefore, these polymers are produced in a roundabout way by polymerization of the carboxylic acid vinyl ester monomers (especially vinyl acetate) and following with transformation of the vinyl ester groups into the wanted vinyl alcohol units by polymer analogous reactions.

We first describe the state of knowledge and our own research on the alcoholysis of ethylene-vinyl acetate copolymers (EVA) in the melt.The kinetics and efficiency of analogous polymer conversions in the extruder are discussed, especially the influence of chain length of the *n*-alcohols used on solubility behavior.

REACTIONS OF THE ACETOXY-HYDROXIDE TRANSFORMATION WITH EVA COPOLYMERS

Based on low molecular weight organic chemistry, there are three possible methods of the acetoxy-hydroxide transformation:

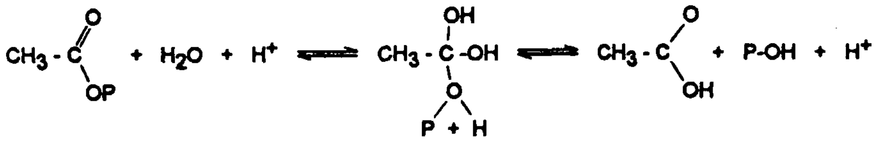
1. Hydrolysis
2. Alcoholysis (transesterification)
3. Aminolysis/ammonolysis

Both ammonolysis and aminolysis of PVAc have not reached technical significance, and the same can be said of EVA copolymers. The existing publications about acetoxy-hydroxide transformation only deal with hydrolysis or alcoholysis.

Hydrolysis

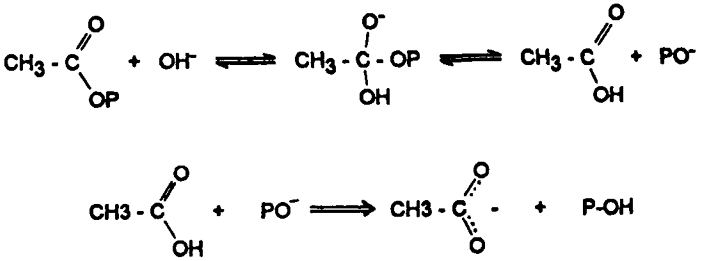
Hydrolysis is the reaction of an ester with water. Generally this reaction runs slowly, even with heat. However, esters are quickly saponified in the presence of strong acids or bases.

Acid-Catalyzed Hydrolysis



P - polymer chain

Base-Catalyzed Hydrolysis (saponification)



Acid-catalyzed hydrolysis is a typical equilibrium reaction which only provides high conversion when there is a large surplus of water.

Base-catalyzed hydrolysis is a nonequilibrium reaction because the last reaction step, the formation of the acetate anion, is irreversible. The added alkaline or earth alkaline hydroxide, which acts as a "catalyst," is consumed during saponification. Complete conversion can be reached after sufficient reaction time and with at least a molar quantity of hydroxide. Saponifications of carboxylic acid esters run faster than acid-catalyzed hydrolysis because the hydroxide ions act with stronger nucleophilicity and have smaller dimensions compared to water. Another advantage of the saponification reaction with hydroxide ions is the noncorrosive effect compared to the strong acids used in acid-catalyzed hydrolysis, and which therefore require special plant equipment.

Because of these technical advantages, our investigations focused on alkaline saponification.

Sakurada [1] carried out the alkaline hydrolysis of polyvinyl acetate in methanol or ethanol, and sometimes with the addition of water at low temperatures. The time-conversion dependence shows an autocatalytic behavior which can be described with a modified second-order kinetic equation:

$$dx/dt = k_0[1 + m(x/a)](a - x)(b - x)$$

where k_0 = starting rate constant
m = autocatalytic effect factor
a = starting VA concentration
b = starting NaOH concentration

The reason for autocatalytic acceleration is apparently a neighboring group effect. Hydroxyl groups in the neighborhood of an acetoxy group increase the hydrolysis.

In contrast, Sliwka [2] explained the autocatalytic behavior of PVAc saponification by steric effects (accessibility of ester groups). At the beginning, the few VA groups outside of the polymer coil react. After diffusion of hydroxide ions, more and more ester groups inside the polymer coil are converted. The following kinetic equation is proposed:

$$-da/dt = kab(1 - D_i/D_o)$$

where D_o = diameter of a spherical polymer coil
D_i = diameter of an inner sphere of polymer coil that does not participate in the reaction
a = VA concentration
b = NaOH concentration

The work of Brandsch [3] showed that the hydroxide ions have entering rates into the EVA copolymer which depend on their concentration. Because of their limited mobility, an inhomogeneous distribution of the hydrolysis product arises. The mixing conditions exert a decisive influence.

Fonseca and coworkers [4] analyzed the kinetic aspects of the acetoxy–hydroxide transformation for EVA copolymers, including the influence of steric and neighboring group effects on the rate of this transformation. It was found that in the conversion of PVA with sodium hydroxide in methanol by alkaline saponification, alcoholysis also proceeds. The reason is the equilibrium reaction

$$OH^- + CH_3OH \rightleftharpoons CH_3O^- + H_2O$$

whereby the methanolate formed catalyzes the transesterification. Water in the reaction system suppresses the alcoholysis.

Rätzsch and Crell [5] studied the alkaline saponification of EVA copolymers in solution. All time–conversion dependencies reported upon the addition of inert EVA solvents show no autocatalytic behavior and follow a second-order kinetic equation. The calculated rate constants of the saponification differ from each other. This is due to the influence of the nature of the solvents. There is no correlation to the Hildebrand solubility parameter or the E_T value of the solvents. Furthermore, it was found that at different chemical compositions of the initial EVA, the saponification rate constant stays almost the same.

Koopmans and colleagues [6] also investigated the saponification of EVA copolymers in a homogeneous phase. The decrease of VA percentage was found to depend on the reaction time. The time–conversion curves were also described by a second-order equation. However, the constancy of the rate parameters for different EVA types and various concentration ratios could not be proved. The reason for this anomaly is complex. Gas chromatographic examinations showed that methyl acetate is produced in the reaction system. This occurs by alcoholysis, as already discovered during PVA saponification.

Further investigations [7] showed that the contribution of alcoholysis to total conversion depends on the type and quantity of alcohol and the KOH concentration. The formation of the alcoholate which catalyzes alcoholysis is of decisive importance.

The equilibrium constant of the reaction

$$OH^- + ROH \rightleftharpoons RO^- + H_2O$$

is 4.5 for methanol, 0.65 for ethanol, and 0.043 for isopropanol [8].

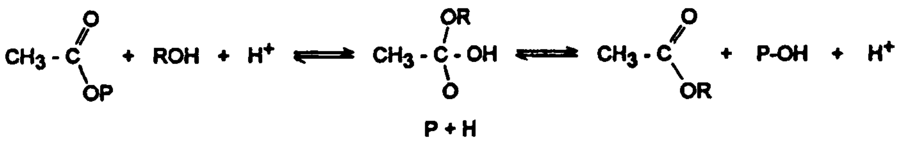
By the use of methanol as a hydroxide solvent, a relative amount of alcoholate is created, but relatively few alcoholates are created when higher molecular weight alcohols are used. This has an automatic effect on the extent of alcoholysis. Thus, alcoholysis and homogeneous alkaline saponification take place simultaneously if there is any alcohol in the reaction mixture. The result is a very complex reaction whose description can only be characterized with a second-order rate equation.

There are other reasons for the considerable differences in the saponification rate with different EVA types. In another publication [9], Koopmans and colleagues explained the increase of the saponification rate constants with growing VA content of the EVA used by an increase in the number of neighboring VA units. These VA units are better able to reach the hydroxide ions because of reduced steric hindrance and increasing polarity. The main consequence is the creation of VAL groups nearby and as a few isolated units. The steric hindrance is seen as the screening of VA groups by ethylene sequences. This grows with increasing ethylene content in the EVA.

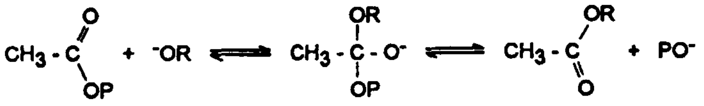
Alcoholysis

During alcoholysis of a carboxylic acid ester, one alcohol is replaced by another. This transesterification of the alcohol component is also catalyzed by acids or bases and is a typical equilibrium reaction.

Acid Catalysis, Mechanism Analogous to Hydrolysis



Base Catalysis by Alcoholate Anions



(1)

$$PO^- + ROH \rightleftharpoons RO^- + P\text{-}OH \qquad (2)$$

The reaction rate is influenced by the steric constitution of the reagents. The growing amount of space filled by the alkyl group in the ester and in the alcohol leads to a decrease of the transesterification rate.

In the case of hydrolysis, base catalysis causes a considerably higher reaction rate than does acid catalysis. Therefore, its use predominates in PVAc and EVA alcoholysis. To continue transesterification according to Eq. (1), it is important to use alcohols with a higher acidity in comparison to the polymer-bound alcohol. Therefore, the re-formation of alcoholate ions by equilibrium reaction (2) is favored.

Besides strong organic and inorganic acids and alkali metal alcoholates, many other transesterification catalysts (such as salts, oxides, metals, metal organic compounds, and organic nitrogen bases) have become well-known from the polyester synthesis according to a summary given in References 10 and 11. Acetates of the metals Zn, Mn, Pb, Ce, Co, and Cd have gained special importance as transesterification catalysts. Titanium alcoholates also show a high efficiency.

Organic tin compounds are used in a Bayer patent [12] as high activity transesterification catalysts in the temperature range from 100 to 180°C for the alcoholysis of polyvinyl esters or vinyl ester copolymers. The required quantity of catalyst is between 0.1 and 1 percent by weight of the polymer. The efficiency of the catalyst depends on the molecular structure. Some of the most active catalysts are dialkyltin oxides. Organotin compounds have the advantage of stability against humidity compared to common alkali alcoholates.

A few articles on alcoholysis have been published. Lambla and colleagues published the results of their investigations concerning the transesterification of EVA copolymers at temperatures of 150 and 190°C [13-15]. Their results involved discontinuous experiments on EVA modification in a kneader (Haake-Plasti-Corder) with the primary alcohol octanol-1 and sodium methanolate or dibutyltin dilaurate. With sodium methanolate the transesterification goes on so fast that the equilibrium state of the reaction is reached within a few minutes. Equilibrium of the alcoholysis could also be achieved in a continuous experiment involving a modification in a twin-screw extruder (ZSK 30) and a residence time of ~80 seconds. However, the catalyst quantity required [more than 1% sodium methanolate by weight of the polymer (EVA with 14 wt% VA)] is considerable.

The authors also refer to the high sensitivity of sodium methanolate to water. Saponification is a side reaction of transesterification if water is present in the reaction system. This side reaction contributed to an additional conversion of 5 to 10%.

Experiments to estimate the reactivities of different alcohols have also been carried out. EVA was converted in an equimolar OH:VA ratio under the same experimental conditions in a kneader with some aliphatic *n*-alcohols, OH-terminated diols with a carbon chain of growing length, as well as with sorbitol as a polyol. Aliphatic alcohols with long alkyl chains (C_8, C_{12}, and C_{16}) reached maximum conversion because they are miscible or compatible. By studying the diffusion of *n*-alcohols in EVA it was concluded that at 170°C the alcohols are soluble in the EVA melt, indicating a homogeneous system as well.

Reaction kinetics was studied in EVA/OcOH with dibutyltin dilaurate as the catalyst using a plasticorder. Alcoholysis with this catalyst proceeds more slowly than with sodium methanolate. Figure 1 shows the time-conversion curve for this system.

From the general reaction scheme of the proceeding reversible transesterification,

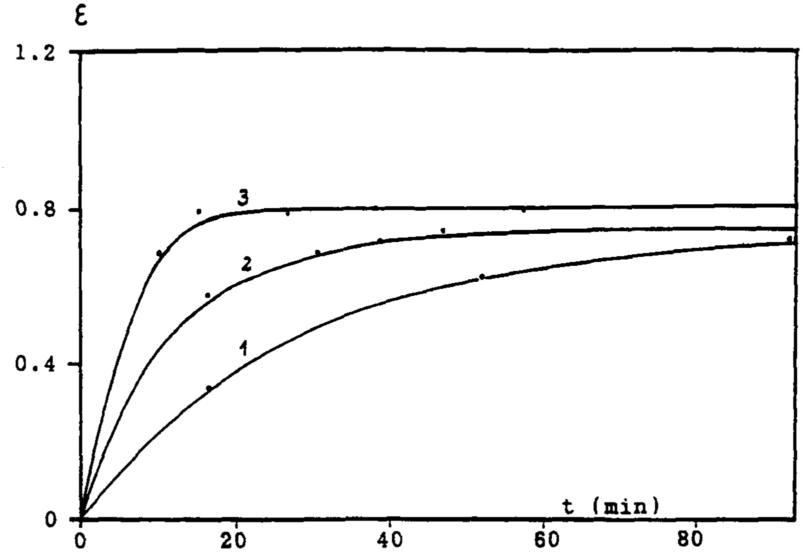


FIG. 1. Presentation of ε vs time *t* for the reaction system EVA (14 wt% VA)/OcOH/DLBDE with 100/21.3/3 by weight in the Plastograph RHEOCORD HAAKE-EC. Temperature: (1) = 150, (2) = 170; (3) = 190°C. (●) Experimental data, (—) calculated curves.

$$\text{A (VAc)} + \text{B (OcOH)} \rightleftharpoons \text{C (VOH)} + \text{D (OcAc)}$$

a second-order rate equation was derived:

$$-dNA/dt = k_1C_AC_B - k_{-1}C_CC_D$$

or

$$d\varepsilon/dt = k_1(a - \varepsilon)(b - \varepsilon) - k_{-1}\varepsilon^2$$

Integration results in

$$\frac{1}{X_1 - X_2} \ln \frac{X_2(X_1 - \varepsilon)}{X_1(X_2 - \varepsilon)} = (k_1 - k_{-1})t$$

where X_1 and X_2 are $\varepsilon^2 - (a + b)m\varepsilon + mab$ and $m = k_1/(k_1 - k_{-1})$, respectively.

By means of the experimental values, the parameters of this equation, the rate constants k_1 and k_{-1}, were determined by numerical calculation. From Fig. 1 it is obvious that the basic kinetic model, which requires a homogeneous reaction system, describes the experiments very well.

We note that the catalyst influence is not considered in the rate equation. The calculated values of the rate constants are only valid for the discrete catalyst concentrations at which the experiments were carried out.

The degree of equilibrium conversions for different starting concentration ratios of octanol/vinyl acetate groups were determined to confirm the validity of the kinetic model as well as the constants. The equilibrium constant for the EVA/OcOH system is $K = 2.4$, which is in very good agreement with calculations based on the rate constants k_1 and k_2.

By means of the research of Lambla and his colleagues, it was proved that it is possible to achieve transesterification of EVA copolymers in the extruder to maximum conversion, i.e., until equilibrium is reached. Furthermore, the attainable limit is given by the determined equilibrium curve. This is valid for EVA-compatible long-chain aliphatic *n*-alcohols as reagents (C number > 6, particularly octanol). Unfortunately, they are not very useful for EVA modification on a technical scale because:

1. Large quantities will be necessary to reach high alcoholysis degrees due to their high molecular weight.
2. They and their acetates are not very volatile, so their separation from EVA-modified product is complicated.
3. Their price is relatively high.

SOLUBILITY OF THE REACTION PARTNERS

Analysis of results from the literature can be summarized in one statement: The efficiency of an alcoholysis method of EVA to EVAL is only given when using short-chain alcohols, but the low solubility of short-chain alcohols in an EVA melt does not permit such a method to be used.

Statements about solubility can be made by using solubility parameters. Accordingly, a liquid is a solvent for a given polymer if the solubility parameters are equal or differ little from each other. The maximum difference of the solubility parameters $|\delta_{\mathrm{Lm}} - \delta_{\mathrm{p}}|$ for which solubility can be predicted is [16]:

$$|\delta_{\mathrm{s}} - \delta_{\mathrm{p}}| = \chi RT/V_{\mathrm{s}} = 3.5 \times 10^3\ \mathrm{J}^{1/2}\cdot\mathrm{m}^{-3/2}$$

where $\chi = 0.5$, correlation parameter for polymer molecules with an infinite molecular weight on the phase surface
$V_{\mathrm{s}} = 100\ \mathrm{cm}^3$, assumed molecular volume of the solvent
$T = 293\ \mathrm{K}$

This value is an approximation for real systems.

In Reference 17 a range from 1.6 to 6.9 × $10^3\ \mathrm{J}^{1/2}\cdot\mathrm{m}^{-3/2}$ is proposed for this maximum difference. Solubility parameters for different polymers and solvents are listed in Table 1.

The third column contains the solubility parameter difference between the alcohols and the EVA used by us with an average VA content of 25 wt%. It can be seen that long-chain alcohols with more than 4 carbon atoms are capable of dissolving EVA. With butanol the maximum difference will be reached or even exceeded, so that no solubility can be expected. For alcohols with less than 4 carbon atoms there are no solvents for EVA copolymers.

These standards cannot be applied to our reaction conditions. The relatively small molecular weight of the EVA copolymers, the small molecular volume of the short-chain alcohols, and the very high reaction temperature at isochoric conditions in the extruder promote solubility. In addition, there is the chemical reaction which changes the polymer as well as the "solvent" and improves compatibility.

TABLE 1. Solubility Parameters of Different Polymers and Alcohols [17][a]

Polymer	δ_p	Alcohol	δ_{ROH}	$\lvert\delta_p - \delta_{ROH}\rvert$
PVAC	19.2	Methanol	29.7	12.6
PE	16.4	Ethanol	26.4	9.3
Elvax 150	16.0–21.7	Propanol-1	24.2	7.1
Elvax 250	17.4–19.4	Butanol-1	23.3	6.2
EVA[b]	17.0–17.25	Pentanol-1	21.7	4.6
		Hexanol-1	21.9	4.8
		Heptanol-1	21.7	4.6
		Octanol-1	21.7	4.0

[a] δ data in $10^3\ J^{1/2} \cdot m^{-3/2}$.

[b] Used EVA copolymers (19 to 32 wt% VA) with the calculated solubility parameters $\delta_{EVA} = m_{VA}\,\delta_{PVAc} + m_E\,\delta_{PE}$, where m = wt% monomer in EVA.

Extensive studies on solubility under similar conditions to our reactions were not made. In the following experiments, emphasis is laid on the study of EVA transesterification with different alcohols under the conditions of reactive extrusion.

METHODS OF PRODUCING EVAL COPOLYMERS

Schillgalies and colleagues [18] made a survey of the production methods of EVAL copolymers. Koopman and colleagues [19] supplied a complete summary and interpretation of patents involving the acetoxy–hydroxide transformation of EVA. Among the 138 patents registered from 1940 to 1980, there are only few describing the modification of EVA in screw reactors [20–23].

Interest in using extruders for chemical modification or synthesis of polymers has increased considerably in the last 10 years. Herrmann [24] pointed out the advantages of screw reactors.

The method of producing EVAL copolymers or partly converted products by reactive extrusion has been described in several patents. In Reference 25 an EVA–ethanol solution with 10–50 wt% EVA was converted in an extruder and then transferred into a coagulation bath. The method reported in References 26 and 27 for this principle is simple. In the extruder the modificator solution, sodium alcoholate dissolved in alcohol, is added in small doses to the molten EVA. After passing the reaction zone where transesterification takes place, the unconverted alcohol and the acetic acid ester formed are removed from the polymer melt by vacuum devolatilization. This procedure seems to be a very elegant method with high efficiency.

Lambla [28] pointed out the difficulties of reactions in polymer melts. Contrary to reactions in solvent, polarity in the molten state is not adjustable. The high viscosity reduces the diffusion processes of the reagents and the accessibility of the reactive groups to a large degree. Therefore, an increase in the miscibility of the reagents or the catalysts in the melt is required in extruders.

EXPERIMENTAL

Based on work concerning the transesterification of EVA in the melt and its solubility behavior, it is believed that problems arise from the use of low molecular weight alcohols because of incompatibility of the reaction partners. Material transport processes can overlap the rate of reaction and reduce it considerably. Consequently, reaction conditions must be provided in such a way that these processes run best. The following conditions improve transport:

Large surface and surface-generation rate
Good mixture of the phases
Low viscosity of the polymer melt
Long-term residence time

The choice of experimental conditions was made based on these conditions. The pilot plant shown in Fig. 2 is based on a twin-screw extruder ZDSK 28 of Werner & Pfleiderer.

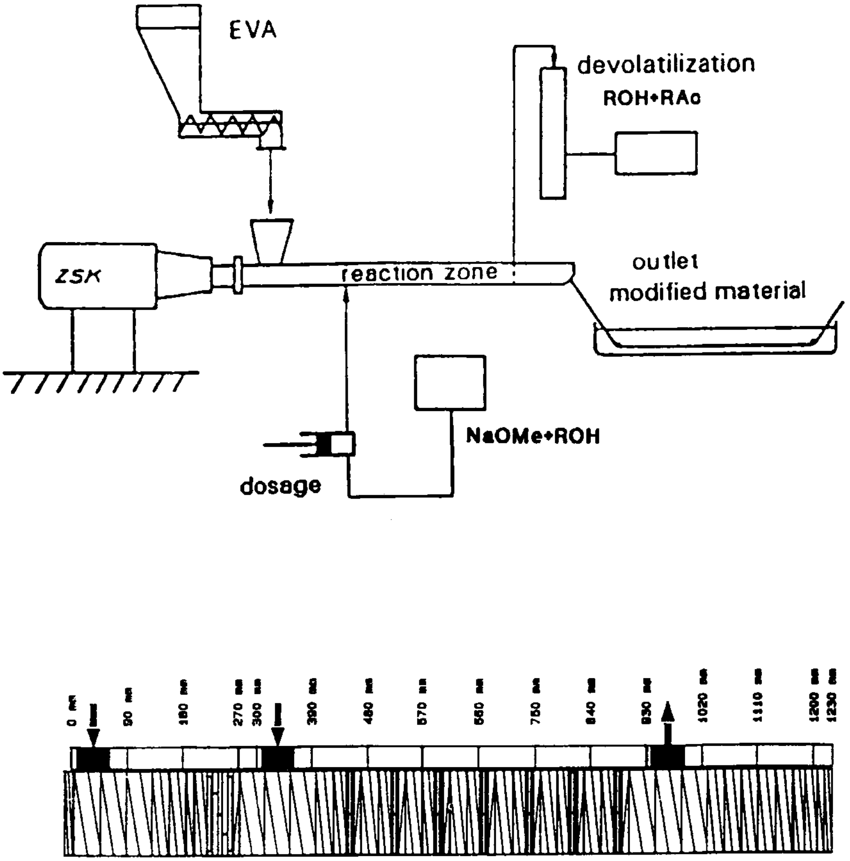


FIG. 2. Pilot plant for the transesterification of EVA copolymers in the reaction extruder with a scheme of the screw geometry.

The ethylene-vinyl acetate copolymers used were supplied by Leuna-Werke AG, Germany. The vinyl acetate content was 19, 24, and 32 wt% as determined by pyrolysis [29]. Butanol and octanol, also from Leuna-Werke AG, were used without further purification. Sodium methanolate was generated in our own laboratory.

RESULTS

Transesterification with Octanol-1

Starting from the work of Lambla, we first carried out conversions of EVA with octanol and NaOMe. On the one hand the aim of these experiments was to compare our results with those of Lambla, and on the other hand it was to test the equilibrium of the transesterification reaction of EVA with OcOH without additional side reactions (saponification) for a larger component ratio.

Attention has to be paid to the differences in the catalysis of Lambla's tests for the reaction conditions and the initial EVA. Our tests should result in an analogous equilibrium curve and equilibrium constant because the position of the chemical equilibrium of a reaction does not depend on the reaction method. The data of our tests can be seen in Table 2.

The general reaction scheme for transesterification is

$$\text{PVAc} + \text{OcOH} \rightleftharpoons \text{PVOH} + \text{OcAc}$$

According to the law of mass action, this results in an equilibrium constant K:

$$K = \frac{[\text{PVOH}]_{\text{eq}}[\text{OcAc}]_{\text{eq}}}{[\text{PVAc}]_{\text{eq}}[\text{OcOH}]_{\text{eq}}} \tag{3}$$

By transforming Eq. (3) for conversion use:

$$K = \frac{U_{\text{eq}}^2}{(1 - U_{\text{eq}})(A - U_{\text{eq}})} \tag{4}$$

TABLE 2. NaOMe-Catalyzed Transesterification of EVA with Octanol in the Twin-Screw Extruder (Q = 3 kg EVA/h)[a]

NaOMe/VA, mol/mol	A	[VA], wt%	U, %	K	MFI, dg/min
–	–	19.00	0	–	57.2
0.095	0.787	8.95	55.3	2.08	12.5
0.08	0.695	9.55	52.2	2.21	14.4
0.070	0.585	10.61	46.6	2.14	14.1
0.057	0.475	11.66	41.0	2.31	13.3
0.045	0.371	13.02	33.6	2.14	20.0

[a] A = initial mole ratio OcOH/VA.

VA = concentration of VA in modification product.

U = degree of conversion.

K = equilibrium constant.

A simple calculation of equilibrium conversion U_{eq} with an already known equilibrium constant K which depends on the initial mole ratio A of OcOH/VA is possible.

Calculated equilibrium curves of the reaction system EVA/OcOH are shown for different temperatures in Fig. 3 by using the equilibrium constants found by Lambla. Obviously, there is no temperature influence. In this figure the conversions of our experiments are marked by asterisks. They are slightly lower, but they follow the shape of Lambla's curves very well.

Confirmation that these measured values follow the law of mass action is provided by mathematical analysis. For each pair of values (A; U) given in Table 1, the equilibrium constant K was calculated according to Eq. (4). It is evident that K values differ only slightly. The equilibrium constant K was calculated as an average value and found to equal 2.18. The position of the transesterification equilibrium for EVA/OcOH at 170°C as found by Lambla was confirmed by our extruder results, too. A further important finding follows from these results. The maximum conversions in our series of experiments were reached with much less catalyst (1.12–0.53 wt%) compared to Lambla (>1.2 wt%). This shows the significant effect of such reaction conditions as extruder configuration, residence time, temperature, and purity of the products.

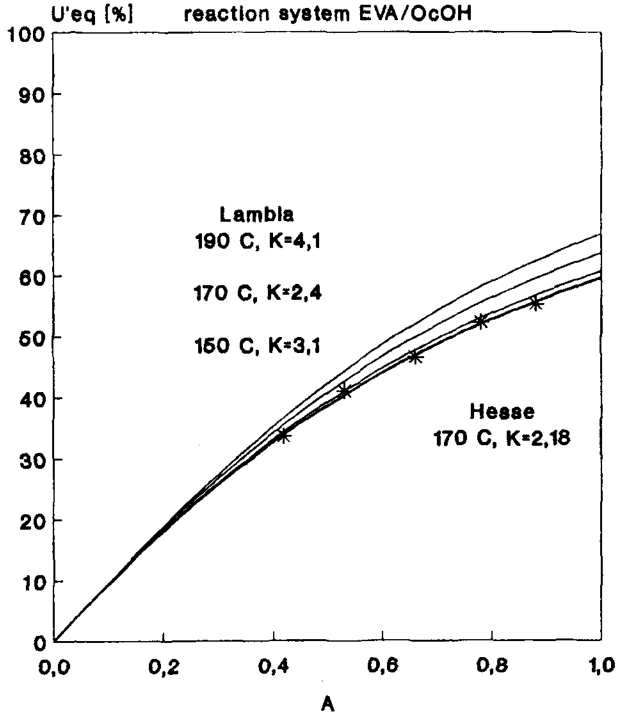


FIG. 3. VA conversion in the equilibrium state of the alcoholysis (U_{eq}) versus the initial molar ratio OcOH/VA (A) used. (—) Equilibrium curves calculated from Lambla's results. (*) Our data..

Transesterification with Butanol-1

From organic chemistry it is known that the reactivity of alcohols increases during transesterification if the C-number of the alkyl decreases. On the other hand, reaction at the EVA copolymer is hindered if short-chain alcohols do not significantly dissolve the polymer. Knowledge about the transesterification of EVA with short-chain *n*-alcohols is extremely incomplete, and the reaction behavior under extrusion conditions is not known. There are questions about transesterification equilibrium and whether it is possible to reach it during reactive extrusion.

An answer should be found in a series of experiments where transesterifications at constant initial mole ratios of EVA and BuOH with a successive increase in NaOMe addition were carried out. The tests were made with the ZDSK28. The dependence of the degree of transesterification, measured at the exit of the extruder, on the catalyst amount is shown in Figs. 4 and 5 for two EVA types with different amounts of VA.

Generally, a catalyst has an accelerating effect on the reaction. An increase in catalyst concentration causes an increase in the reaction rate, so conversion at a constant reaction time should increase enormously. However, this behavior is not observed. At the beginning, all dependencies show a retarding period in which

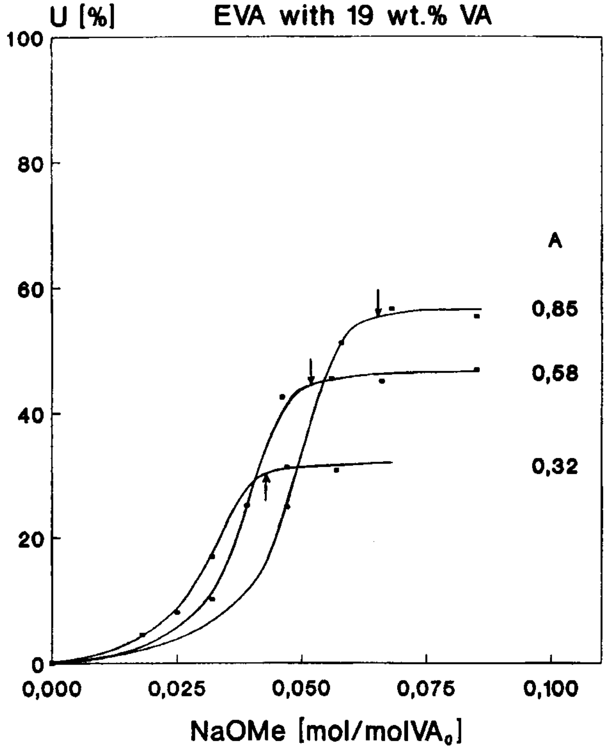


FIG. 4. Dependence of the degree of conversion of VA (*U*) on the added catalyst quantity NaOMe at different initial molar ratios BuOH/VA (*A*).

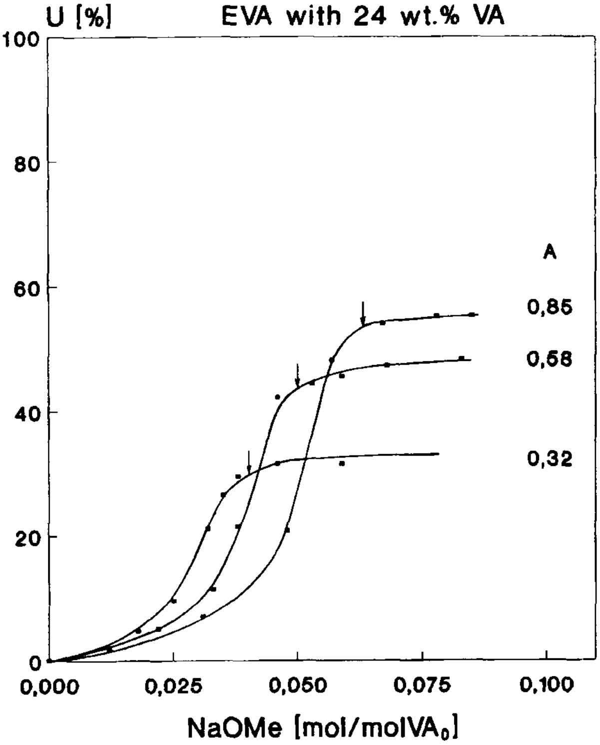


FIG. 5. Dependence of the degree of conversion of VA (*U*) on the added catalyst quantity NaOMe at different initial molar ratios BuOH/VA (*A*).

conversion increases only slightly with increasing catalyst addition. Surprisingly, the more BuOH added to the reaction system, the larger is this retarding period.

This is either a self-acceleration effect at work or we are dealing with a heterogeneous system in which mass transfer of the catalyst from the liquid butanol phase in the EVA melt determines the reaction rate. Further investigations showed that contaminations due to the use of technical BuOH are the main reason for this reaction.

There are some impurities in BuOH, water, aldehydes, and ketones which destroy the alcoholysis catalyst NaOMe. The reaction with water leads to NaOH and finally via VA saponification to NaAc. Aldehydes and ketones enter into aldol reactions in an alkaline medium, water is set free, or they react and consume NaOMe with the existing esters via a Claisen condensation to give stable Na-enolate compounds. From this it is clear why the observed retardation period is extended by increased BuOH addition.

Only after the contaminants have completely reacted is a "normal" increase of the curves found. Small additions of NaOMe lead to larger conversion profits. This is a reflection of the efficiency of the catalyst. The higher the BuOH concentration, the sharper is the slope. This is caused by BuOH excess leading to a higher reaction rate.

Finally, the curves quickly reach a conversion limit which depends on the quantity of BuOH used. Any further increase of the catalyst concentration shows no effect. Thus, it can be assumed that transesterification equilibrium has been reached.

It is very simple to cause alcoholysis in the extruder if the reaction is carried out at its conversion limit where variations of the catalyst concentration no longer have a significant influence on the extent of transesterification. Thus, at a BuOH concentration corresponding to the conversion limit, products with a defined chemical structure can be produced. Therefore, knowledge of the catalyst quantity necessary for reaching this conversion limit is of great technical interest. The minimum catalyst quantities for both EVA types can be estimated from Figs. 4 and 5 by approximation (see arrows at the curves). Data are contained in Table 3.

More catalyst is necessary to reach the conversion limit with an increase in BuOH content. It is obvious that these minimum quantities are essentially determined by the extent of the retarding period, i.e., the purity of the materials used.

Figure 6 shows the conversion limits reached in our experiments in relation to the initial BuOH concentration. From this figure it is evident that all points are fitted by a single curve, which means that for all the EVA types under investigation, the conversion limit is 1. The same function of the BuOH/VA ratio represents the law of mass action. For the alcoholysis of EVA with BuOH, an equilibrium constant of $K = 2.35$ was found. This result proves that transesterification equilibrium of EVA with BuOH can be reached during the residence time in the extruder. Thus, the production of EVA/VAL terpolymers with any wanted composition is possible. The necessary initial ratio of BuOH/VA can be calculated by using Eq. (4).

It seems that BuOH produces compatibility at higher temperatures because there are no irregularities in reaction behavior for the different EVA types under our test conditions. This is also confirmed by solubility tests. Boiling resulted in clear butanol solutions of EVA copolymers with 32 and 24 wt% VA and a slightly cloudy solution of the EVA copolymer with 19 wt% VA.

Kinetics of the Alcoholate-Catalyzed EVA Alcoholysis with BuOH

Knowledge of the rate at which alcoholysis in the extruder occurs is of significant importance for the technical realization of EVA modification in order to produce defined materials. The building-up of the reactor, its screw form, the

TABLE 3. Minimum Quantity of Catalyst (NaOMe) to Reach Equilibrium Conversion during Extrusion

Initial molar ratio BuOH/VA (A)	Minimum quantity of NaOMe $[\text{mol/mol VA}]_{t=0}$ EVA 19 wt% VA	EVA 24.3 wt% VA
0.32	0.043	0.040
0.58	0.052	0.050
0.85	0.065	0.062

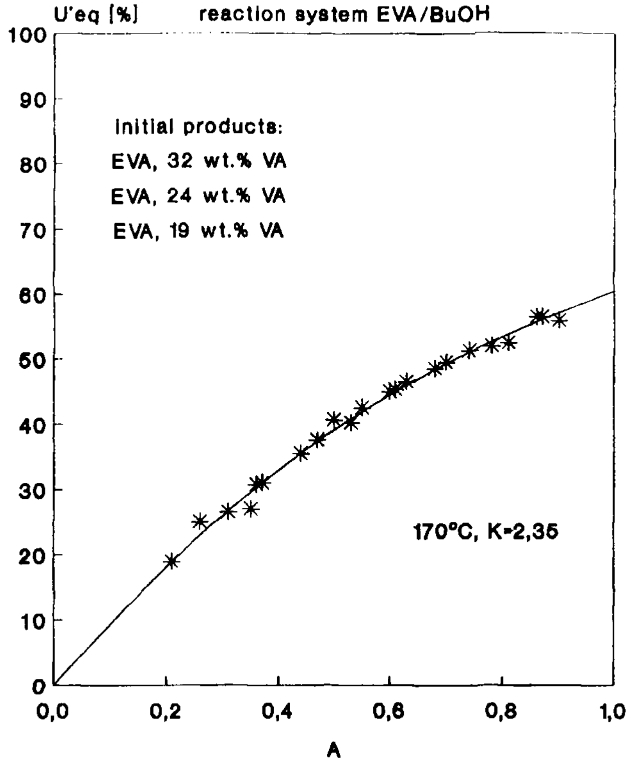


FIG. 6. Equilibrium curve of BuOH-EVA alcoholysis. Conversion limits (U_{eq}) versus the initial molar ratio BuOH/VA (A). Values of three different EVA products, resulting in the equilibrium constant $K = 2.35$.

transport conditions, and the mixing behavior can be coordinated according to the rate equation. That is an important precondition to optimize the process to reach the maximum space-time efficiency. Therefore, we utilized experiments for kinetic evaluation.

Deduction of the Rate Equation

A complicated nonintegrable time principle results because of the mechanism of alcoholate-catalyzed transesterification. Therefore, a simpler rate equation was derived from the general reaction scheme

$$\text{PVAc} + \text{ROH} + (\text{NaOMe}) \rightleftharpoons \text{PVOH} + \text{RVAc} + (\text{NaOMe})$$

From stoichiometry, the catalyst does not appear in the reaction scheme and is expected to be zeroth order in the rate equation. However, the concentration of the catalyst influences the reaction rate. In our case it is expected that the time principle is first order, as usual. For transesterification reactions in polyester synthesis, the catalysts tetrabutyl- and tetrapropyltitanate were used as first order [30, 31]. For complicated reaction mechanisms the catalyst concentration can also enter the rate equation as a higher order.

Our general rate equation for the build-up of vinyl alcohol units is

$$\frac{d[\mathrm{PVOH}]}{dt} = k_1[\mathrm{NaOR}][\mathrm{PVAc}][\mathrm{ROH}] - k_{-1}[\mathrm{NaOR}][\mathrm{PVOH}][\mathrm{RAc}] \qquad (5)$$

where initial state $t = 0$, [PVOH] = 0, and [RAc] = 0.

To simplify Eq. (3), it is transformed into the conversion rate:

$$\frac{d[\mathrm{PVOH}]}{dt}\,\frac{[\mathrm{PVAc}]_0}{[\mathrm{PVAc}]_0} = (k_1[\mathrm{PVAc}][\mathrm{ROH}] - k_{-1}[\mathrm{PVOH}][\mathrm{RAc}])[\mathrm{NaOR}]\,\frac{[\mathrm{PVAc}]_0^2}{[\mathrm{PVAc}]_0^2}$$

$$\frac{d}{dt}\,\frac{[\mathrm{PVOH}]}{[\mathrm{PVAc}]_0} = \left(k_1\,\frac{[\mathrm{PVAc}]}{[\mathrm{PVAc}]_0}\,\frac{[\mathrm{ROH}]}{[\mathrm{PVAc}]_0} - k_{-1}\frac{[\mathrm{PVOH}]}{[\mathrm{PVAc}]_0}\,\frac{[\mathrm{RAc}]}{[\mathrm{PVAc}]_0}\right)[\mathrm{NaOR}][\mathrm{PVAc}]_0$$

$$\frac{[\mathrm{PVOH}]}{[\mathrm{PVAc}]_0} = \frac{[\mathrm{RAc}]}{[\mathrm{PVAc}]_0} = U;\ \frac{[\mathrm{PVAc}]}{[\mathrm{PVAc}]_0} = 1 - U;\ \frac{[\mathrm{ROH}]}{[\mathrm{PVAc}]_0} = \frac{[\mathrm{ROH}]_0}{[\mathrm{PVAc}]_0} - U = A - U$$

$$\frac{dU}{dt} = (k_1(1 - U)(A - U) - k_{-1}U^2)C \qquad (6)$$

where U = PVAc conversion (degree of alcoholysis or transesterification)
A = initial molar ratio ROH/PVAc
C = $(\mathrm{NaOMe})(\mathrm{PVAc})_0$ = constant
(NaOMe) = catalyst concentration used
$(\mathrm{PVAc})_0$ = initial concentration of vinyl acetate groups in the reaction mixture
k_1, k_{-1} = rate constants in $\mathrm{L^2\cdot mol^{-2}\cdot min^{-1}}$

Integration of Eq. (4) for the conversion rate [32] leads to

$$1 \int_{U=0}^{U} \frac{dU}{k_1(1 - U)(A - U) - k_{-1}U^2} = \int_{t=0}^{t} Cdt$$

$$\frac{1}{\sqrt{-\Delta}} \ln \frac{2(k_1 - k_{-1})U - k_1(1 + A) - \sqrt{-\Delta}}{2(k_1 - k_{-1})U - k_1(1 + A) + \sqrt{-\Delta}} - \frac{1}{\sqrt{-\Delta}} \ln \frac{-k_1(1 + A) - \sqrt{-\Delta}}{-k_1(1 + A) + \sqrt{-\Delta}} = Ct$$

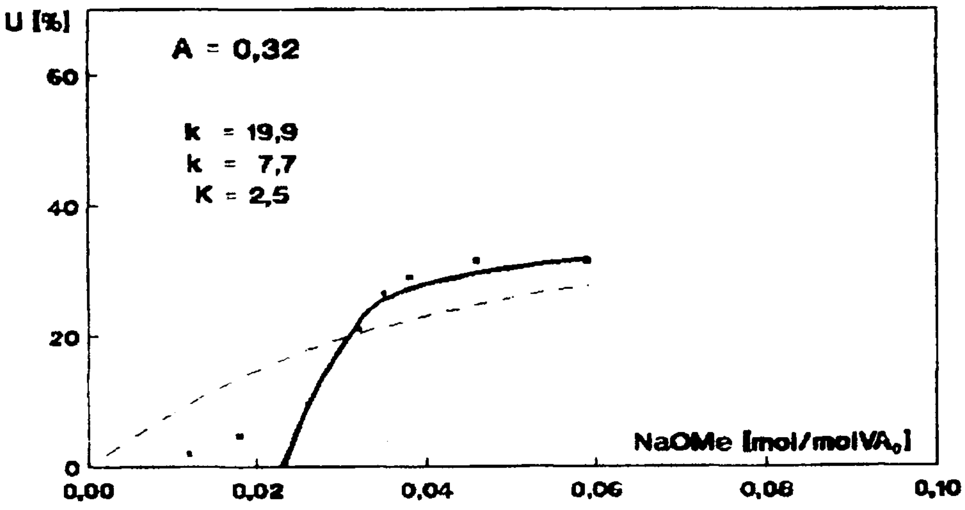
By solving this equation for U, the time-conversion dependence of alcoholysis results:

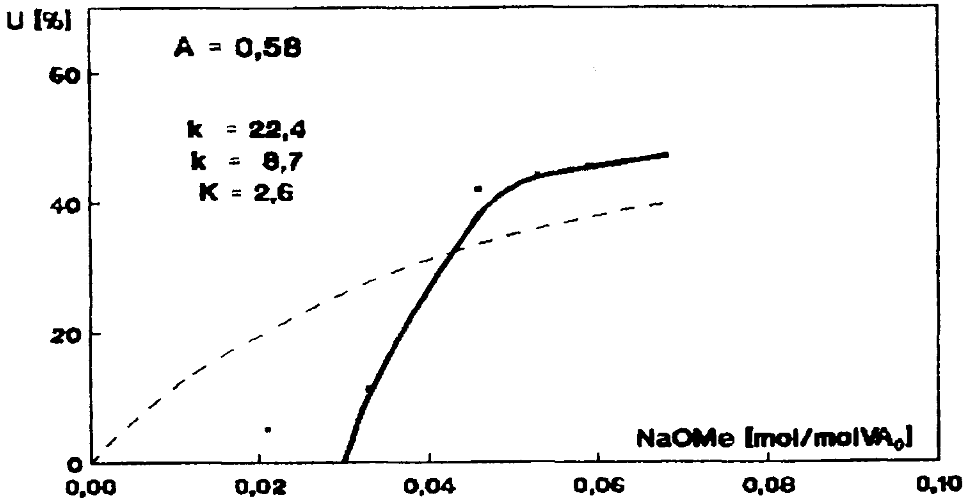
$$U = \frac{2k_1A}{\dfrac{(e^{\sqrt{-\Delta}Ct} + 1)}{(e^{\sqrt{-\Delta}Ct} - 1)} + k_1(1 + A)} \qquad (7)$$

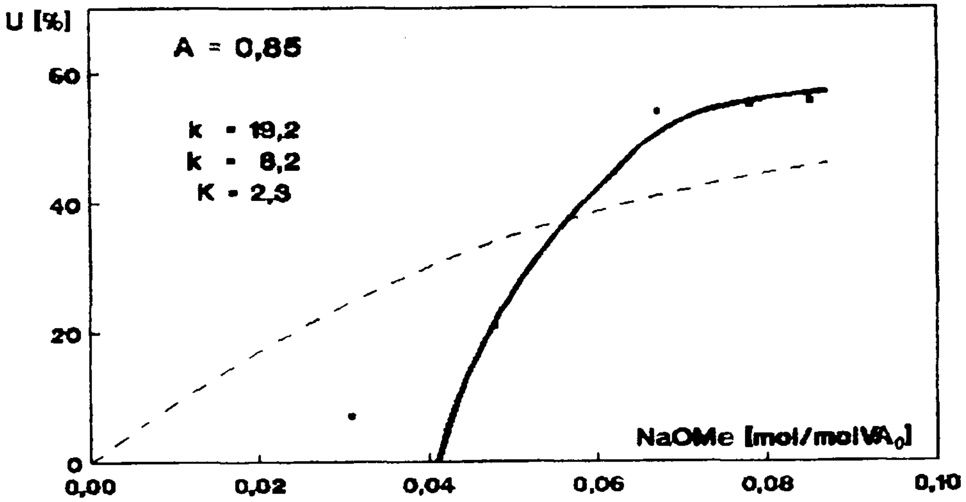
$$\sqrt{-\Delta} = 4k_1(k_1 - k_{-1})A - k_1^2(1 + A)^2$$
$$= 4k_1^2(1 - 1/K)A - k_1^2(1 + A)^2$$

For both of the following extremes, the integrated general rate equation gives good solutions:

1. At a mole ratio of $A = 0$ (which means no addition of alcohol), the result is $U = 0$
2. At reaction time $t = \infty$, the term $(e^{\sqrt{-\Delta}Ct} + 1)/(e^{\sqrt{-\Delta}Ct} - 1) = 1$, and Eq. (5) changes to the law of mass action:


U [%]
A = 0,32
k = 19,9
k = 7,7
K = 2,5
60
40
20
0
0,00
0,02
0,04
0,06
0,08
0,10
NaOMe [mol/molVA$_0$]


U [%]
A = 0,58
k = 22,4
k = 8,7
K = 2,6
60
40
20
0
0,00
0,02
0,04
0,06
0,08
0,10
NaOMe [mol/molVA$_0$]


U [%]
A = 0,85
k = 19,2
k = 8,2
K = 2,3
60
40
20
0
0,00
0,02
0,04
0,06
0,08
0,10
NaOMe [mol/molVA$_0$]

$$\frac{k_1}{k_{-1}} = K = \frac{U_{eq}^2}{(1 - U_{eq})(A - U_{eq})}, \quad \text{with } U = U_{eq} \tag{8}$$

where K = equilibrium constant
U_{eq} = equilibrium conversion

This model assumes a homogeneous reaction system, i.e., under the reactive extrusion conditions, the reaction partners have to be completely miscible. Heterogeneity effects must not be superimposed on the alcoholysis. Another precondition is constant alcoholate functionality during the reaction; this means the side reactions which lead to the destruction of alcoholysis catalyst are negligible.

Experimental data based on Eq. (7) can be used to determine the rate constants. The usual time-conversion dependencies are used. However, alcoholysis proceeds so fast that it is almost impossible to follow this process analytically. Therefore, lab-scale experiments in this solvent failed. However, degrees of conversion with various quantities of NaOMe catalyst were determined from knowledge of all the other free variable reaction parameters: reaction time, initial VA concentration, and quantity of alcohol used.

When the experimental parameters are put into Eq. (7), determination of the rate constants by fitting the model to the experimental data ($[\text{NaOMe}]_i$; U_i) is possible if the assumed rate equation adequately reflects the real situation.

For curve fitting, two-dimensional simplex-optimization was used [33]. It provides the two rate constants, k_1 and k_{-1}, of the alcoholysis.

There is also the possibility of including the already determined equilibrium constant K in the calculation. Thus, the fitting procedure is reduced to the optimization of one parameter.

The optimization criterion in both cases is the least-squares approach.

Analysis of the Experiments

The reaction system EVA/BuOH is certainly a homogeneous mixture under extrusion conditions. Thus, an essential precondition for the validity of the rate equation is fulfilled, and good conformity of model and experimental data can be expected. For the rate equation, curve fitting by parameter optimization to the experimentally determined dependencies, as shown in Fig. 7, was realized.

It is obvious from all three series of measurements that the general rate equation derived cannot describe the experimentally found dependence of the conversion on the catalyst concentration used. The reason for this is the retardation behavior seen at the beginning of the curves.

As already explained, the atypical behavior of the alcoholysis is caused because undesired side reactions destroy the catalyst. These reactions originate from

---

FIG. 7. Model curves found by parameter optimization, dependence of the conversion (U) on the quantity of catalyst (NaOME) at three different initial molar ratios BuOH/VA (A). (- -) Curves of the model Eq. (5), not adequate. (—) Curves of the model Eq. (5) with the destruction of NaOME by contamination; adequate. k_1 = 20.18; k_1 = 8.04; K = 2.51.

contamination of the BuOH used. This contamination is not taken into consideration in our kinetic model, and this is a systematic lack in our model.

However, after receiving kinetic information from our "technical" experiments about the alcohol-catalyzed transesterification of EVA with BuOH in the extruder, we have chosen to ignore the retardation phase, i.e., the retardation period is not taken into account for kinetic analysis. Consequently, a reduced catalyst concentration has to be used. The newly fitted model curves are shown in Fig. 7 as full lines. These curves are well described by the general rate equation. The rate constants of the three curves, which were determined independently of each other, correspond approximately. Therefore, it can be assumed that the kinetic model for BuOH alcoholysis of EVA by reactive extrusion (with the above-mentioned restrictions) is effective. By applying our model, the following rate constants were determined:

$$k_1 = 20.18; \qquad k_{-1} = 8.04\ L^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}; \qquad K = 2.51$$

It is encouraging that the equilibrium constant K of the reaction system EVA/BuOH, which had already been determined by use of conversion limits, was also found by calculation of the kinetic parameters.

The k-parameters can be considered as approximate values, and they provide the order of magnitude at which BuOH alcoholysis operates.

REFERENCES

[1] I. Sakurada, *Pure Appl. Chem.*, *16*, 243 (1968).

[2] W. Sliwka, *Angew. Makromol. Chem.*, *4/5*, 310 (1968).

[3] J. Brandsch, *Preprints MACRO Mainz*, Vol. 1, 1979, pp. 117–20; *Abstracts MACRO 83, Bucharest*, Sect. 1, pp. 142–145; *Acta Polym.*, *38*(1), 24 (1987).

[4] C. Fonseca, J. G. Fatou, and J. M. Perena, *Angew. Makromol. Chem.*, *190*(3216), 137–155 (1991).

[5] M. Rätzsch and G. Crell, *Plaste Kautsch.*, *22*, 243 (1975).

[6] R. J. Koopmans, R. Van der Linden, and E. F. Vansant, *Bull. Soc. Chim. Belg.*, *91*(6), 531 (1982).

[7] R. J. Koopmans, R. Van der Linden, and E. F. Vansant, *Ibid.*, *92*(2), 83 (1983).

[8] S. Patai, in *The Chemistry of the Hydroxyl Group: Part 2*, Wiley, New York, 1971, p. 1109.

[9] R. J. Koopmans, R. Domisse, F. Alderweireldt, E. F. Vansant, and R. Van der Linden, *Eur. Polym. J.*, *19*(2), 165 (1983).

[10] H. Ludewig, *Polyesterfasem—Chemie und Technologie*, Akademie-Verlag, Berlin, 1975, p. 117.

[11] Houben-Weyl, *Methoden der organischen Chemie, Bd. E20/Teil 1, Makromolekulare Stoffe*, Georg Thieme Verlag, Stuttgart, 1987, p. 606.

[12] DE OS 3528490 A1 (1985), Bayer AG.

[13] A. Boilloux, J. Druz, and M. Lambla, *Polym. Process Eng.*, *4*(2–4), 235 (1986).

[14] M. Lambla, J. Druz, and A. Bouilloux, *Polym. Eng. Sci.*, *27*(16), 1221 (1987).

[15] M. Lambla, in *Polymerreaktionen und reaktives Aufbereiten in kontinuierlichen Maschinen*, VDI-Verlag, Düsseldorf, 1988, pp. 297–317.

[16] E. Schröder, G. Müller, and K.-F. Arndt, *Leitfaden der Polymercharakterisierung*, Akademie-Verlag, Berlin, 1982, pp. 292–294.

[17] H.-G. Elias, *Makromoleküle*, 2nd ed., Hüttig & Wepf Verlag, Basel-Heidelberg, 1972.

[18] J. Schillgalies, H. Hoffmann, and M. Fedtke, *Plaste Kautsch.*, *27*, 61 (1980).

[19] R. J. Koopmans, R. Van der Linden, and E. F. Vansant, *Polym. Eng. Sci.*, *22*(10), 645 (1982).

[20] British Patent 1,106,489 (1968), Monsanto.

[21] US Patent 3,547,858 (1969).

[22] Japanese Patent 72-030932 (1972), Toray Industries.

[23] German Patent 107,938 (1974), Leuna Werke.

[24] H. Herrmann, in *Polymerreaktionen und reaktives Aufbereiten in kontinuierlichen Maschinen*, VDI-Verlag, Düsseldorf, 1988, pp. 1–6.

[25] Japanese Patent 62-116614-A (1985), Nippon Synth. Chem. Ind.

[26] German Patents 206 900, AT 15.3.82; 243 287 A1, AT 15.12.85; 252 834 A1, AT 29.9.86.

[27] German Patent 3525559 (1985), ATOCHEM.

[28] M. Lambla, In *Polymerreaktionen und reaktives Aufbereiten in kontinuierlichen Maschinen*, VDI-Verlag, Düsseldorf, 1988, pp. 7–18.

[29] H. Beck, M. Gebauer, G. Hoffmann, and A. Hesse, *Plaste Kautsch.*, *37*(9), 292 (1990).

[30] L. Yurramendi, M. J. Barandiaran, and J. M. Asua, *Polymer*, *29*(5), 871 (1988).

[31] J. Hsu and K. Y. Choi, *J. Appl. Polym. Sci.*, *33*, 329 (1987).

[32] I. N. Bronstein and K. A. Semendjajew, *Taschenbuch der Mathematik Staatl.*, 6th ed., Verlag für Techn.-Theoret. Literatur, Moscow, 1956, p. 299.

[33] Autorenkollektiv, *Technisch-chemisches Praktikum*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1977, pp. 225–265. P. F. A. Van der Wiel, R. Maassen, and G. Kateman, *Anal. Chim. Acta*, *153*, 83 (1983).