The Controlled Solvolysis of Ethylene−Vinyl Acetate Copolymers

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ABSTRACT: The basic “hydrolysis” of ethylene−vinyl acetate copolymers (EVA) leads to ethylene−vinyl alcohol copolymers (EVOH) or ethylene−vinyl acetate−vinyl alcohol terpolymers which can be used for their surface properties or for further chemical modification. The controlled basic solvolysis of EVA takes place via a complicated nonstoichiometric mechanism. The solvolysis by anhydrous methanol catalyzed by sodium methoxide has been investigated thoroughly. This reaction is capable of fully converting acetate groups; the solvolysis of an acetate group next to another acetate (in EVV triads) is faster than that for isolated vinyl acetate (EVE triads) and proceeds immediately to the neighboring acetate group. The rate constants of each elementary step have been determined with the help of numerical simulations of kinetics data. In particular, the forward rate constant, k_+, of the S_N2 attack of the methoxide ion on vinyl acetate strongly depends on solvent quality (methanol content), i.e., on polymer coil expansion. When sodium hydroxide is used as a base, the reaction system is more complex because of the additional steps and equilibria involving water. The most prominent difference with respect to anhydrous conditions is partial solvolysis of acetate groups, even when fully converted. Indeed, the reaction stops when the reactive species have been fully converted into acetate ions of low reactivity. The numerical simulation of the kinetics agreed with the experimental data, but the large number of reaction steps and equilibria did not allow reliable determination of the rate constants.

Introduction

Vinyl acetate monomers are widely used as a source of vinyl alcohol units in (co)polymers. For instance, poly(vinyl alcohol)[1] is produced by the hydrolysis of poly(vinyl acetate). Even in this case, hydrolysis has to be controlled. The nonpolar poly(vinyl acetate) turns progressively into a more polar polymer when hydrolyzed, but the fully hydrolyzed polymer is insoluble in water.[2] Hydrophilic gels can be prepared from fully hydrolyzed PVAc.[3] For application as a dispersant, the water-soluble form of poly(vinyl alcohol) is obtained by partial hydrolysis of PVAc.

In the same way, ethylene−vinyl alcohol copolymers (EVOH) are obtained by the hydrolysis of ethylene−vinyl acetate copolymers (EVA). Because of its excellent barrier properties, EVOH is useful in food packaging applications.[4] EVOH or the terpolymers resulting from the partial hydrolysis of EVA are also used in polymer blends.[5,6] Finally, EVOH can be used for further chemical modifications by grafting alcohol groups.[7−9]

Several reports on puzzling results obtained with different batches of poly(vinyl alcohol) that should have been identical[10−12] call for more careful control of hydrolysis. The amount of residual vinyl acetate in the poly(VA-*co*-VAc) copolymer known as poly(vinyl alcohol) has great importance in applications such as dispersion or emulsion polymerization.[13]

No clear interpretation of the self-acceleration of the hydrolysis of poly(vinyl acetate) has been given, although this phenomenon has been well-known for a long time. The origin of this self-acceleration is the higher reactivity of ester groups located next to an alcohol.[14] However, several other effects appear to contribute, and the exact mechanism is still being debated. In particular, several authors have ascribed the acceleration to the polymer coil expansion as the vinyl acetate units are converted into their more polar vinyl alcohol units.[15,16] Only semiempirical formal descriptions of the reaction kinetics have been proposed. Sakurada et al. wrote an effective rate constant k_{eff} of the hydrolysis reaction which was no longer constant but increased as a function of conversion ξ: $k_{\mathrm{eff}} = k_0(1 + m\xi)$, where the empirical parameter m accounted for the acceleration.[2,17,18] Since hydrolysis takes place in the vicinity of the hydrolyzed regions, hydrolyzed blocks form on the polymer chain,[19] giving an amphiphilic character to the partially hydrolyzed polymer.[20,21]

The EVA copolymer is a good model for investigating the hydrolysis of poly(vinyl acetate), because the mechanism is much less complex and the analysis of the partially hydrolyzed polymers is also simpler. In particular, EVA's with a low vinyl acetate content contain only isolated vinyl acetate units in EVE triads and pairs of neighboring vinyl acetate units in EVV triads (E = ethylene unit, V = vinyl acetate unit). Sequences with three contiguous vinyl acetate units (EVVVE) or more are present at an insignificantly low level. The hydrolysis of the EVE and EVV sequences can be easily monitored in a kinetic experiment because their ^{1}H and ^{13}C NMR lines are resolved. The ethylene units are chemically neutral under reaction conditions and act as a diluent along the polymer chain. The investigation of the hydrolysis of EVA is simpler than that of PVAc but shares certain characteristics. This should help in the appraisal of the much more complex hydrolysis of PVAc.

There are only few studies on the mechanism and kinetics of the widely used basic solvolysis of EVA in toluene/methanol mixed solvent, and no report on the control of partial solvolysis exists. It should be noted

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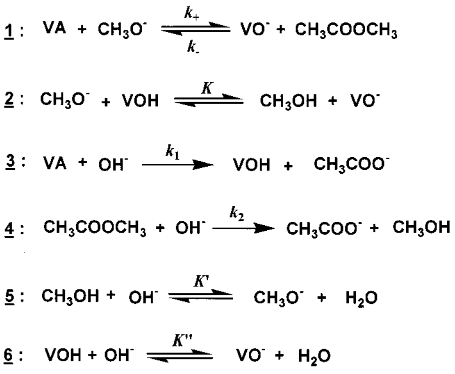
Scheme 1: Mechanism of the Solvolysis of EVA



that the often used term “hydrolysis” is unsuitable, since the solvent mixture does not contain water; “solvolysis” or “alcoholysis” would be more appropriate. In an experimental investigation of the basic hydrolysis of EVA by potassium hydroxide, Koopmans et al.[22−24] reported the main features and proposed a series of reactions and acid−base equilibria which essentially showed the complexity of the mechanism. Thus, the reaction does not follow the simple second-order kinetics which was proposed in early works.[25] The rate constants, which were calculated from the data at low conversion by assuming a second-order kinetic law, were not constant but depended on the reagent concentrations. The reaction is not stoichiometric since the degree of hydrolysis at full conversion exceeds the base-to-vinyl acetate mole ratio. The “hydrolysis” involves the ester cleavage by both the hydroxide and methoxide ions. The authors have studied the influence of several parameters but could not reach clear-cut conclusions. The proposed mechanism was not validated by the experimental data and there was no quantitative interpretation of the kinetic data in terms of rate constants.

For the solvolysis of EVA by sodium (or potassium) hydroxide in toluene/methanol mixture, the mechanism is written as shown in Scheme 1, where VA = vinyl acetate units, VOH and VO^- = vinyl alcohol units in their alcohol or alcoholate form. Notice that the equilibria 2, 5, and 6 are not independent since $K = K''/K'$. Equilibrium 2 was written because it can take place even in the absence of water. The present mechanism was correctly rewritten from Koopmans et al.[22−24] who ignored the protonation equilibria of VO^- (6 and 2) and wrote reaction 3 erroneously.

It is noteworthy that quite different results are obtained according to the reaction conditions, although the same general mechanism is obeyed. Thus, in the simplest case where alkaline hydroxide is used in a non protic solvent, the sole nucleophilic species are OH^- ions and only reaction 3 takes place. This case has been studied by Rätzsch and Crell[25] for EVA’s with different vinyl acetate contents; they found a simple stoichiometric second-order reaction having the same rate constant as for the saponification of isopropyl acetate. However, this process is of little practical use because alkaline hydroxides have very low solubility in aprotic solvents. The same results are obtained when the solvent is either water or a water-rich mixture with an aprotic solvent (e.g. water−acetone). However, current processes make use of alcohol solvents, possibly as mixtures with water or an organic solvent in order to ensure the solubilization of all reagents throughout the reaction. In this case, both hydroxide and alkoxide ions act as nucleophiles and the full mechanism given above has to be taken into account. The reaction is no longer stoichiometric[22−24] but is more or less catalytic; it does not reach completion when low amounts of base are used. The latter case concerns the solvolysis by alkoxide ions under anhydrous conditions, in binary mixtures of alcohol and an organic solvent. This case involves only reactions 1 and 2. According to our findings reported in the present paper, it differs from the previous “wet” process because it is genuinely catalytic and the solvolysis can reach completion. The last two processes have been studied in the present work.

The present study deals with the basic solvolysis of EVA in toluene/methanol mixed solvent. Several open questions are addressed in a detailed kinetic investigation. In particular, the solvolysis of EVV sequences has been studied with respect to that of the EVE sequences, the mechanistic differences between the solvolysis by sodium methoxide in anhydrous conditions and by sodium hydroxide are disclosed. Finally, the rate and equilibrium constants have been determined, allowing a detailed discussion of the influence of the reaction conditions.

Materials and Methods

The Ethylene−Vinyl Acetate Copolymer. The commercial EVA referenced as CP7018 was a random copolymer of low molar mass having 12 mol % (28 wt %) of vinyl acetate units. The distribution of the VA units was random because ethylene and vinyl acetate have similar reactivities in radical polymerization.[26] The molar masses as given by size exclusion chromatography were $M_N = 2400$ g/mol and $M_W = 10800$ g/mol. This grade was chosen because the low molar mass enabled accurate high-resolution NMR characterization.

Kinetic Measurements. A 30 cm^3 sample of a 20 wt % solution of the EVA CP7018 in dry toluene was heated to 40 °C under a dry argon atmosphere in a 100 cm^3 three-necked flask equipped with a septum, an argon inlet and outlet, and a magnetic stir bar. The concentration of acetate groups was thus 0.5 mol/L. A solution of either sodium methoxide or hydroxide in methanol was added with a syringe into the reactor at time $t = 0$. Aliquots of the reaction medium (2 cm^3) were taken at different times and poured into a large volume of methanol containing hydrochloric acid. The acidic medium stopped the reaction immediately and the polymer precipitated. The polymer was filtered and dried overnight at 50 °C in vacuo.

Analysis of the Partially Hydrolyzed EVA. IR Spectroscopy. This method was widely used for the analysis of partially hydrolyzed PVAc. The band at 1735 cm^{-1} corresponding to the stretching of the carbonyl allows the quantitative determination of the residual acetates. IR spectra were recorded with a Nicolet Magna 560 in transmission mode for polymer films cast from a hot TCE solution onto KBr pellets. In the present case, the ester band of EVA at 1739 cm^{-1} split into two bands for polymers above 30% conversion. The new band at 1718 cm^{-1} grew at the expense of that at 1739 cm^{-1} as the conversion was increased. This was attributed to ester groups bound to alcohol groups by means of hydrogen bonding in the pure polymer.[19,20] Therefore this phenomenon means that the Beer−Lambert law is not obeyed. This prohibits the use of IR spectroscopy for the quantitative determination of the acetates, unless prior calibration can be done, provided calibration samples are available, or reference is made to a different technique.[27,28]

Thermogravimetric Analysis. The titration of the residual acetate can be made by the detection of acetic acid evolved by thermolysis of the EVA.[29] Thus, in a thermogravimetric analysis, acetic acid is eliminated at 360−450 °C before the thermal degradation of the polyethylene parts at 450−550 °C. The weight loss between 200 and 450 °C allows the determination of the vinyl acetate content in EVA.[30] Measure-

Table 1. Assignment of the ^{1}H or ^{13}C NMR Spectra of the CHOC(O)CH_3 and CHOH Fragments in TCE/C_6D_6 (2/1) Mixture at 360 K (ppm from TMS)

	observed nucleus	^{1}H NMR	^{13}C NMR
acetate	**CHOC(O)*CH*$_3$** of EVE	1.87	20.7
	CH(OAc)*CH*$_2$CH(OAc) of EVV	2.20	39.4
	***CH*OC(O)CH$_3$** of EVE	4.88	73.6
			73.9
	***CH*OC(O)CH$_3$** of EVV	4.95	70.2 (meso)
			71.2 (rac)
	C=O		169.5
alcohol	***CH*OH** of EHE	3.50	71.6
	***CH*OH** of EHH	3.75	69.1
		3.85	72.7

ments were carried out with a Du Pont Instruments TGA 2950 themogravimetric analyzer between 30 and 600 °C with a heating rate of 40 °C/min under helium atmosphere.

^{1}H and ^{13}C NMR. The NMR data were recorded using a Bruker AC250 spectrometer for solutions in tetrachloroethylene/benzene-d_6 (2/1) mixture (TCE/C_6D_6) at 360 K. The chemical shifts given in ppm from TMS, were measured from the line of TMS internal reference for ^{1}H NMR and from the line of TCE (120.75 ppm from TMS) for ^{13}C NMR. These experimental conditions were selected because the polymers hydrolyzed to various extents were soluble and the NMR lines were narrow. The spectral assignments of small polyethylene fragments studied in this solvent mixture[31] were identical with those of Hansen et al.[32] in 1,2-dichorobenzene-d_4, and the same optimal parameters for the quantitative acquisition in ^{13}C NMR were used.[31] However, the chemical shifts were strongly affected by the presence of the aromatic C_6D_6, so that they could not be compared with those of the literature measured in nonaromatic solvents. The advantage of this exotic solvent mixture was high resolution: the ^{1}H NMR lines of EVA solutions were quite narrow, allowing accurate determination of their areas for the quantitative analyses. For instance, DMSO-d_6 in which all the polymers were also soluble, gave broad lines which partially overlapped. This problem has already been encountered by Wu[33] who had to reacetylate the partially hydrolyzed EVA with perdeuterated acetic anhydride prior to its NMR analysis. The ^{1}H and ^{13}C NMR spectra were quite complex because the long polyethylene sequences (10 E units on average) showed the same features as for low-density polyethylene.[34−36] For our present purpose, the only spectral data pertaining to the VA and VOH units is discussed in the following. The lines of the ^{1}H and ^{13}C NMR spectra of the EVA where only EVE and EVV triads appeared, were unambiguously assigned (Table 1) with the help of reference works.[36,37] The ^{1}H NMR lines of the methine corresponding to the EVE (4.80 ppm) and EVV (4.85 ppm) triads were poorly resolved and could not be integrated separately with accuracy. It is worth noticing that this spectral region was not disturbed by lines corresponding to double bonds[32] formed by disproportionation chain termination reactions, because such reactions were absent. Thus, the main chain termination process was the transfer to a chain transfer agent added in order to obtain low molar masses. The relative abundance of EVV triads was estimated from the ^{13}C NMR data recorded under quantitative acquisition conditions. The area of these EVA lines decreased as the solvolysis extent increased and new lines corresponding to the vinyl alcohol units appeared. A singlet at 3.50 ppm as the major line and two smaller lines of equal intensity at 3.75 and 3.85 ppm appeared in the ^{1}H NMR spectra. Only three lines appeared in the ^{13}C NMR spectra: the major additional line at 71.6 ppm and two smaller lines of equal intensity at 69.1 and 72.7 ppm (Figure 1). The major lines obviously pertain to the EVE sequences hydrolyzed into EHE (H stands for vinyl alcohol unit). However, four additional lines were expected for the solvolysis products of the EVV triads: two for the EVH triads and two for the EHH triads (meso and racemic). 2D-NMR showed the correlation of the ^{1}H NMR and ^{13}C NMR lines: the pairs of ^{1}H−^{13}C correlated lines were 3.50−71.6 ppm for the EHE triads and 3.75−69.1 and 3.85−72.7 ppm for the hydrolyzed EVV triads. The proximity of the ^{1}H NMR lines of the EHE and hydrolyzed EVV triads strongly suggested that the latter were fully hydrolyzed EVV, namely EHH triads. Definitive proof of this assignment came from the comparison of the solvolysis degrees as estimated from thermogravimetric analysis and ^{1}H or ^{13}C NMR: good agreement with these two independent measurements could be achieved if the two supplementary small lines were assigned to EHH triads. EVH sequences were never observed. The spectral assignments are summarized in Table 1. The ^{1}H NMR lines of the different methine protons at 3.50, 3.75, 3.85, 4.88, and 4.95 ppm were used for the calculation of the conversion in the kinetic experiments.

Synthesis of Model Compounds and Their Solvolysis. 2,4-Diacetoxypentane was prepared from the reaction of 2,4-pentanediol (mixture of its optical isomers) with acetyl chloride.[38]

^{1}H NMR in $CDCl_3$ (ppm from TMS): 1.23 and 1.24 (CH_3-CH, 6H, 2 doublets, $^3J_{H-H}$ = 6.33 Hz); from 1.6 to 2.0 (central CH_2, 2H, complex pattern of sharp lines); 2.01 and 2.03 (CH_3C(O)O, 6H, 2 singlets); 4.97 (*CH*OAc, 2H, sextuplet, $^3J_{H-H}$ = 6.33 Hz).

^{13}C NMR in $CDCl_3$ (ppm from TMS): 19.975; 20.33; 21.06; 21.18; 41.71; 42.18; 66.99; 67.85; 170.32; 170.41.

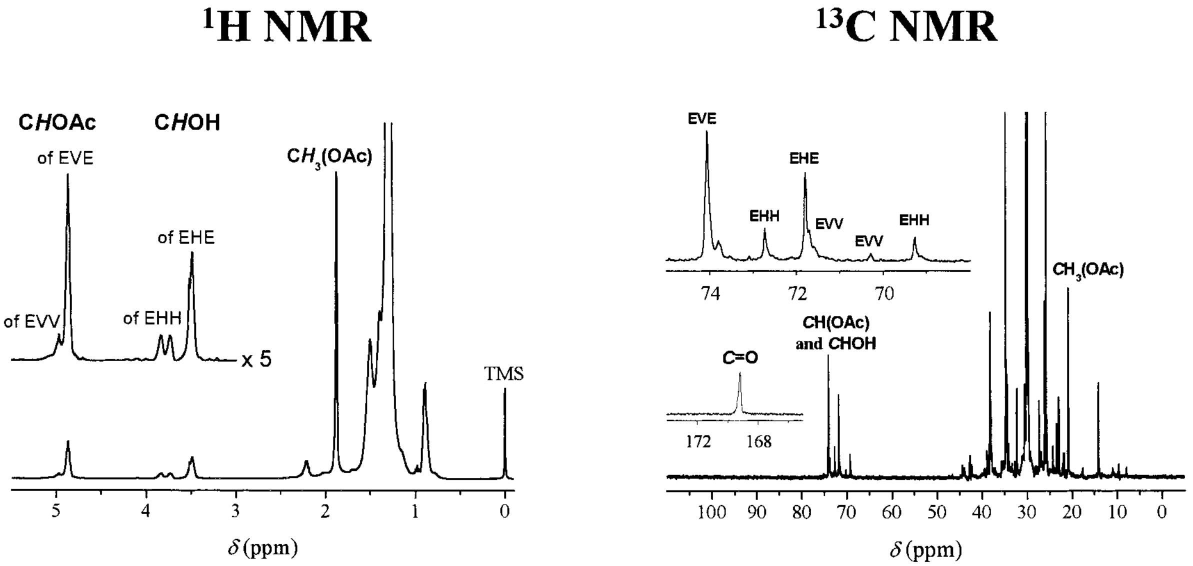


Figure 1. ^{1}H and ^{13}C NMR spectra of partially (34%) hydrolyzed EVA.

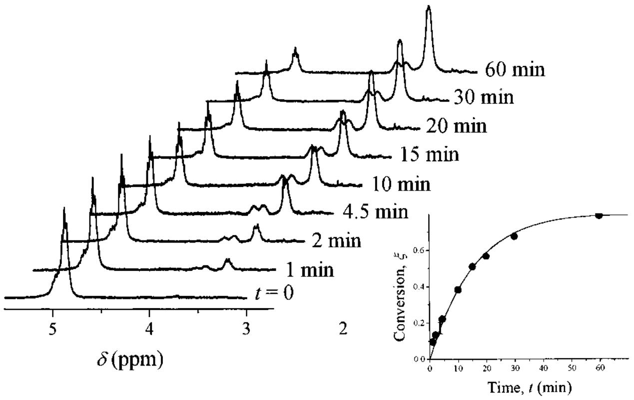


Figure 2. ^{1}H NMR monitoring of a solvolysis kinetic experiment (run 3).

4-Acetoxy-2-pentanol was prepared from 2,4-pentanediol by means of its ethyl orthoacetate intermediate according to a synthesis procedure described in the literature.[39]

^{1}H NMR in $CDCl_3$ (ppm from TMS): 1.2 (CH_3CH, 6H, 3 doublets); from 1.5 to 1.9 (central CH_2, 2H); 2.03 and 2.06 ($CH_3C(O)O$, 3H, 2 singlets); 3.00 and 3.35 (CHOH, 1H, 2 broad singlets); 3.7 to 4.0 (CHOH, 1H); 5.0 to 5.2 (CHOAc, 1H).

^{13}C NMR in $CDCl_3$ (ppm from TMS): 20.06; 20.55; 21.14; 21.24; 23.11; 23.53; 23.93; 45.02; 45.78; 63.52; 64.96; 68.34; 69.24; 170.73; 171.64.

The kinetic studies of the solvolysis of 2,4-diacetoxypentane and 4-acetoxy-2-pentanol were carried out in a toluene-d_8/methanol mixture under the same conditions as for one of the solvolysis runs of the EVA. The reactions were carried out in the NMR tube, allowing direct monitoring of the reaction by ^{1}H NMR. The kinetics were measured for conversions below 30% because of the low solubility of the reaction product 2,4-pentanediol.

Solvolysis of EVE and EVV Triads

The solvolysis of the EVV triads takes place according to two successive steps as

$$\mathrm{EVV} \rightarrow \mathrm{EVH} \rightarrow \mathrm{EHH}$$

The ^{1}H and ^{13}C NMR lines of both the EVH and EHH triads should be observed in the kinetic investigation of the reaction, but only the lines of the EHH triads were observed (see assignment of the NMR lines in the experimental part). EVH triads were never observed throughout reaction, whatever the experimental conditions. This showed that the solvolysis of the EVH triads was much faster than that of the EVV triads. Thus, the solvolysis of acetate groups next to an alcohol group was very fast. This is the first direct observation of this phenomenon, which was proposed as the origin of the self-acceleration of the hydrolysis of PVAc by Sakurada.[14,17] The first step controlled the rate of solvolysis of the EVV triads.

The faster solvolysis of the second acetate group in EVV triads could be disclosed because the NMR lines of the EVH were sought specifically. This could not be observed in earlier kinetic experiments in which the overall acetate cleavage was measured, because the solvolysis of the first acetate in the EVV triads was rate-determining. On the same basis, model studies on small organic molecules representing the EVV fragments (2,4-diacetoxypentane) do not show any self-acceleration because the first attack is rate-determining. It has often been concluded in the literature that the self-acceleration of the solvolysis was solely due to an expansion the polymer coil because this point has been missed.[16]

The rate of solvolysis of the grouped acetate functions was also faster than that of the isolated acetates. Thus, the solvolysis of the EVV and EVE triads could be observed in a kinetic experiment because the ^{1}H NMR lines of the formed EHH and EHE triads were resolved (Figure 2). In a simple comparison of the conversion, the solvolysis of the first acetate of the EVV triads was faster than that of the EVE triads (Figure 3). The ratio of the initial rates was essentially independent of the reaction conditions; a value between 1.5 and 2 was found for the different conditions given in Table 2. The same result was found by observing the ratio of the forward rate constants k_+ of reaction 1 in Scheme 1 (Figure 3) which were determined at low conversions, as explained in the next section. However, a slight but significant variation of this ratio with respect to the reaction conditions could be observed, the highest values of 2 being observed for the highest methanol contents.

Finally, the solvolyses of small model organic molecules that mimic the EVV and EHV triads have been investigated using the same experimental conditions as for the solvolysis of EVA. Thus, the solvolysis of the EVV analogue 2,4-diacetoxypentane was faster than with the EVA polymer and a low but significant (less than 10%) concentration of the monoester intermediate could be

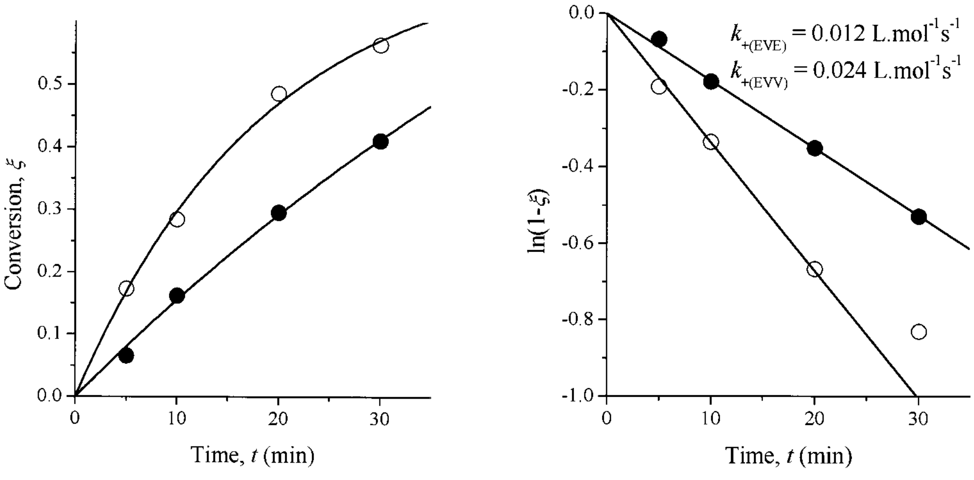


Figure 3. Left: Conversion of the EVE (●) and EVV (○) triads as determined from the ^{1}H NMR lines of the EHH and EHE triads for run 9 (Table 2). Right: Semilog plot allowing the determination of the rate constant k_+ from its slope at small conversions (see text).

Table 2. Results of the Kinetic Investigation for Different Reaction Conditions[a]

run no.	[MeOH] (mol/L)	[MeONa] (mol/L)	k_+ (L mol^{-1} s^{-1})	k_- (L mol^{-1} s^{-1})	K	$k_{+(\mathrm{EVV})}/k_{+(\mathrm{EVE})}$
1	0.816	0.0192	0.057	0.05	2	1.5
2	0.815	0.0190	0.066	0.04	3	1.2
3	1.36	0.0318	0.028	0.01	1	1.5
4	1.57	0.0245	0.043	0.008*	10*	1.9
5	2.03	0.0303	0.029	0.003*	9*	1.8
6	2.28	0.0357	0.022	0.008	1.5	1.4
7	2.86	0.0469	0.013	0.02	2.5	1.4
8	2.93	0.0236	0.014	0.15*	0.2*	1.9
9	3.56	0.0286	0.010	0.02	2.5	2.0
10	3.56	0.0288	0.009	0.00003*	8*	1.8

[a] The concentration of acetate groups was 0.50 mol/L in all experiments. k_+ was determined from the slope d[ln(1 − ξ)]/dt with 10% accuracy. The values of k_- and K, which were obtained from the minimum of the error maps, were of very poor accuracy. In particular, the values marked with an asterisk corresponded to error maps that did not show a single minimum.

observed throughout the reaction. There was no accumulation of the intermediate, showing that its solvolysis was faster than its formation. Hence, the small model molecule showed the same feature as the EVA polymer but the acceleration by the neighboring OH group was less. The solvolysis of 4-acetoxy-2-pentanol (EVH analogue) as measured in a separate kinetic experiment was 3 times faster than for 2,4-diacetoxypentane. This shows that the proximity of the alcohol group contributes to the acceleration, but the magnitude of this effect as measured with models cannot account for the full effects observed with the polymers.

Solvolysis by Sodium Methoxide in Anhydrous Conditions.

To evaluate the relative importance of each elementary step in the complex mechanism shown in Scheme 1, the values of the reaction rate constants and equilibrium constants were determined from the kinetic data. This quantitative interpretation could be made in the case of the solvolysis by sodium methoxide under anhydrous conditions where only the forward and backward reactions 1 and the equilibrium 2 were present. All the other reactions in Scheme 1 involve hydroxide ions or water which were not present in the reaction medium. This case is thus simple enough to be controlled, since only the two rate constants k_+ and k_- and the equilibrium constant K have to be determined.

The full kinetics equations and the method of solving them is reported in the Appendix. In the low conversion limit, the integration of the rate gives

$$\ln(1\text{-}\xi) = -\,k_+\,[\mathrm{MeONa}]\,t \qquad (7)$$

where ξ is the conversion and [MeONa] is the concentration of sodium methoxide added at the beginning of the reaction. The slope of the plot of ln(1 − ξ) as a function of time t gives the rate constant k_+ (Figures 3 and 4). This is the same equation as for a simple stoichiometric second-order solvolysis which was often assumed in previous works. The rate constants that can be found in the literature are thus identical with k_+ if the reactions were run in anhydrous conditions; but the mechanism is not a stoichiometric second-order reaction. The rate constant k_+ was determined from the overall conversion. This is an average of the values of the EVE and EVV triads as

$$k_+ = x_{\mathrm{EVE}}\,k_{+(\mathrm{EVE})} + x_{\mathrm{EVV}}\,k_{+(\mathrm{EVV})} \qquad (8)$$

where x_{EVE} and x_{EVV} are the mole fraction of vinyl acetate units involved in EVE and EVV triads ($x_{\mathrm{EVE}} = 0.76$ and $x_{\mathrm{EVV}} = 0.24$). For $k_{+(\mathrm{EVV})}/k_{+(\mathrm{EVE})} = 2$, $k_{+(\mathrm{EVV})} = 1.6k_+$ and $k_{+(\mathrm{EVE})} = 0.8k_+$. Once k_+ has been found, the values of k_- and K can be estimated by looking for the best fit of the calculated kinetics (see Appendix) with the experimental data. The influences of variations of k_- and K on the simulated kinetics were quite similar, so that different pairs of values (k_-, K) could fit to the data as well. As a consequence, accuracy was poor. A rigorous process of searching for the best fit consisted in a systematic calculation of the mean square deviation between the calculated and the experimental data points: an error map was calculated for each kinetic run and the (k_-, K) domain, giving the minimum error was determined (see Appendix). The depths of the minimum in the error maps were rather flat, but the agreement with the experimental data was very good. An example is given in Figure 4.

The results of these data analysis are given in Table 2. The very good agreement with the experimental data shows that the mechanism has been written correctly. The values of k_+ could be determined with fairly good accuracy. On the contrary, the values of k_- and K, which correspond to the minima of the error maps, must be considered as orders of magnitude. A better way of looking at the result was to compare the error maps themselves. Thus, the minima of all the error maps corresponded k_- and K coordinates of 0.02 L mol^{-1} s^{-1} and 2, respectively. Within experimental accuracy, the backward reaction rate and the acid − base equilibrium do not seem to depend on the reaction conditions. $K = 2$ shows that the acidities of methanol and vinyl alcohol are of comparable strength in the reaction conditions, the secondary alcohol VOH being slightly more acidic than the primary alcohol MeOH. In a nonpolar solvent, the acidities should resemble those in the gas phase[40] and they have been measured extensively by mass spectrometry techniques.[41] Combining the tabulated data of methanol and of the secondary alcohol 2-propanol taken in place of VOH, K assumes the large value $K = 5 \times 10^3$. Conversely, methanol is more acidic than 2-propanol in the polar aprotic solvent DMSO: $K = 5.6 \times 10^{-2}$.[42] The present value of K lies between, it is closer to that in a polar solvent although toluene is the major component of the solvent mixture. This suggests the formation of a micropolar environment at the reaction site. Although methanol is a poor solvent of EVA because of the polyethylene parts, a preferential solvation of the vinyl acetate and vinyl alcohol units by methanol can be proposed.

The forward reaction rate definitely depends on the chemical composition of the solvent. Thus, k_+ significantly decreases as a function of the methanol content in the toluene-methanol solvent mixture (Figure 5).

The solvolysis reaction should be faster in a more polar solvent, but the presence of methanol paradoxically slows down the reaction rate. However, methanol is a poor solvent of EVA. The collapse of the macromolecular chains due to the presence of a poor solvent hinders the solvolysis reaction because the polyethylene segments prevent the diffusion of reagents for the reaction site. The picture that can be proposed is a protective polyethylene cap around the isolated vinyl

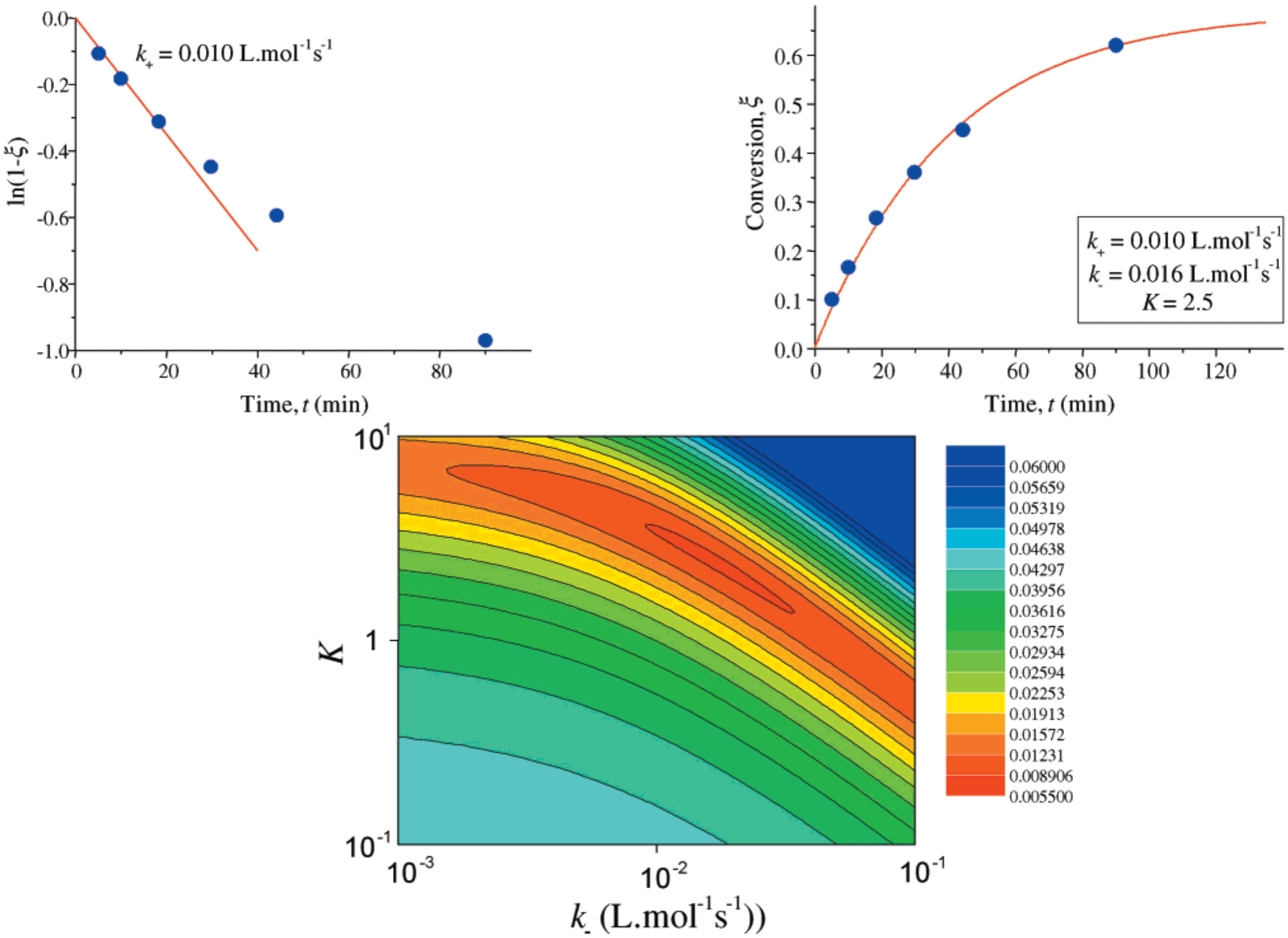


Figure 4. Search of the best fit to the data points for run 9 (Table 2). Top left: plot of ln(1 − ξ) against *t* allowing the determination of the rate constant k_+ from the slope at small conversions. Bottom: error map for the determination of k_- and *K*. Top right: Conversion as a function of time showing the overall agreement of the theory (full line) with the experiment (dots).

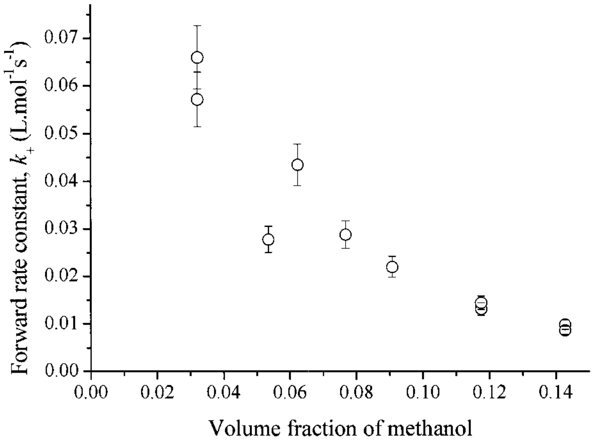


Figure 5. Variation of the forward rate constant k_+ as a function of the chemical composition of the solvent (toluene + methanol).

acetate units. This is a classical picture in which the reaction site is buried inside a collapsed nonpolar coil.[15,23−25] The presence of the polyethylene segments slows down the reaction because they are nonpolar. In the case of the acid-catalyzed methanolysis of vinyl chloride−vinyl acetate copolymers, Pichot et al. have observed an acceleration of the reaction by the presence of the vinyl chloride units because they are polar comonomers.[43] The values of k_- and *K* do not seem to depend essentially on the methanol content. This was expected for *K* since steric hindrance does not influence an acid base equilibrium constant. The backward reaction involves the nonpolar methyl acetate as a reagent which is freer with regards to diffusion in a polyethylene rich medium than the very polar sodium methoxide.

Solvolysis by Sodium Hydroxide

When sodium hydroxide was added in place of sodium methoxide as a source of basic species, the reaction of hydroxide ions with methanol yielded methoxide and water. Both hydroxide and methoxide ions are able to cleave the ester function. The difference with respect to the previous case is that the two nucleophiles compete in the ester cleavage and additional acid−base equilibria are involved. The acidities of methanol and water are not very different,[44,45] so that both hydroxide and methoxide ions were present in significant amounts in the reaction medium. The simultaneous ester cleavage by hydroxide and alkoxide ions has also been observed for small organic esters in water/alcohol mixed solvent.[46] An important difference lies in the nature of the reaction products. Thus, the ester cleavage by the hydroxide ions yields the alcohol and the acetate ion, which is a poor nucleophile as compared to hydroxide and alcoholate ions. The nucleophilic hydroxide ions were converted into species of very low reactivity, so that the total concentration of active nucleophiles in the reaction medium decreased as a function of conversion. The reaction then stopped when these nucleophiles were consumed. Conversely, in the previous case, the ester cleavage by methoxide ions was a transesterification

Table 3. Results of the Kinetic Investigation for Different Reaction Conditions[a]

run no.	[MeOH] (mol/L)	[NaOH] (mol/L)	$k_{+\mathrm{eff}}$ (L mol^{-1}s^{-1})	solvolysis rate at full conversion (yield)
11	1.35	0.025	0.061	0.52
12	2.03	0.025	0.045	0.65
13	3.56	0.025	0.0076	0.70
14	3.56	0.050	0.0076	0.72

[a] The concentration of acetate groups was 0.50 mol/L in all experiments. $k_{+\mathrm{eff}}$ was determined from the slope d[ln(1 − ξ)]/dt with 10% accuracy.

which yielded a new ester and alcoholate. The new alcoholate was still nucleophilic, and the concentration of nucleophiles remained constant throughout the reaction: the transesterification was catalytic.

The experimental kinetic measurements have indeed shown the loss of the catalytic character of the reaction when passing to the solvolysis by means of sodium hydroxide. But the reaction was not stoichiometric; the transesterification still contributed to the solvolysis. As expected, the larger the methanol content, the larger the contribution of the transesterification, and the larger was the solvolysis yield at full conversion for a given overall nucleophile concentration (added NaOH). There are actually three variables which do not influence the reaction course in an independent manner; they are the concentrations of EVA (the vinyl acetate concentration), sodium hydroxide, and methanol. The ratio of the added sodium hydroxide to methanol sets the relative amounts of hydroxide and methoxide ions in the reaction medium according to equilibrium 5, and subsequently the relative contributions of basic hydrolysis (by OH^-) and transesterification (by MeO^-). But the extent of ester cleavage at full conversion (solvolysis yield) also depends on the relative amounts of sodium hydroxide and vinyl acetate groups. Finally, it has been shown in the previous section that the reaction rate depends on the solvent composition through the methanol volume fraction (or methanol concentration).

The effect of the concentration of sodium hydroxide at constant EVA and methanol concentrations was straightforward: the reaction rate was simply proportional to [NaOH] (Table 3, runs 13 and 14). This was expected despite the complexity of the mechanism, since the rate of each elementary step was proportional to the concentration of OH^-. The differences of solvolysis yields reported in Table 3 were not significant because the reactions were very slow in runs 13 and 14 at high methanol content (17%). The yield obviously increases as a function of added sodium hydroxide and reaches 100% when the amount of sodium hydroxide is stoichiometric. Experiments at lower methanol contents and higher NaOH concentrations gave unambiguous evidence of the increase of yield, but the faster reaction rates did not allow kinetic measurements.

The effect of the methanol content at constant concentrations of EVA and NaOH was 2-fold. The contribution of transesterification was larger at higher methanol contents because the hydroxide−methoxide equilibrium 5 was shifted toward methoxide. The yield was then larger. But the presence of the methanol poor solvent of the EVA slowed the reaction. The decrease of the effective second-order rate constant $k_{+\mathrm{eff}}$ in runs 11, 12, and 13 reflects this behavior. The kinetic curves of Figure 6 run across one another because of this duality.

Finally, the sodium hydroxide and methanol contents were varied concomitantly, keeping constant the ratio NaOH/MeOH and the EVA concentration (0.5 M). A 10 wt % (2 mol/L) solution of NaOH in MeOH was used, giving a NaOH/MeOH mole ratio of 0.08. The measurements were carried out at rather large concentrations of NaOH and low methanol contents, so that full conversions were reached within less than 1 h. However, kinetic measurements could not be performed, so only the solvolysis yield was measured at full conversion. In every case, the solvolysis rate at full conversion was larger than what could be expected on the basis of a stoichiometric reaction. The larger deviation relative to the stoichiometry was obtained at vanishing NaOH and MeOH contents (Figure 7). The competition between hydrolysis by OH^- ions and transesterification was not simply controlled by the NaOH to MeOH ratio; the amount of NaOH with respect to the stoichiometry was also a relevant parameter. These conditions were well suited for partial solvolysis of EVA on a preparative scale, the solvolysis degree being controlled by means of the NaOH content.

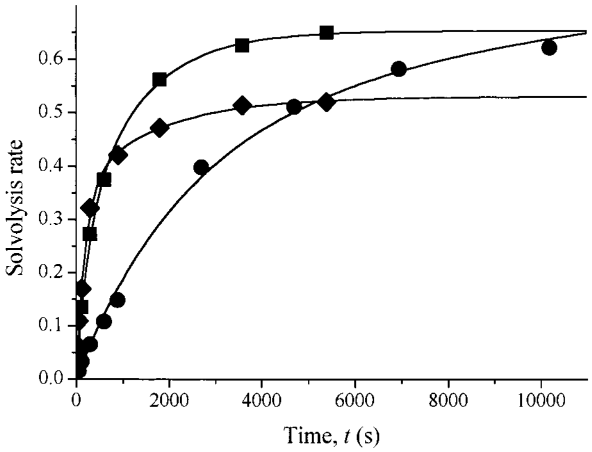


Figure 6. Kinetic measurements of the solvolysis rates for different methanol contents, keeping constant the concentrations of EVA (0.5 M) and NaOH (0.05 M). Key: (◆) run 11; (■) run 12; (●) run 13. They correspond to methanol volume fractions of 5%, 8%, and 17%, respectively.

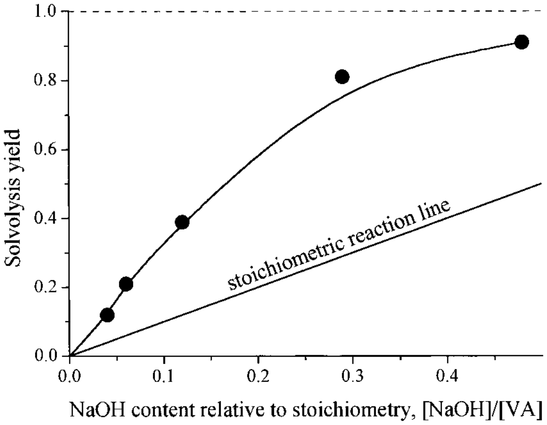


Figure 7. Departure from the stoichiometry. Solvolysis yield as a function of the NaOH content at constant NaOH/MeOH (0.08 mol/mol) and EVA concentration (0.5 M).

The calculation of the kinetics could be carried out in the same way as for the solvolysis by sodium methoxide (anhydrous medium), but the number of parameters was larger because of the larger number of reactions and equilibria involved. It was easy to account for the experimental data with the numerical calculation, but the set of parameters that gave a good fit to the

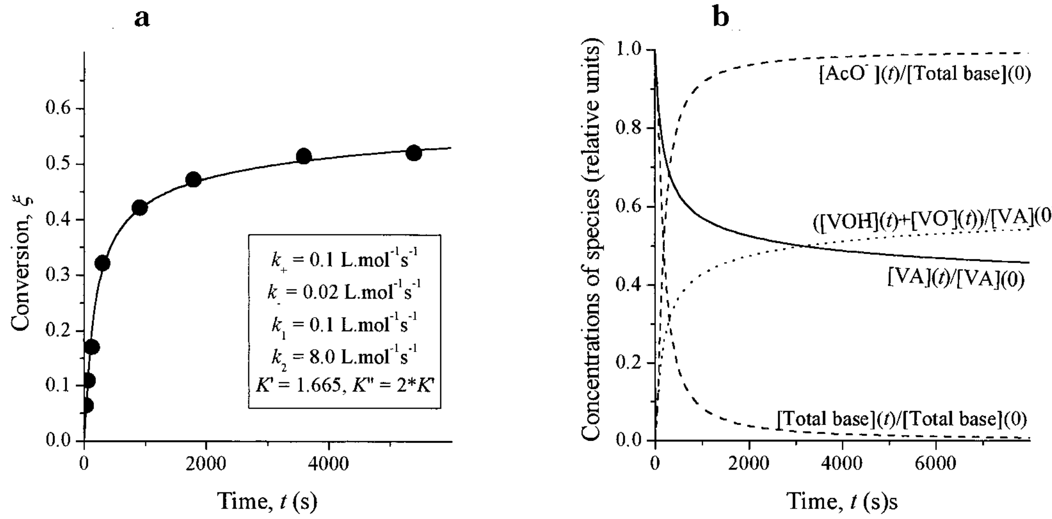


Figure 8. Example of simulated data which fit correctly with the experimental data of run 11 with realistic rate and equilibrium constants. (a) Calculated conversion ξ = 1-[VA](t)/[VA](0) (full line) compared to the experimental data (black dots). (b) Relative concentrations of some chemical species of interest: residual vinyl acetate groups [VA](t)/[VA](0) (solid line), total vinyl alcohol groups formed ([VOH](t) + [VO$^-$](t))/[VA](0) (dotted line), residual total basic species ([MeO$^-$](t) + [VO$^-$](t) + [OH$^-$](t))/([MeO$^-$](0) + [OH$^-$](0)) (decreasing dashed line) and inert acetate ions formed [AcO$^-$](t)/([MeO$^-$](0) + [OH$^-$](0)) (increasing dashed line).

experimental data was not unique because the number of free parameters was too large. Thus the rate and equilibrium constants could not be determined.

The data at low conversions obeyed a second-order kinetics law as in the anhydrous medium but the ester cleavage took place by the simultaneous attacks by OH$^-$ (reaction 1) and MeO$^-$ (reaction 3). An effective second-order rate constant could be deduced from a plot of ln(1 − ξ) against time. It is related to the real rate constants by $k_{+\mathrm{eff}} = \alpha k_+ + (1 - \alpha)k_1$ where α is the fraction of OH$^-$ ions converted into MeO$^-$ ions according to equilibrium 5. The values of $k_{+\mathrm{eff}}$ are given in Table 3. In principle, systematic kinetic measurements at low conversion should allow the determination of k_+, k_1, and K'; but our present set of data was not large enough. Nonetheless, the simulations accounted correctly for the experimental data: the way the kinetics vary as a function of the chemical composition of the reaction medium was the same as that described above, and the limitation of the yield at full conversion was also predicted. As an example, the experimental data of run 11 (Table 3) were simulated with a set of rate and equilibrium constants of realistic magnitude; the variations of concentrations of all species during the course of the reaction came out of the calculation. Thus, k_- was fixed as the value determined in the anhydrous case which was independent of the reaction conditions ($k_- = 0.02$ L mol^{-1} s^{-1}); K' was taken from the value determined in water-methanol mixed solvent[44] ($K' = 0.03 \times 55.5 = 1.665$), and K'' was chosen such that $K = K''/K' = 2$ as in the anhydrous case. Finally, k_1 and k_+ were kept identical because they are of the same order of magnitude.[46] Their exact value was adjusted to get a good fit with the experimental data ($k_+ = k_1 = 0.1$ L mol^{-1} s^{-1}). The value of k_2 was also adjusted and quite a large value ($k_2 = 8.0$ L mol^{-1} s^{-1}) resulted from the fit. Indeed both the methyl acetate and hydroxide ions involved in reaction 4 were small molecules which gave faster reactions than those involving polymers. The interesting feature shown in Figure 8 was the decrease of the concentration of the nucleophilic species MeO$^-$, VO$^-$, and OH$^-$ to the benefit of the nonnucleophilic acetate ions. It also can be seen that the reaction stopped when the overall concentration of nucleophiles was vanishing, their conversion into acetate having reached completion. However, this set of reaction parameters which accounted for the experimental data was not unique, so that it was not possible to determine and discuss their values.

Conclusions

The basic "hydrolysis" of ethylene−vinyl acetate copolymers (EVA) is quite versatile. The competition between the catalytic solvolysis path by alcoholate and the stoichiometric path by hydroxide allows very different kinetic behaviors and final products according to reaction conditions.

In the "anhydrous process", where the acetate groups are cleaved by an alcoholate in the alcohol, a catalytic transesterification takes place. The reaction can reach completion but is quite slow because of the macromolecular nature of one of the reagents. The rate constants could be determined from the kinetic experimental data. It is noteworthy that the forward rate constant k_+ strongly depends on the polymer coil expansion, showing that access of the reagents to the reaction site was severely limited. The solvolysis of the EVV triads is faster than the isolated vinyl acetate groups in EVE triads, and the solvolysis of the first acetate group in a EVV triads causes the very fast solvolysis of the remaining one.

In the "wet process", where the base is sodium hydroxide, additional reactions and equilibria are operative. Even when water is not loaded in the reactor, it is formed by the reaction of hydroxide and methanol (equilibrium 5). The major difference is the loss of the catalytic character of the solvolysis; the reaction stops at partial conversion when the base has been fully converted into acetate ions. The reaction yield depends on the competition between transesterification by methoxide ions and hydrolysis by hydroxide ions. The control of the hydrolysis with the chemical composition of the reaction medium is therefore easy, since the reaction stops at the stage of partial hydrolysis.

Regarding the solvolysis of poly(vinyl acetate), it can be extrapolated that the self-catalysis of the reaction by the neighboring alcohol groups does occur; it could be observed directly on EVA for the first time because resolution of the ^{1}H NMR data was high enough. But the polymer coil expansion that can vary during the reaction course (in the case of PVAc) also contributes to the kinetics. To the question, "does the self-acceleration in the hydrolysis of PVAc originate from the catalysis by the neighboring alcohols or from the enhanced accessibility to the ester groups as the polymer turns more hydrophilic", the answer is "Both contribute significantly". However, the idea of polymer coil expansion in good solvent is misleading, because the reaction medium is in the semidilute regime in most cases.

Appendix

Calculation of the Solvolysis Kinetics of EVA. In the case of the solvolysis of EVA by sodium methoxide under anhydrous conditions (toluene−methanol mixture), only the forward and backward reactions 1 and the equilibrium 2 (Scheme 1) are operative. The concentration of any chemical species can be calculated as a function of time by solving the following equations: the rate equation, the mass action law for the equilibrium and the materials balance equations

The rate equations read

$$\frac{\mathrm{d[AcOMe]}}{\mathrm{d}t} = \frac{\mathrm{d[VO^-]}}{\mathrm{d}t} = -\frac{\mathrm{d[VA]}}{\mathrm{d}t} = -\frac{\mathrm{d[MeO^-]}}{\mathrm{d}t} = \mathrm{[VA](0)}\frac{\mathrm{d}\xi(t)}{\mathrm{d}t}$$

where ξ is the conversion

$$\xi(t) = \frac{\mathrm{[AcOMe]}(t)}{\mathrm{[VA](0)}} = 1 - \frac{\mathrm{[VA]}(t)}{\mathrm{[VA](0)}}$$

Thus

$$\frac{\mathrm{d}\xi(t)}{\mathrm{d}t} = k_+(1-\xi)\mathrm{[MeO^-]} - k_-\xi\mathrm{[VO^-]}$$

The acid−base equilibrium is written as

$$K = \frac{\mathrm{[MeOH][VO^-]}}{\mathrm{[VOH][MeO^-]}}$$

The materials balance equations for each species are

$$\mathrm{[VA] + [AcOMe] = [VA](0)} \text{ for acetates}$$

$$\mathrm{[VA] + [VOH] + [VO^-] = [VA](0)} \text{ for vinyl groups}$$

$$\mathrm{[MeOH] + [MeO^-] + [AcOMe] = [MeOH]_{total}} \text{ for methyl groups}$$

and

$$\mathrm{[MeO^-] + [VO^-] = [Na^+]} \text{ for anions (electroneutrality)}$$

Two methods can be used for solving this set of equations: Either the integration of the differential equation $\mathrm{d}\xi(t)/\mathrm{d}t = \mathrm{f}(\xi, k_+, k_-, K) = k_+(1-\xi)\mathrm{[MeO^-]} - k_-\xi\mathrm{[VO^-]}$, or a step-by-step numerical simulation of the reaction.

Method by Integration. The first-order differential equation was integrated numerically:

$$\int_0^\xi \frac{\mathrm{d}\xi}{\mathrm{f}(\xi, k_+, k_-, K)} = t$$

where the integration constant was zero since the initial conditions were $\xi(0) = 0$.

$\mathrm{[MeO^-]}$ and $\mathrm{[VO^-]}$ were expressed as a function of the conversion ξ by solving the system of five equations (mass action law + four materials balance equations) for the five concentrations [MeOH], $\mathrm{[MeO^-]}$, [VOH], $\mathrm{[VO^-]}$, and [AcOMe], giving

$$\mathrm{[MeO^-]} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad \text{with } a = K - 1$$

$$b = (K-1)\{\xi \times \mathrm{[VA](0)} - \mathrm{[Na^+]}\} + \mathrm{[MeOH]_{total}}$$

$$c = \mathrm{[Na^+]}\{\xi \times \mathrm{[VA](0)} - \mathrm{[MeOH]_{total}}\}$$

$$\mathrm{[MeO^-]} = \mathrm{[Na^+]}\left\{1 - \frac{\xi \times \mathrm{[VA](0)}}{\mathrm{[MeOH]_{total}}}\right\} \text{ if } K = 1$$

$\mathrm{[VO^-] = [Na^+] - [MeO^-]}$ and the three other concentrations could also be readily calculated.

Step-by-Step Numerical Simulation of the Reaction. Knowing the species concentrations at a given time t, the rate of reaction 1 is

$$v(t) = k_+\mathrm{[VA]}(t) \times \mathrm{[MeO^-]}(t) - k_-\mathrm{[VO^-]}(t) \times \mathrm{[AcOMe]}(t)$$

At $t_1 = t + \Delta t$, a very short time Δt later, the conversion $\xi(t + \Delta t) = \xi(t) + \Delta\xi$ increases according to reaction 1 as

$$\xi(t+\Delta t) = \xi(t) + \left\{\frac{k_+\mathrm{[VA]}(t) \times \mathrm{[MeO^-]}(t) - k_-\mathrm{[VO^-]}(t) \times \mathrm{[AcOMe]}(t)}{\mathrm{[VA](0)}}\right\} \times \Delta t$$

and the concentrations of all species are given by

$$\mathrm{[VA]}(t_1) = \mathrm{[VA]}(t) - v(t) \times \Delta t,\ \mathrm{[MeO^-]}(t_1) = \mathrm{[MeO^-]}(t) - v(t) \times \Delta t,\ \mathrm{[VO^-]}(t_1) = \mathrm{[VO^-]}(t) + v(t) \times \Delta t \quad \text{and} \quad \mathrm{[AcOMe]}(t_1) = \mathrm{[AcOMe]}(t) + v(t) \times \Delta t$$

The concentrations of the MeOH and VOH which are not directly involved in reaction 1 do not vary in this step but the acid−base equilibrium 2 is no longer satisfied. A reequilibration step at constant time which keeps the overall concentrations of methanol and vinyl alcohol ($\mathrm{[MeOH] + [MeO^-] = MeOH_{total}}$ and $\mathrm{[VOH] + [VO^-] = VOH_{total}}$) is then performed according to the analytical solution of the mass action law and electroneutrality equations

$$\mathrm{[MeO^-]} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad \text{with } a = K - 1,\ b = K \times \mathrm{VOH_{total}} + \mathrm{MeOH_{total}} - (K-1)\mathrm{[Na^+]}$$

and

$$c = -\mathrm{MeOH_{total}} \times \mathrm{[Na^+]};\ \mathrm{[MeO^-]} = \frac{-c}{b} \quad \text{if } K = 1$$

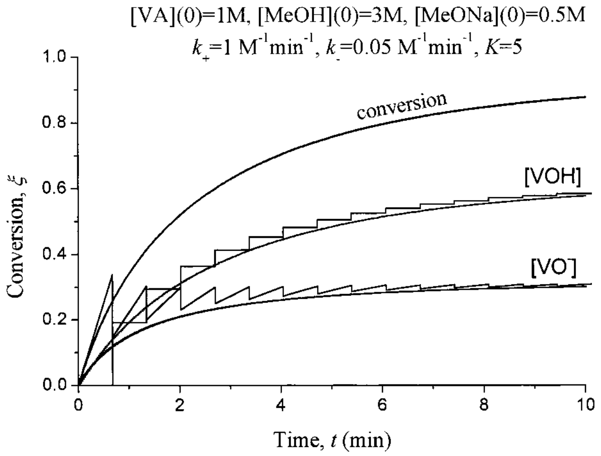


Figure 9. Results of a numerical simulation as explained in the text. The serrated lines are the concentrations of VOH and VO$^-$ as calculated with a large time step whereas the lines that appear continuous were calculated with a small time step.

The simulation of the reaction course was performed step-by-step from the initial conditions [VA](0), [MeOH](0), and[MeO$^-$](0) = [Na$^+$]. The result of such a simulation is given in Figure 9 where the conversion and the concentrations of VO$^-$ and VOH have been calculated for different time steps Δt; the variations of the concentrations of VO$^-$ and VOH at the reaction and reequilibration steps can be seen for the calculation performed with large time steps. The two methods gave identical results, but only the numerical simulation could be extended to the case of solvolysis with sodium hydroxide.

A similar simulation could be done for the solvolysis with sodium hydroxide where the 6 reactions and equilibria of Scheme 1 have to be taken into account. In this simulation, the reequilibration step was also calculated numerically because of the complexity of the equations.

Comparison with the Experiment. To find out the best fit of the simulated kinetic with the experimental data, error maps were calculated. In the case of the solvolysis in anhydrous conditions, k_+ could be determined from the slope of $\ln(1 - \xi)$ as a function of time t and the values of k_- and K remained to be determined. Thus, the mean square deviation for a kinetic experiment with N data points

$$\text{error} = \frac{1}{N-2}\sqrt{\sum_{i=1}^{N}(\xi_{i,\,\text{exp}} - \xi_{i,\text{calc}})^2}$$

was plotted as a function of k_- and K, giving an error map as shown in Figure 4.

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