Characteristics of the alkaline hydrolysis of N-vinyl and acrylic polymers

N. A. Lavrov

St Petersburg State Technological Institute (Technical University)

The carrying out of reactions in chains of polymers containing different functional groups makes it possible to expand the range of known polymers and to produce new polymeric materials with valuable properties. Taking into account the selective susceptibility of different polymers to acidic and alkaline hydrolysis and the influence of the reaction conditions (the medium, the concentration of the hydrolysing agent, the temperature) on the stability of the monomer units, it is possible to carry out the targeted hydrolysis of copolymers with retention or modification of individual units. In the course of the present work, a study was made of features of the alkaline hydrolysis of homopolymers based on N-vinyl and acrylic polymers: poly-N-vinylsuccinimide (PVSI), poly-N-vinyl-3(5)-methylpyrazole (PVMP), poly-2-hydroxyethyl methacrylate (PHOEMA), polybutyl acrylate (PBA), VSI-HOEMA, VMP-HOEMA, and VSI-BA copolymers, and also polyvinyl acetate (PVA) and VMP-BA and HOEMA-VA copolymers in aqueous and in aqueous organic media.

It is known [1] that, when reactions are carried out in PVSI chains, the imide ring readily opens under the action of solutions of alkalis and organic primary and secondary amines, with the formation of water-soluble derivatives of N-vinylamidosuccinic acid (VASA):

\[
\text{CH}_2 - \text{CH} - \text{NH - C} = \text{O} \quad \text{NaOH} \quad \text{CH}_2 - \text{CH} - \text{NH - C} = \text{O}
\]

By carrying out ion exchange on a KU-2 cation exchanger, or using the high-voltage electrodialysis method [2], hydrolysed units are converted from saline into acidic form:

\[
\text{CH}_2 - \text{CH} - \text{NH - C} = \text{O} \quad \text{KU-2} \quad \text{CH}_2 - \text{CH} - \text{NH - C} = \text{O}
\]

The hydrolysis of PVSI with a 5% aqueous solution of sodium hydroxide at 60°C is completed within 1 h [3]. At higher concentrations of the hydrolysing agent and elevated temperatures, the hydrolysis of PVSI is more extensive, with the formation of polyvinylamine. For example, during the hydrolysis of PVSI with a 10N aqueous solution of NaOH at 85–90°C for 30 h, a polymer containing up to 82% primary amine groups is obtained [4]. The formation of amine groups was also observed using concentrated acids as the hydrolysing agent at temperatures of 110–180°C [1], while, under milder conditions, the imide ring in VSI polymers does not open during acidic hydrolysis.

The selective resistance of the imide ring to the action of hydrolysing agents makes it possible to produce different polymer analogues on the basis of VSI polymers. For example, in a study of the acidic and alkaline hydrolysis of VSI–VA copolymers it was established [5] that, depending on the hydrolysis conditions, various products are formed. When acidic hydrolysis is carried out under certain conditions, the imide ring does not open and the reaction proceeds only by the VA units. In alkaline solutions, saponification proceeds by both functional groups:
In previous studies, the hydrolysis of PVSI was carried out in aqueous media under heterogeneous conditions. In the present work, a study was made of the alkaline hydrolysis of homopolymers and copolymers of VSI both under heterogeneous and under homogeneous conditions in aqueous organic media, varying the nature of the organic solvent and the reaction temperature.

The hydrolysis of PVSI can be regarded as a reaction of nucleophilic substitution. Carbon atoms of the carbonyl groups, which have a large deficit of electrons (charges on atoms of +0.896 and +0.912), undergo attack by the nucleophilic agent — the hydroxyl ion. The organic solvent, being a cocomponent of the medium, not only creates conditions for a homogeneous reaction but also, interacting with VSI units in the macrochain, can affect the hydrolysis rate. The organic solvents used were dioxane, dimethylformamide (DMF), and dimethyl sulphoxide (DMSO), in which PVSI and products of alkaline hydrolysis are soluble.

It was established [6] that, with increase in the dielectric permittivity of the organic solvent used (dioxane 2.21, DMF 37.78, DMSO 46.45 [7]), the initial rate of the reaction increases (Figure 1). The rate constants of the reactions at 20°C were as follows: in dioxane 0.19 l mol⁻¹ s⁻¹, in DMF 0.43 l mol⁻¹ s⁻¹, and in DMSO 0.87 l mol⁻¹ s⁻¹, with a PVSI concentration of 0.023 mol l⁻¹ and a sodium hydroxide concentration of 0.034 mol l⁻¹.

The higher rate of acidic hydrolysis in the presence of DMSO can be explained by the interaction between carbonyl groups of the VSI units and sulphoxide groups of the DMSO molecules, leading to charge redistribution on the atoms and promoting acceleration of the attacking action of the hydroxyl ions on the carbon atoms of the carbonyl groups by the following scheme:

\[
\text{CH}_3-\text{CH}_{\delta+}-\text{CH}_2-\text{CH}_{\delta+}-\text{CH}_3
\]
\[
\text{CH}_3-\text{CH}_{\delta+}-\text{CH}_2-\text{CH}_{\delta+}-\text{CH}_3
\]

Carrying out the process under homogeneous conditions makes it possible to achieve almost 100% conversion of the VSI units into units of VASA salt within 45–60 min.

The alkaline hydrolysis of PVSI obeys the kinetic laws governing second-order reactions. The activation energy of PVSI hydrolysis in an aqueous dioxane medium amounts to 36.5 kJ mol⁻¹ [8].

From published data it is known that acrylate and methacrylate polymers are noted for considerably greater hydrolytic stability. In [9] it was shown that alkaline hydrolysis of PHOEMA proceeds at a sufficient rate only at temperatures above 100°C. However, the authors of this study confined themselves only to an examination of the qualitative features of the hydrolysis of PHOEMA.

In the present investigations, a study was made of the kinetics of alkaline hydrolysis of PHOEMA and VSI–HOEMA copolymers at lower temperatures. It was established (Figure 2) that at 20°C the hydrolysis of PHOEMA does not occur even under homogeneous conditions. With increase in temperature, the reaction proceeds at a low rate.

Reactions of alkaline hydrolysis of poly(meth)acrylates generally obey the kinetic laws governing second-order reactions, for which the rate constant is calculated by means of the formula [10]

\[
k = \frac{2.303}{\tau(b-a)} \ln \left( \frac{a(b-x)}{b(a-x)} \right)
\]

where \(a\) is the initial concentration of polymer (mol l⁻¹), \(b\) is the initial concentration of alkali (mol l⁻¹), \(x\) is the concentration of hydrolysed units of the polymer (mol l⁻¹), and \(\tau\) is the duration of the reaction (s).
For the hydrolysis of PHOEMA, a rectilinear time dependence of \(\lg (b - x)/(a - x)\) is observed (Figure 3), which is a necessary condition for carrying out second-order reactions [10]. The rate constant of the reaction at 60°C amounted to \(2.3 \times 10^{-4}\), and at 80°C it was \(1.1 \times 10^{-3}\) l mol\(^{-1}\) s\(^{-1}\).

Comparison of the results obtained with data on the hydrolysis of PVSI indicates that, under identical concentration conditions, the rate constant of the alkaline hydrolysis of PVSI even at 20°C is almost 800 times higher than that of the alkaline hydrolysis of PHOEMA at 80°C.

This gives grounds for assuming that, in the case of the hydrolysis of VSI-HOEMA copolymers at 20°C, the reaction will occur only by the imide units of VSI, whereas HOEMA units will not be hydrolysed.

A study of the kinetics of hydrolysis of copolymers and the results of studying the products obtained by means of IR spectroscopy confirmed the correctness of this assumption.

It was established [11] that the dependence of the degree of hydrolysis of copolymers on the duration of the process is determined by the composition of the copolymers and by the conditions under which the process is carried out (Figure 4). Homogeneous hydrolysis (Figure 4a), which can be realised in a wide range of compositions of the copolymers in mixtures of water with polar organic solvents (DMSO, DMF), proceeds considerably more rapidly than does heterogeneous hydrolysis (Figure 4b), which can be carried out directly in aqueous solutions of alcalis. However, a characteristic of both homogeneous and heterogeneous hydrolysis is the fact that the maximum achievable degree of hydrolysis does not exceed the content of VSI units in the copolymer, i.e. almost complete splitting of the VSI units is observed, while the HOEMA units are not hydrolysed. From Figure 4 it can be seen that, after the achievement of a 70–80% degree of hydrolysis of VSI units, slowing down of the reaction occurs, which is characteristic of reactions of hydrolysis of (co)polymers of VSI. As hydrolysed units are formed in the copolymer chain, remaining unhydrolysed groups may turn up between two ionised COO\(^{-}\) groups, which repel HO\(^{-}\) ions, preventing their interaction with the carbon atom of the carbonyl group. To obtain a 100% degree of hydrolysis, the reaction must be carried out at a higher temperature, which promotes greater mobility of macromolecules of the side groups.

Carrying out hydrolysis under homogeneous conditions makes it possible to achieve an almost 100% conversion of VSI units into VASA units within a comparatively short time (Figure 4a), whereas the process of conversion under heterogeneous conditions proceeds much more slowly (Figure 4b).

However, homogeneous hydrolysis has an essential shortcoming, consisting in the need to isolate the reaction product by precipitation in a 20–30-fold volume of acetone in view of the impossibility of carrying out the reaction of ion exchange in an aqueous organic medium, and therefore heterogeneous hydrolysis is technologically more convenient.

In the IR spectrum of the hydrolysed copolymer, the 1750 cm\(^{-1}\) absorption band characteristic of the carbonyl group of the imide ring is absent, and 1630 and 1550 cm\(^{-1}\) absorption bands appear, corresponding to vibrations of the amide group \(-\text{CONH}-\), and a 2600 cm\(^{-1}\) band corresponding to vibrations of the \(-\text{OH}\) group in the carboxyl group (Figure 5).
Thus, carrying out the hydrolysis of VSI–HOEMA copolymers in aqueous or aqueous organic mixtures at 20˚C, it is possible to carry out a targeted reaction only by the VSI units, leaving the HOEMA units unchanged, producing compounds containing ionogenic carboxyl and non-ionogenic hydroxyl groups:

![Figure 4](image)

**Figure 4** Dependence of degree of hydrolysis X (%) of VSI–HOEMA (co)polymers in 2.5:1.0 DMSO–water mixture (a) and in water (b) on duration of process τ (h) at 20˚C. Composition of VSI–HOEMA (co)polymers (mole fractions): 1 — PHOEMA; 2 — 0.07:0.93; 3 — 0.45:0.55; 4 — 0.70:0.30; 5 — PVSI. Concentration: (co)polymer 0.023 mol l⁻¹; NaO 0.034 mol l⁻¹

![Figure 5](image)

**Figure 5** IR spectra of VSI–HOEMA copolymer containing 0.70 mole fractions of VSI units (1) and product of its alkaline hydrolysis in acid form (2). Tr — transmission (%); ν — wave number (cm⁻¹)

Considering that one of the methods of producing soluble VSI–HOEMA copolymers is based on copolymerisation in a DMSO solution, it is possible to combine the processes of synthesis and hydrolysis of copolymers in the same reactor, initially carrying out copolymerisation, and then, without isolating the copolymer, introducing an aqueous solution of alkali and carrying out hydrolysis [12].

The alkaline hydrolysis of VSI–BA copolymers proceeds in a similar way. In view of the higher hydrolytic stability of BA units (the rate constants of hydrolysis of PBA in a dioxane–water mixture amounted to 7.68 x 10⁻⁵ l mol⁻¹ s⁻¹ at 20˚C, to 2.47 x 10⁻⁴ at 40˚C, and to 8.09 x 10⁻⁴ l mol⁻¹ s⁻¹ at 60˚C with a PBA concentration of 0.022 mol l⁻¹ and a sodium hydroxide concentration of 0.033 mol l⁻¹), the reaction proceeds mainly by VSI units. BA units are retained in hydrolysed copolymers, as indicated by the presence in the IR spectra of a 1460 cm⁻¹ band corresponding to the –C₄H₉ group, and here the intensity of the 1100–1150 cm⁻¹ and 1250–1300 cm⁻¹ bands characteristic of acrylates hardly varies.

The activation energy of the hydrolysis of VSI–BA copolymers in a dioxane–water mixture in the temperature range 20–60˚C amounted to 38.4–38.8 kJ mol⁻¹ [13]. That is, as during the hydrolysis of VSI–HOEMA copolymers, in the case of alkaline hydrolysis of VSI–BA copolymers it
is possible to carry out targeted saponification only of the VSI units, retaining the BA units, with the production, after ion exchange, of VASA–BA copolymers. The solubility of VASA–HOEMA and VASA–BA copolymers in water or in aqueous organic mixtures is determined by the content of VASA units. Water-soluble copolymers should contain at least 0.60 mole fractions of VASA.

The VMP units in the polymer chain, in contrast to VSI units, possess a higher hydrolytic stability. The alkaline hydrolysis of homopolymer VMP at 20–90°C does not occur either under heterogeneous conditions (in aqueous solutions of sodium hydroxide) or under homogeneous conditions (in aqueous methanol solutions of sodium hydroxide). The IR spectrum of the hydrolysed polymer (Figure 6) is identical to the spectrum of the initial polymer, and it retains the 1530 cm⁻¹ absorption band corresponding to stretching vibrations of substituted heteroaromatic five-membered rings and the 780 cm⁻¹ absorption band corresponding to out-of-plane vibrations of the ring.

It was established that, at a temperature of up to 60°C, heterogeneous alkaline hydrolysis of VMP–HOEMA copolymers hardly occurs.

In order to select the conditions of alkaline hydrolysis of VMP–VA and HOEMA–VA copolymers, a study was made of the kinetics of alkaline hydrolysis of homopolymer VA in aqueous methanol media.

It is known that PVA is hydrolysed fairly readily under homogeneous conditions in a methanol solution, and the rate constant of hydrolysis amounts to 5.7 ¥ 10⁻³ l mol⁻¹ s⁻¹ [14]. In carrying out the present work it was noted [15] that, as the homogeneity of the medium deteriorates by the addition of water to the methanol solution of the alkali, the rate of the reaction decreases (Figure 7a). In an aqueous solution of alkali, the rate of the reaction is minimum. Increase in temperature promotes an increase in the hydrolysis rate (Figure 7b).

![Figure 6](image)

**Figure 6** IR spectrum of hydrolysed PVMP. *Tr* — transmission (%); *ν* — wave number (cm⁻¹)

![Figure 7](image)

**Figure 7** Dependence of degree of hydrolysis X (%) of PVA on duration of reaction τ (min). PVA concentration 0.09 mol l⁻¹. *a* — in 0.1N aqueous methanol solution of NaOH at temperature of 20°C; water:methanol ratio: 1 — 38:62; 2 — 50:50; 3 — 87:13. *b* — in 0.1N aqueous solution of NaOH; reaction temperature: 1 — 60°C, 2 — 20°C.
The values of the rate constants of the hydrolysis of PVA are presented in Table 1. They are in good agreement with published data [14] and indicate that the rate constant of hydrolysis of VA units, $k$, under homogeneous conditions at 30 $^\circ$C is almost 6 times higher than that of the hydrolysis of HOEMA units under homogeneous conditions at 80 $^\circ$C. As the water content of the aqueous methanol solution increases, the values of $k$ decrease. However, even in this case their values at 20 $^\circ$C are comparable with the rate constants of the hydrolysis of HOEMA units under homogeneous conditions at 60–80 $^\circ$C. Under heterogeneous conditions, PHOEMA is not hydrolysed at the given temperature, which is confirmed by data of IR spectroscopy.

The difference in the values of the rate constants of hydrolysis of HOEMA and VA units in homopolymer chains creates conditions for targeted hydrolysis by the VA units during the combined saponification of VA and HOEMA units in the copolymer. It was established in experiments that, during the heterogeneous hydrolysis of copolymers with a 0.1N aqueous solution of NaOH, only the VA units are hydrolysed. In view of the fact that the relative activity of HOEMA in copolymerisation is considerably higher than the activity of VA ($r_{\text{HOEMA}} = 14.26$, $r_{\text{VA}} = 0.01$), the microstructure of the copolymers consists mainly of single VA units separated by a few HOEMA units. This facilitates the interaction of VA units with the HO$^-$ ion and makes it possible to carry out their practically 100% hydrolysis. Therefore, the maximum achievable degree of hydrolysis corresponds to the content of VA units in the copolymer (Figure 8).

Thus, it was established that the heterogeneous alkaline hydrolysis of HOEMA–VA copolymers makes possible targeted modification by the VA units with the formation of copolymers of vinyl alcohol (VAL) with HOEMA:

![Figure 8](image-url)
By varying the composition of the polymers and the degree of hydrolysis, it is possible to produce copolymers of VAl with HOEMA that are soluble in water, in organic solvents (DMF, DMSO, pyridine), or in aqueous organic mixtures (water–ethanol, water–acetone, water–DMF, etc.).

Only VA units are hydrolysed in copolymers of VMP with VA [16]. Here, the hydrolysis rate of VMP–VA copolymers is higher than that of VA homopolymers synthesised under similar conditions (Figure 7a and Figure 9). This seems to be due to the greater accessibility of the VA units in the copolymer to the action of the hydrolysing agent, which is due to the microstructure of the macrochains ($r_{VMP} = 6.90$, $r_{VA} = 0.03$). Single VA units, alternating with blocks consisting of VMP units, are hydrolysed more readily, and their maximum achievable degree of hydrolysis is close to the content of VA units in the copolymers, reaction by which proceeds with an almost 100% degree of conversion. As a result of the hydrolysis of VMP–VA copolymers, VMP–VAl copolymers are formed:

They comprise a white or yellowy powder. Depending on the composition, it is possible to produce products that are soluble in organic solvents or in water.

Thus, the use of alkaline hydrolysis opens up wide scope for modifying the copolymers studied. As a result of the investigation carried out, the conditions for homogeneous and heterogeneous hydrolysis have been determined, and the rate constants of hydrolysis of (co)polymers in various media have been calculated. It has been shown that, by varying the composition of the (co)polymers being hydrolysed and the process conditions, it is possible to carry out targeted hydrolysis, modifying or retaining the individual monomer units in the macrochain, with the production both of water-soluble (co)polymers and of (co)polymers that are insoluble in water but soluble in aqueous organic mixtures. The production of copolymers with new functional groups makes it possible to broaden the area of practical application of known copolymers.

REFERENCES


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