

# Alcoholysis of Copolymers of Vinyl Acetate with Itaconic Acid

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## Synopsis

We studied alcoholysis of vinyl acetate and itaconic acid (up to 8.5 mol %) copolymers. We obtained the copolymers both by single and continuous addition of the second comonomer, and carried out the alcoholysis in methanol and methanol-gasoline medium at temperature 30°C using sodium hydroxide as catalyst. We established that the presence of itaconic sequences in the vinyl acetate polymer chain in an amount of 1.5–2 mol % causes significant reduction in the viscosity of methanol solutions without greatly affecting the molecular weight of the copolymer. The alcoholysis of random copolymers, containing not more than 4 mol % itaconic sequences takes place at a higher rate. The vinyl acetate-vinyl alcohol copolymer, containing groups of itaconic acid has better surface activity. This is more clearly expressed in the case of random copolymers.

## INTRODUCTION

The most widely used commercial method for the production of poly(vinyl alcohol) (PVAL) is the alkaline alcoholysis of poly(vinyl acetate) (PVA). Compared to the other processes, this method has several advantages, with respect to both the kinetics of the process and the quality of the product.<sup>1</sup>

The rate of alcoholysis and the structure of the obtained PVAL are closely related to the solvation of the functional groups present.<sup>2</sup> The solvation of PVA is carried out through the hydrogen bond between the carbonyl group of the vinyl acetate sequences and the hydroxyl group of methanol. The presence of itaconic acid (IA) sequences in the polymer chain should have a significant effect on the degree of solvation and this might lead to changes in the rate of alcoholysis. On the other hand, it should be expected that the presence of anionic hydroxyl groups in PVAL will improve its surface-active, resp. dispersing, properties.<sup>3</sup>

Partially alcoholized poly(vinyl acetate) containing 27–30 mol % residual acetate groups (ester value 250–300) greatly reduces the surface tension on the phase boundary for vinyl chloride–water systems and for this reason is used as stabilizer in vinyl chloride polymerization.<sup>4,5</sup> There are, however, some problems arising during the preparation of such products, mainly connected with filtration and drying stages, due to the fact that in the reaction medium particles swell and stick to one another. Besides that, when producing lower molecular polymers the loss with filtrate is rather heavy. In order to avoid these problems, the alcoholysis should preferably take place in a methanol–aliphatic hydrocarbon medium (heptane, hexane, gasoline).<sup>6</sup> The solubility of these compounds in methanol is limited and they do not dissolve either the initial or the final product. In such a reaction medium the phase transition

takes place at a lower degree of alcoholysis, which facilitates the production process. It was established that in a methanol-gasoline medium the alcoholysis rate is higher due to the reduced degree of solvation.<sup>1</sup>

The aim of our study is to investigate the kinetics of alkaline alcoholysis of vinyl acetate copolymers with small amounts of itaconic acid in a methanol-gasoline medium as well as the comonomer's influence on the surface-active properties of the obtained products.

### EXPERIMENTAL

The initial copolymers of vinyl acetate (VA) and IA were prepared in methanol solution at monomers/solvent ratio 2:1. The reaction was initiated by bis(*tert*-butyl cyclohexyl) peroxydicarbonate, 0.2% based on monomers. IA was added in two different ways, at the beginning of the process and continuously throughout it in an amount not exceeding 8.5 mol %, based on monomer mixture.<sup>7</sup>

The weight-average molecular weights of the initial products were determined by gel-permeation chromatography using polystyrene standards, tetrahydrofuran as eluent, and at temperature 45°C. The viscosity of the polymerizate at 20°C was determined using a Hoeppler viscosimeter.

The alcoholysis was carried out in methanol and methanol-gasoline medium at a temperature of 30°C, with polymer/solvents ratio 1:5 and sodium hydroxide as catalyst (7% methanol solution). The catalyst was added after neutralizing the itaconic groups with the catalyst solution. The process was terminated by introducing glacial acetic acid until pH 7 was established. The obtained suspension was filtrated, washed, and dried under vacuum at 50°C. The rate of alcoholysis was determined by the changes in the ester value, defined in accordance with standard BDS 9306-71.

The synthesis was performed using monomer grade VA and IA comonomers. Methanol, sodium hydroxide, and acetic acid were analytically pure products and extraction gasoline was bp 67-85°C fraction.

The surface tension was determined on 1% aqueous solutions of vinyl alcohol copolymers using Tensiometer K 8600E in accordance with BDS 12281-81.

### RESULTS AND DISCUSSION

The presence of small amounts of itaconic groups in vinyl acetate polymer chains significantly changes the degree of solvation. This agrees with the fact that the viscosity of the obtained polymer solutions is reduced, while at the same time the molecular weight of the corresponding products remains almost unchanged, as illustrated in Table I.

As a result of the reduced degree of solvation, the intra-molecular hydrogen bonds between carbonyl groups of acetates and the already formed—OH groups are strengthened. Thus the reactivity of the ester groups, resp. the rate of alcoholysis, is also increased (Fig. 1).

It should be expected that the way of distribution of itaconic sequences along the polymer chain will affect the rate of the process. In the case of products, obtained by single IA addition, the rate of the alcoholysis remains almost the same (curves 2 and 3). For products with random distribution,

TABLE 1  
Effect of IA on Viscosity of the  
Polymerizate and Molecular Weight  
of the Copolymer

IA content (mol %)	Method of IA addition	Viscosity of polymerizate (Pa s)	$\bar{M}_w$
—	—	88.0	144,000
2	Single	21.0	130,000
2	Continuous	17.8	143,000

prepared by continuous IA addition throughout the polymerization process, the rate of alcoholysis increases. This increase is more evident in the initial stage of the process (curve 1). The above indicates that the carboxyl ions affect the activity of the neighboring acetate groups.

It was of interest to compare these results with the results, obtained during the alcoholysis of vinyl acetate copolymer, containing 2 mol % maleic groups. PVAL, based on such a product, is recommended as an excellent stabilizer for suspension polymerization of vinyl monomers.<sup>3</sup> It was established that the alcoholysis of VA and maleic anhydride copolymers proceeds at a lower rate compared with the corresponding IA copolymer (curves 2 and 6). Probably the different effect of itaconic and maleic groups on the kinetics of the process is due both to steric differences and the different degree of dissociation of the salts formed in the alkaline medium.

When the content of IA in the copolymer exceeds 4 mol %, the introduction of the alkaline solution in the reaction medium causes salting out of the sodium salt formed. Actually the process is carried out in suspension and at a lower rate (curves 4 and 5) because of the troubled access to the catalyst. In this case also the rate of the alcoholysis of random copolymers is higher

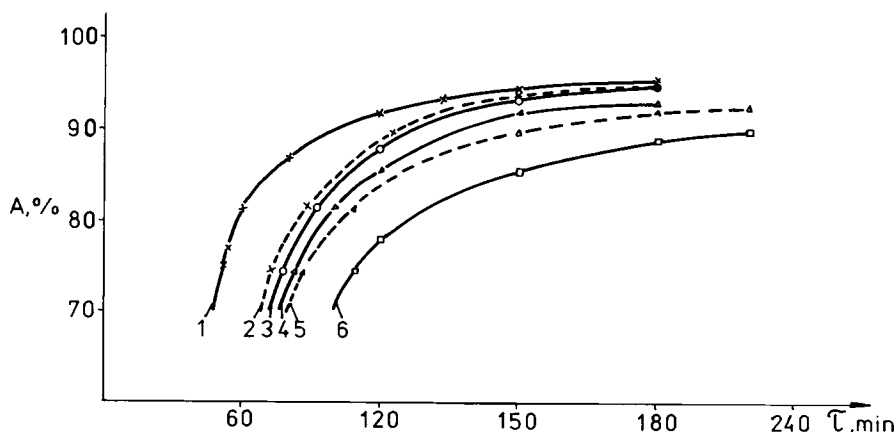


Fig. 1. Kinetics of alcoholysis of VA copolymers with IA and MA Polymer ÷ solvent ratio, 1 ÷ 5; temperature, 30°C; catalyst, 0.4%; (1) 2 mol % IA, continuous addition; (2) 2 mol % IA, single addition; (3) VA homopolymer; (4) 8.5 mol % IA, continuous addition; (5) 8.5 mol % IA, single addition; (6) 2 mol % MA, single addition.

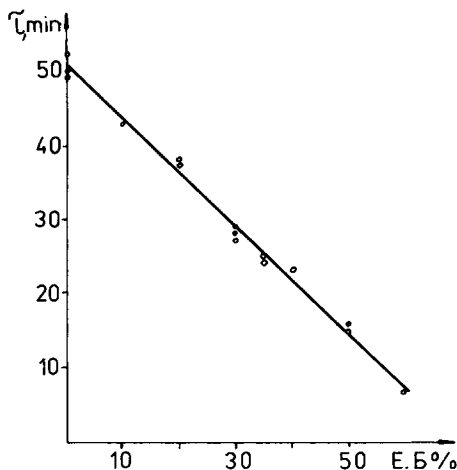


Fig. 2. Effect of EG concentration on phase transition time Polymer ÷ solvents ratio, 1 ÷ 5; temperature, 30°C; catalyst, 0.5%; itaconic sequence content in the copolymer, 2 mol %.

compared to that of products, obtained by adding the whole amount of comonomer at the beginning of the process.

In order to isolate copolymers with high residual acetate group content (27–30%), the process was carried out in a medium of methanol and extraction gasoline (EG). As the content of EG in the solvent mixture increases, the solubility of the copolymer in the system decreases and the phase transition (gel forming) takes place at higher residual acetate group content. In this way powdered products with low alcoholysis degree can be obtained. The time from catalyst addition to gel formation is reversely proportional to EG content (Fig. 2).

The solubility of EG in methanol is limited—29–30%. When greater amounts are used, the process takes place in heterogeneous medium. Due to the relative increase of the concentration of PVAI solution, the alcoholysis rate increases, depending on the EG content (Fig. 3, curves 1–3).

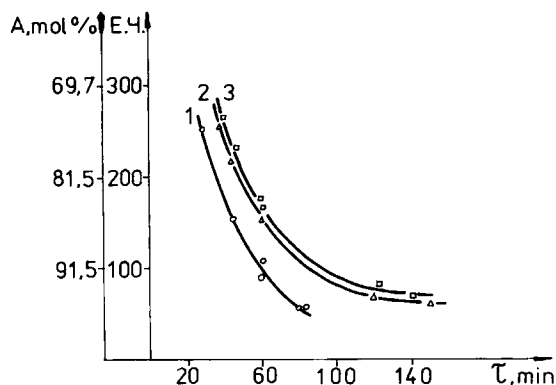


Fig. 3. Effect of EG concentration in the solvent mixture on the kinetics of the alcoholysis. Polymer ÷ solvents ratio, 1 ÷ 5; temperature, 30°C; catalyst, 0.5%; IA content, 2 mol %; (1) 50% EG; (2) 35% EG; (3) 30% EG.

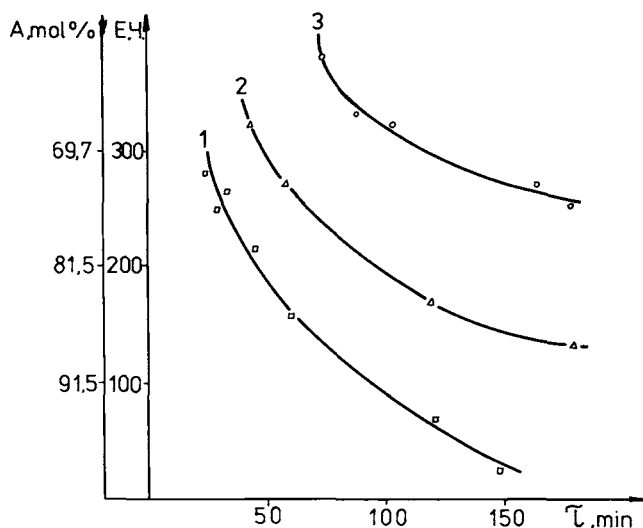


Fig. 4. Effect of catalyst concentration on the rate of the alcoholysis process. Polymer ÷ solvents ratio, 1 ÷ 5; temperature, 30°C; EG, 30%; itaconic sequence content, 2 mol %; (1) 0.5% catalyst; (2) 0.3% catalyst; (3) 0.2% catalyst.

The effect of catalyst amount on the kinetics of the process for EG content 30% was studied (Fig. 4). At 0.5% catalyst, the alcoholysis takes place very intensively. Small deviations in the reaction time lead to significant changes in the chemical composition of the product (curve 1). At 0.2% catalyst, much more time is necessary for the preparation of the same product in comparison

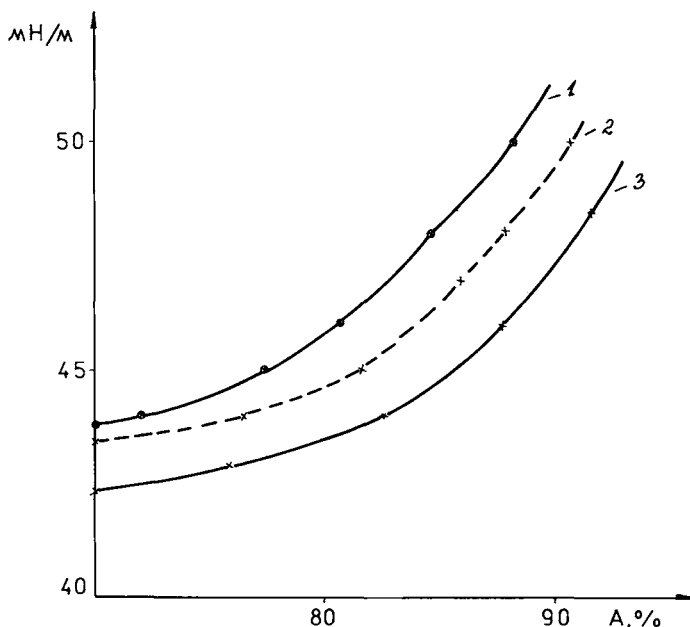


Fig. 5. Dependence between surface tension of 1% solutions of vinyl alcohol copolymers and the degree of alcoholysis: (1) without IA; (2) 2 mol % IA, single addition; (3) 2 mol % IA, continuous addition.

with the first case (curve 3). When 0.3% catalyst was used, the process rate was high and at the same time smooth enough to be interrupted when the desired degree of alcoholysis was reached (curve 2).

The surface activity of poly(vinyl alcohol) products is of great importance when they are used as stabilizers of disperse systems. The content of residual acetate groups, resp. the degree of alcoholysis [ $A$  (%)], has significant effect on this activity. As the percentage of unreacted acetate groups increases, the surface activity becomes higher (Fig. 5, curves 1–3). The results from our investigations showed that the presence of IA in the polymer chain enhances the surface activity (curves 2 and 3) in respect to polymers, which do not contain IA at the same degree of alcoholysis (curve 1). The amount and the way of distribution of itaconic sequences in the copolymer also affects the surface activity. The even distribution of the comonomer along the polymer chain reduces to a greater extent the surface activity of the aqueous solutions (curve 3). Amounts such as 2 mol % are found to be effective.

### CONCLUSION

By introducing IA in the vinyl acetate polymer chain in an amount 1.5–2 mol %, the viscosity of methanol solutions is greatly reduced without affecting the molecular weight of the polymer.

The alcoholysis of polymers with random distribution of the itaconic sequences (up to 4 mol %) takes place at a higher rate.

The vinyl acetate–vinyl alcohol copolymers, containing IA, have a better surface activity. This is more clearly expressed in the case of random copolymers.

### References

1. M. E. Rosenberg, *Polimeri na Osnove Vinilacetata*, Chimia, Leningrad, 1983, p. 174.
2. V. A. Kuznetzova, M. E. Rosenberg, et al., *Viskomol. Soed.*, **23** (A) (8), 1770 (1981).
3. U. S. Pat. 4380442 (1983).
4. Nilsson et al., *J. Vinyl Technol.*, **7** (3), 112–119 (1985).
5. D. Padovan, D. Woods, Hamilton, ON, Canada, JChE Symposium Series, N. 252, 1986, pp. 91–99.
6. Invention certificate USSR, 211091 (1969).
7. L. Kotzeva and R. Mateva, *J. Polym. Sci.*, to appear.

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