

Gel-free process of synthesis of poly(vinyl alcohol)

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It is known that the synthesis of poly(vinyl alcohol) (PV) by alcoholysis of poly(vinyl acetate) (PVA) in MeOH in the presence of alkaline catalysts is accompanied by a sharp change in the phase state of the system resulting in gel formation.^{1,2} A consequence of this very undesirable process is a decrease in the reaction rate and the limiting degree of conversion. It has been considered until recently that the necessary conditions for a high conversion of alcoholysis to attain are the use of anhydrous alcohol (total water content in the system <0.7 wt.%)¹ and an elevated temperature (40–60 °C) of the last step of the reaction. The process of PV synthesis by alkaline hydrolysis of PVA in water is also known.³ It occurs from the very beginning under heterogeneous conditions and is also accompanied by gel formation. The duration of the process is several hours. An excess of alkali (>1.1 moles per mole of elementary units) is required to achieve a high degree of conversion.

We established that, when water-alcoholic mixtures are used as media, the polymer-analogous transformation of PVA into PV in the presence of NaOH occurs with a high rate up to a high degree of conversion even at 20 °C without gel formation. In a typical experiment in a reactor with a stirrer, the time of synthesis was 30 min. The initial PVA was used as a 10% solution in a water-alcoholic mixture, and MeOH, EtOH, PrOH, or PrⁱOH served as alcohols. The alcohol/water ratio was varied from 40/60 to 90/10 wt.%, and the consumption of alkali (NaOH) ranged from 0.3 to 1 mole per mole of elementary units of vinyl acetate (VA). For the EtOH/H₂O (40 : 60 wt.%) system, the consumption of alkali corresponding to the achievement of 99.5% and 45.0% conversion was 0.5 and 0.3 moles per mole of elementary units, respectively. It follows from these data that in water-alcoholic media the alkaline hydrolysis of PVA occurs in addition to alcoholysis, both reactions making comparable contributions to the total conversion. Evidently, the change in the kinetic parameters of the process is caused by a change in the phase state of the system.

In order to confirm this assumption, we studied the triple phase diagrams for the initial PVA (Fig. 1) and copolymer containing 50% acetate groups in H₂O—EtOH

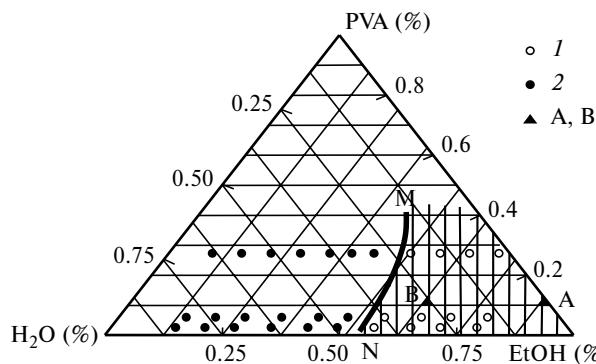


Fig. 1. Phase diagram of the PVA—EtOH—water system with experimental points corresponding to the solubility (1) and insolubility (2) zones. Points A and B are the beginning of the reaction route for saponification in a medium of anhydrous alcohol (A) and in a water-alcoholic medium (B).

mixtures (Fig. 2). The phase evolution of the reaction system with an increase in the conversion of saponification can be monitored by the transition of the binodal from the position NM (see Fig. 1) to the position N'M' (see Fig. 2). The binodal position was determined by the method of turbidity points. The route of PVA alcoholysis

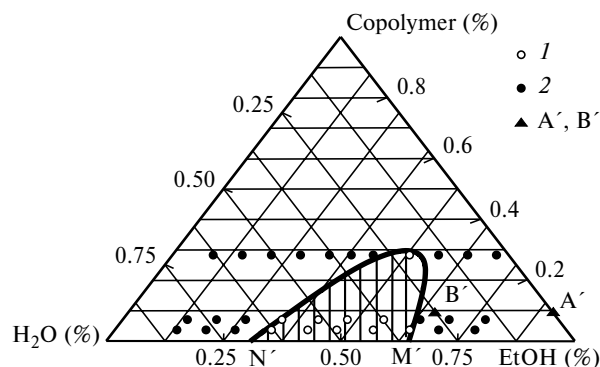


Fig. 2. Phase diagram for the copolymer containing 50% residual acetate groups. Experimental points correspond to the solubility (1) and insolubility (2) zones. Points A' and B' are the points of the reaction route for the 50% conversion of saponification in a medium of anhydrous alcohol (A') and in a water-alcoholic medium (B').

in the absence of water corresponds to the transition from point A, which is localized in the solubility zone of the diagram of the initial system (see Fig. 1) to point A' in the insolubility zone (see Fig. 2). Point A' is situated at a long distance to the binodal, namely, in the region where the probability of spinodal decay and related gel formation is high.⁴ When the process occurs in the presence of 26 wt.% water, the reaction route is reflected by the transition from point B (see Fig. 1) to point B' (see Fig. 2). In this section of the reaction route point B exists either in the solubility zone or shifts to the insolubility zone but is localized near the binodal where the probability of spinodal decay is low. Thus, controlling the phase state of the system, one can perform the process of PV synthesis *via* the mixed mechanism with a high rate and without gel formation.

References

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