

Reaction of polyvinyl alcohol with aluminum isopropoxide

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REACTION OF POLYVINYL ALCOHOL WITH ALUMINIUM ISOPROPOXIDE

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Abstract—The uncatalyzed and oxalic acid catalyzed modification of polyvinyl alcohol (PVA) with aluminium isopropoxide have been studied for reaction in a suspension of powdered PVA in boiling benzene. Isopropyl alcohol (IPA) formed during the reaction was removed by continuous distillation of an IPA-benzene mixture. The reaction was initially quite fast but slowed up rapidly and practically stopped when only 4–12% of the OH-groups had reacted. Thermogravimetric analysis (TGA) showed that products with 6.8 mole Al/100 mole VA exhibit a significant rise in decomposition temperature from 250 to 285°. The characteristics are attributed to the occurrence of vicinal OH-groups in PVA.

INTRODUCTION

We have reported the reaction of aluminium alkoxides with free OH-groups present in polyvinyl butyral [1, 2]. The modified polymer showed interesting properties including improved thermostability [3]. It appeared that the stability increased substantially by converting only very few OH-groups into alumoxy groups, suggesting that specific OH-groups are involved. It seemed to be interesting to study the incorporation of aluminium into polyvinyl alcohol (PVA) by reaction with aluminium alkoxides and to examine the products. Many modifications of PVA involving reactions of OH-groups have been studied, including esterification, sulphonation and phosphorylation [4] but reaction with aluminium alkoxides has not been reported.

EXPERIMENTAL

Reagents and solvents

The following (*pro analysi*) reagents and solvents were used: benzene, oxalic acid (Merck), aluminium isopropoxide m.p. 124° (Merck-Schuchardt), polyvinyl alcohol (Elvanol 71-30, Dupont, average degree of polymerization 1800, technical grade, powdered, particle size 5–10 μ).

Reaction of polyvinyl alcohol with aluminium isopropoxide

The reaction was carried out in suspension using a flask fitted with stirrer, thermometer and fractionating column (40 cm). PVA (1 mole of VA units) was introduced into the flask and a filtered solution of Al-isopropoxide (from 0.1 mole to 1 mole) in 600 ml benzene, was added. Then the suspension was stirred and heated.

The isopropyl alcohol (IPA) formed during the reaction was removed directly from the flask by continuous distillation of an IPA (b.p. 82.3°)—benzene (b.p. 80.1°) mixture at a constant rate of 0.5 cm³/min. These components form an azeotrope (b.p. 71.5°; 39.4 mole % IPA). During the reaction, benzene was added to compensate for loss by distillation. The first distillate was collected at approx 74°, then

the temperature rose as the IPA content of the distillate decreased, and finally practically pure benzene distilled off.

During the entire course of the reaction, the composition of the distillate was determined by GLC (Figs 1 and 2). The GLC analysis of the distillate was carried out on a gaschromatograph with a flame ionization detector (Hewlett-Packard type 5750, with carrier gas helium, liquid phase squalane, column temperature 130°). Retention times and peak areas were recorded on an electronic integrator (Hewlett-Packard type 3382). The distillate composition was confirmed by i.r.-analysis (Hitachi Grating Infrared Spectrophotometer, type EPI-G04).

After 5 hr (except for experiment 2, after 8 hr) the reaction was stopped and the product was filtered off, washed

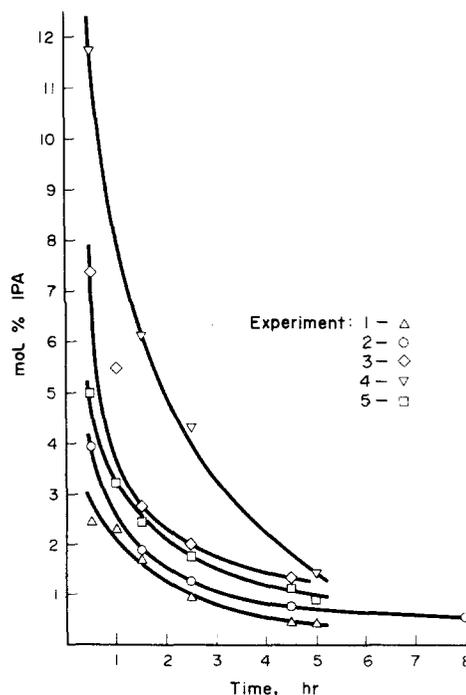


Fig. 1. IPA content of the instantaneous distillate, as a measure of the rate of conversion of OH-groups in PVA vs reaction time for experiment 1–5 (Table 1).

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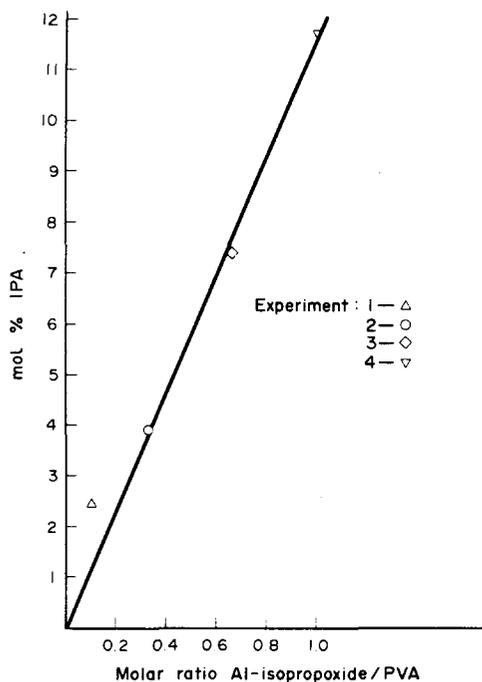


Fig. 2. IPA content of the distillate instantaneously collected after 30 min reaction time, as an approximate measure of the initial rate of conversion of OH-groups in PVA vs the initial molar ratio Al-isopropoxide/PVA for experiments 1-4 (Table 1).

with benzene and dried for 48 hr at 60° under vacuum. The aluminium content (*a*) of the polymer obtained was determined by calcination [5].

The results of the experiments and some blank determinations are given in Table 1. Determination of IPA in the total amount of distillate permits calculation of the degree of substitution (*s*) of the OH-groups in PVA (mono-, bi- and trifunctional reaction of Al-isopropoxide). From the latter value (*s*) combined with the weight % Al in the polymer (*a*), the average functionality (*n*) of Al-isopropoxide in reaction with OH-groups in PVA can be calculated from Eqn (1).

$$n = \frac{s(2700 - 204a)}{a(4400 - 60s)} \quad (1)$$

The number of moles Al/100 mole VA units (*s/n*) was calculated (Table 1).

Thermogravimetric analysis of the products

Dynamic TGA analysis was performed on a Mettler Vacuum Thermoanalyzer, heating rate 15°/min, in argon atmosphere (see Table 1).

RESULTS AND DISCUSSION

The reaction cannot easily be carried out in solution since suitable common solvents for PVA and Al-isopropoxide are not available. In some solvents (e.g. acetylacetone, ethyl acetoacetate, toluene and DMF) only dark products were obtained. The reaction was also carried out by melting a mixture of PVA and Al-isopropoxide. Although reaction occurred, the i.r. spectra of the products showed double bonds indicating decomposition. The best results were obtained in suspension by carrying out the reaction of PVA with Al-isopropoxide in boiling benzene.

The presence of strongly acidic catalysts e.g. hydrochloric acid cause discolouration of the reaction mixture and the products, but oxalic acid did not induce any unfavourable effects.

The products (PVA modified with Al-isopropoxide) appeared to be slightly soluble only in hot dichloroacetic acid, whereas the unmodified PVA was readily soluble in hot water, hot DMF, acetylacetone and cold dichloroacetic acid.

From the data in Table 1, it is evident that an increase of the Al-isopropoxide/PVA ratio does not significantly affect the aluminium content (*a* or *s/n*) of the products, at least for the uncatalyzed reactions and for the conditions studied. On the other hand, increase of the Al-isopropoxide/PVA ratio leads to an increased IPA production, i.e. increased degree of substitution (*s*) of OH-groups in PVA. As a consequence, the functionality (*n*) of Al-isopropoxide in reaction with OH-groups increases from 1.0 to 2.8 (maximum value 3.0).

As in many other modification reactions of PVA [6], the catalyst plays an important part. For the acid-catalyzed reaction (experiment 5), the Al-content of the product (*a* or *s/n*) increases significantly whereas the functionality (*n*) is the same as in the corresponding uncatalyzed reaction (cf. experiments 2 and 5).

Evidently, the catalyst increases the Al-content but does not affect the relative occurrence of primary, secondary and tertiary reactions of Al-isopropoxide

Table 1. Summary of experimental and computed data for some typical experiments

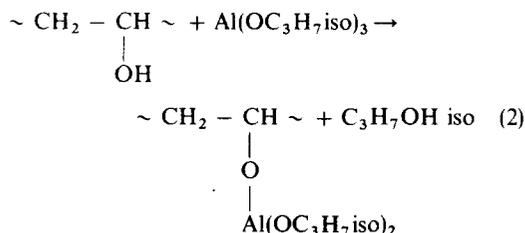
Exp. number	Initial molar ratio of Al-isopropoxide/PVA*	Al-content of products (<i>a</i>) in wt %	Degree of substitution of OH-groups in PVA† (<i>s</i>) in %	Functionality of Al-isopropoxide in reaction‡ (<i>n</i>)	Mole Al/100 mole VA (<i>s/n</i>)	Primary decomp. temperature, TGA (°C)
1	0.10	2.33	4.4	1.0	4.4	—§
2	0.33	2.76	5.9	1.1	5.4	250
3	0.66	2.77	8.2	1.6	5.1	250
4	1.00	2.46	11.6	2.8	4.1	250
5	0.33	3.41	7.5	1.1	6.8	285
6	PVA	0.00	0.0	—	—	250
7	Benzene + Al-isopropoxide	—	—	—	—	—

* 1 mole PVA = 1 mole VA units in 600 ml reaction mixture. † Calculated from the IPA content of the total distillate. ‡ Calculated according to Eqn (1). § Not determined. || Oxalic acid (3g) present as catalyst.

with PVA, while Al-isopropoxide seems to autocatalyze the secondary and tertiary reactions preferentially, at practically constant Al-content.

Figure 1 shows that in all cases the reaction rates decrease rapidly; after approx 5 hr, practically no further reaction occurs. The IPA production (see Fig. 2) suggests first order kinetics in Al-isopropoxide concentration but it should be noted that the reaction system is heterogeneous.

Examination of the TGA results (Table 1) reveals that only the catalyzed modification of PVA, leads to more thermostable products containing 6.8 mole Al/100 mole VA units. The reproducibility of the rise in decomposition temperature from 250 to 285° has been confirmed. Assuming only monofunctional reaction according to Eqn (2),



it follows that, in the product from experiment 5, one out of every fifteen OH-groups of PVA has reacted with Al-isopropoxide. It seems possible that only a few OH-groups, viz. those in the "head-to-head" configuration, are responsible for the primary decomposition on heating and that these vicinal OH-groups react with Al-isopropoxide more readily than the others.

This interpretation agrees with the conclusions of Flory and Leutner [7] about anomalous additions in vinyl polymerization. They reported that 2% anomalous additions, corresponding to 4% vicinal OH-groups, are likely in vinyl acetate polymerization. Since we have found a somewhat higher degree of alumoxy substitution (6.8%) necessary to give increased thermostability, it is probable that the alumoxy modification also stabilizes other labile OH-groups, e.g. end-groups and groups adjacent to unhydrolysed acetate groups, amounting to approx 2%.

The physical properties of alumoxy-polyvinyl alcohol will be further investigated. In addition, the reaction of PVA with other aluminium alkoxides will be dealt with.

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