Chemistry

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Abstract

Full Text

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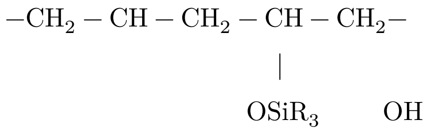
ON THE SYNTHESIS OF SILICON DERIVATIVES OF POLYVINYL ALCOHOL

Polyvinyl alcohol, as is known, is by its structure a 1,3-glycol containing a small amount of 1,2-glycol units.

For the purpose of modifying the properties of polyvinyl alcohol, the preparation of various silicon derivatives of it is of interest. There is no information in the literature on the preparation of such derivatives.

We undertook an attempt to obtain silicon derivatives of polyvinyl alcohol (organosilicon ethers) of the general formula:



$$-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}-\underset{\mathrm{OSiR_3}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{OH}}{\mathrm{CH_2}}-$$

where R is alkyl, aryl, or aralkyl.

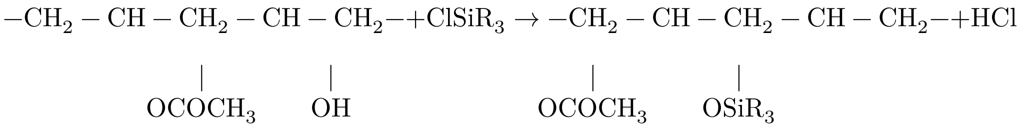
For obtaining such derivatives of polyvinyl alcohol, the following reactions were employed: a) interaction of chlorosilanes with polyvinyl alcohol and its alcoholates in a heterogeneous medium; b) interaction of chlorosilanes with partially saponified polyvinyl acetate in a homogeneous medium; c) interaction of trialkylaminosilanes with polyvinyl alcohol in a pyridine medium. In carrying out the reactions of chlorosilanes with polyvinyl alcohol and its alcoholates, difficulties arise because chlorosilanes readily react with water, pyridine, formamide, and other agents used for dissolving (or swelling in them) polyvinyl alcohol.

In view of the above, an attempt was made to carry out a heterogeneous reaction of anhydrous polyvinyl alcohol, its alcoholate, and an alkaline derivative (containing 7-8 mole % Na), synthesized by the described methods ([1]), with alkylchlorosilanes in benzene. For the reaction, polyvinyl alcohol obtained by alkaline methanolysis from polyvinyl acetate (with a viscosity of 20 cP and a content of residual acetyl groups of 1.03 mole %) was used. The reactions were conducted with stirring of finely ground powders, suspended in benzene, of polyvinyl alcohol, its alcoholate, and the alkaline derivative in a mixture with trimethylchlorosilane (2–4 moles per one unit of polyvinyl alcohol) at temperatures from 20 to 70° for 7–24 hr.

Under the conditions of the heterogeneous reaction, it was not possible to achieve any appreciable replacement of the hydroxyl groups of polyvinyl alcohol by alkylsilicon radicals.

In order to ensure homogeneity of the reaction, partially saponified polyvinyl acetates, retaining solubility in benzene, were subsequently used. They were obtained by known methods—by catalytic alkaline alcoholysis in absolute methanol (^{2}). To preserve solubility in benzene, it is necessary to carry out alcoholysis to a content of no more than 10 mole % of hydroxyl groups in the polyvinyl acetate chain.

The reaction of interaction with trialkylchlorosilanes (used in excess) was carried out in a solution of such partially saponified polyvinyl acetates in benzene or in a mixture of benzene with dioxane (for polyvinyl acetates containing 10 mol. % hydroxyl groups). The experiments were carried out in an absolutely anhydrous medium and were performed in a three-necked flask equipped with a reflux condenser, a calcium chloride tube, a stirrer, and a dropping funnel. In this case the reaction proceeds according to the scheme



$$-CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-+ClSiR_3 \rightarrow -CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OSiR_3}{\underset{|}{CH}}-CH_2-+HCl$$

To bind the liberated HCl, finely powdered magnesium carbonate was suspended in the reaction medium. The product obtained was precipitated from the filtered solution with petroleum ether and purified by twofold dissolution in dioxane and precipitation with water.

The results of some experiments are presented in Table 1.

Table 1

No.	Duration of reaction, h	Part. sap. PVA*, g	TMCS, g**	TMCS / part. sap. PVA	Medium	Reaction temp., °C	Yield of reaction products, g	Si content, mol. %	Substituted OH groups, % for silicon
1	7	2	10.8	50 : 1	Benzene	60	1.5	1.32	17.6
2	78	4	21.5	55 : 1	Benzene	20	2.7	4.8	64
3	46	2	12	60 : 1	Benzene	40	1.3	2.3	30.5

No.	Duration of reaction, h	Part. sap. PVA*, g	TMCS, g**	TMCS / part. sap. PVA	Medium	Reaction temp., °C	Yield of reaction products, g	Si content, mol. %	Substituted OH groups, % for silicon
4	52	3	18	60 : 1	Benzene in the presence of $MgCO_3$	50	1.63	5	66.7
5	75	3.4	4	4 : 1	Benzene in the presence of $MgCO_3$	20	2.8	3.8	52

* Partially saponified polyvinyl acetate.
** Trimethylchlorosilane.

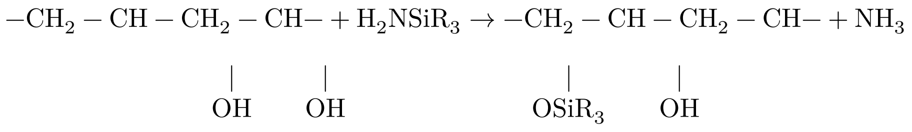
Note. The initial part. sap. PVA had a characteristic viscosity of 0.37 and contained, in experiments Nos. 1-4, 7.8 mol. %, and in experiment No. 5, 7.3 mol. % hydroxyl groups.

Thus, under the adopted conditions, 50-70% of all free hydroxyl groups of partially saponified polyvinyl acetate were substituted. The addition of powdered magnesium carbonate, used by us to bind the liberated HCl, plays a very large role, ensuring the attainment of a higher degree of substitution of the hydroxyl groups.

No noticeable destruction of the chains is observed in this case, as was established by comparing the characteristic viscosity of the initial partially saponified polyvinyl acetate in acetone ($[\eta] = 0.37$) and of the reaction product with a silicon content of 4.8 mol. % ($[\eta] = 0.43$). The copolymers obtained with a silicon content of 4-5 mol. % have an elevated glass-transition temperature: $T_c = 38^\circ$, as against $T_c = 28^\circ$ for polyvinyl acetate. The increase in the glass-transition temperature is evidently associated with the presence of hydroxyl groups and the formation of hydrogen bonds between chains.

Work on obtaining such copolymers is being continued with a smaller amount of trimethylchlorosilane introduced into the reaction (down to the theoretical amount). In an analogous manner, the reaction is carried out with partial acetals of polyvinyl alcohol that are soluble in benzene and dioxane.

As is known, aminosilanes readily react with low-molecular alcohols with the formation of orthosilicic acid esters (3). An analogous reaction was used by us to obtain the corresponding derivatives of polyvinyl alcohol according to the scheme:



$$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}- + H_2NSiR_3 \rightarrow -CH_2-\underset{OSiR_3}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}- + NH_3$$

For the reaction, polyvinyl alcohol with *M* 27,000, containing 1.03% residual acetate groups, and triethylaminosilane, obtained by the interaction of triethylchlorosilane with liquid ammonia (4), were used.

Triethylaminosilane had the following characteristics: b.p. 134–139°, Si content 21.99% (calculated 22.06%), n_D^{20} 1.4259.

The reaction was carried out in the same apparatus as in the interaction of partially saponified polyvinyl acetate with alkylchlorosilane. The reaction was conducted in a medium of dry pyridine (in which polyvinyl alcohol swells and triethylaminosilane dissolves), under conditions of complete protection from moisture from the air. The polyvinyl alcohol was first swollen in pyridine for 18–20 hr at normal temperature or for 2–3 hr at 100°, and the reaction mixture was stirred for a definite time.

Table 2

Results of experiments on the preparation of triethylsilyl ethers of polyvinyl alcohol

No.	PVA*, g	Amount of TEAS**, g	PVA / TEAS	Reaction temperature, °C	Reaction duration, hr: heating	Reaction duration, hr: total	Degree of substitution, mol. %	OH content, mol. %
1	2.65	8	1 : 1	80	12, 44	44	26.4	
2	5	25	1 : 1.38	100	5	168	13.7	
3	1	6.5	1 : 2	100	4	4	19.6	
4	2.23	4.2	1 : 0.7	80	16	48	17	
5	0.9	4.81	1 : 1.8	100	12	46	36.3	61
6	4	24.15	1 : 2	100	14	192	45	37.2

No.	PVA*, g	Amount of TEAS**, g	PVA / TEAS	Reaction temperature, °C	Reaction duration, hr: heating	Reaction duration, hr: total	Degree of substitution, mol. %	OH content, mol. %
7	0.9	12.53	1 : 4	100	12	48	44.5	51.4
8	3	19.5	1 : 2	100	22	110	49.7	34.9
9	1	6.3	1 : 2	100	34	168	78	
10	2	13.7	1 : 2	100	53	168	61.6	35.7

* Polyvinyl alcohol
** Triethylaminosilane

Note. The total duration of the reaction includes the time during which the reaction mixture was kept at ordinary temperature in the intervals between heating periods.

After approximately 1.5-2 hr the reaction mixture became completely homogenized. Isolation of the reaction product was carried out by precipitating it with various organic liquids, since, depending on the degree of substitution, the solubility of the products varies greatly. Thus, for example, for a polymer with a content of 15 mol. % Si, petroleum ether was used as the precipitant. The isolated product was subjected to two repeated precipitations, washed, and dried in vacuum; it was then analyzed for Si content (by combustion in the presence of HNO_3 and H_2SO_4 and calcination at 1000°) and for free hydroxyl groups (by Verley' s method).

It was established that under the indicated conditions a silicon-organic ether of polyvinyl alcohol is formed. Since detection of the ammonia liberated during the reaction in pyridine medium is difficult, special experiments were set up on the interaction with triethylaminosilane of a silicon-organic ether of polyvinyl alcohol, prepared beforehand by the method described above, containing 28.7-31 mol. % Si and soluble in dioxane and benzene. When the reaction with triethylaminosilane was carried out in benzene, qualitative and quantitative liberation of ammonia and an increase in the degree of substitution of the hydroxyl groups of polyvinyl alcohol were observed.

The results of some experiments are given in Table 2. As can be seen from this table, triethylsilyl ethers of polyvinyl alcohol with various degrees of substitution (up to 78 mol. %) were obtained.

The solubility data for some of the products obtained, given in Table 3, show that already upon introduction of 13 mol. % triethylsilyl groups the product is insoluble in water and soluble in certain organic solvents. At a content of 31.6

mol. % triethylsilyl groups, the polymer is completely soluble in benzene, and at a content of 61.6 mol. % of such groups—in petroleum ether. The observed the property of solubility of triethylsilyl ethers of polyvinyl alcohol—solubility in benzene at a content of 70 mol. % free hydroxyl groups and in aliphatic hydrocarbons at a content of 40 mol. % free hydroxyl groups—has not so far been observed for other derivatives of polyvinyl alcohol and is of interest from both theoretical and practical standpoints.

Table 3

Solubility of triethylsilyl ethers of polyvinyl alcohol

No.	Si content, mol. %	Water	Methanol	Ethanol	Acetone	Pyridine	Dioxane	Benzene	Petroleum ether	Dichloroethane	Chloroform
1	13.7	−	s	−	−	+	+	−	−	s	−
2	19.6	−	+	s	−	+	+	s	−	s	−
3	31.6	−	−	+	+	+	+	+	−	+	+
4	44.4	−	−	−	−	+	+	+	−	+	+
5	61.6	−	−	−	−	+	s	+	+	+	+
6	78	−	−	−	−	−	−	+	+		

Note. Plus means soluble, minus—insoluble, s—swells.

Table 4

Properties of the triethylsilyl ether

No.	Si content, mol. %	ρ_s	tg δ	ε	T_c, °C	Tensile strength, kg/cm^2	Relative elongation, %
1	13.7				65	280	13
2	30	$2.5 \cdot 10^{16}$	0.035	5	36	212	64
3	45	$5.5 \cdot 10^{16}$	0.025	4.8	Balsam-like		

For tablets ($d = 10$ mm; $h = 5$ mm) pressed from polymers with an Si content of 6 to 30 mol. %, water absorption upon immersion in water for 24 h decreases from 10 to 0.1%.

When a product containing 61.5 mol. % Si was saponified by Price’ s method with 0.3% NaOH (alcohol solution) in benzene for 6 days at 18°, a precipitate formed, which after drying was dissolved in water and precipitated in acetone. The product obtained showed an Si content of 0.8 mol. %, indicating practically complete saponification of the triethylsilyl groups under these conditions.

To study the thermal properties, tablets were pressed from the products obtained. The softening temperature on a plate for polymers containing 13–15 mol. % Si was 125°. However, with an increase in the amount of triethylsilyl groups, the polymer acquires greater softness at normal temperature.

The glass-transition temperature (determined in the Marei apparatus), as is seen from Table 4, decreases with increasing degree of substitution. For tensile testing, films were cast on water and mercury (casting the film on glass could not be carried out because of the high adhesion of the polymer to glass). Some indices of mechanical strength and dielectric properties are given in Table 4.

Triethylsilyl ethers of polyvinyl alcohol at a degree of substitution of 30 mol. % and higher are distinguished by strength sufficient for many applications and by sufficiently high dielectric indices.

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Note: Figure translations are in progress. See original paper for figures.