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Abstract

Full Text

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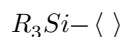
and E. A. CHERNYSHEV

POLYMERIZATION AND COPOLYMERIZATION OF UNSATURATED ORGANOSILICON COMPOUNDS.

p-TRIALKYLSILYLSTYRENES

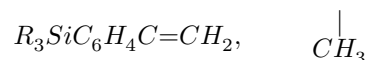
The most important factors determining the ability of substituted ethylenes to undergo polymerization are: the nature, number, mutual arrangement, and bulk of the substituents located at the carbon atoms joined by the double bond ⁽¹⁾.

We have previously shown ⁽²⁾ that trialkylvinylsilanes, or, as they may be called, trialkylsilylethylenes, $R_3SiCH=CH_2$, can polymerize by a radical mechanism with the formation of viscous products having a polymerization coefficient of 12-18. The introduction of a second substituent into this molecule in the β -position leads to a considerable decrease or complete suppression of the ability to polymerize. Thus, for example, 1-triethylsilyl-2-methylethylene $(C_2H_5)_3SiCH=CH-CH_3$ and 1,2-bis(triethylsilyl)ethylene $(C_2H_5)_3SiCH=CHSi(C_2H_5)_3$ polymerize only to dimers ⁽³⁾, while 1-dimethylpropylsilyl-2-phenylethylene $(CH_3)_2C_3H_7SiCH=CH-C_6H_5$ is incapable of polymerization ⁽²⁾. Replacement of the group R_3Si in the vinylsilane molecule by the group



leads to the formation of the compound $R_3SiC_6H_4CH=CH_2$, which readily polymerizes to a glassy product ⁽⁴⁾.

Introduction of a methyl group in the α -position into this molecule should cause a decrease in the ability to polymerize, since steric hindrance is thereby created. Indeed, as we established in the present investigation, *p*-triethylsilyl- α -methylstyrene



although it polymerizes by a radical mechanism to a glassy product, requires the use of pressure.

Thus, the ability of silicoolefins to polymerize is determined by the same factors as in the case of hydrocarbon unsaturated compounds.

We have previously published works⁽²⁻⁴⁾ in which extensive material was presented concerning the preparation of low-molecular-weight, oil-like polysilanes. The present investigation is devoted to the preparation of high-molecular-weight polysilanes and to the study of their properties. Under standard conditions—at a pressure of 6000 atm and at atmospheric pressure, in the presence of 1 mole % initiator—the polymerization of *p*-trialkylsilylstyrenes, $R_3SiC_6H_4CH=CH_2$, where $R = CH_3$ and C_2H_5 , *p*-triethylsilyl- α -methylstyrene, and the copolymerization of *p*-triethylsilylstyrene with styrene were investigated.

Whereas the alkylalkenylsilanes studied by us earlier⁽²⁻⁴⁾ required the application of pressure for the formation of polymers, *p*-trialkylsilylstyrenes polymerize under the same conditions also at atmospheric pressure. However, the use of pressure in this case leads to a considerable increase in the molecular weight of the polymers (Table 1). We have also established that *p*-triethylsilyl- α -methylstyrene polymerizes under a pressure of 6000 atm to a solid product of lower molecular weight and with lower

at a higher rate in comparison with *n*-triethylsilylstyrene. The intrinsic viscosities $[\eta]$ of toluene solutions of the polymers of *n*-triethylsilylstyrene and *n*-triethylsilyl- α -methylstyrene are, respectively, 0.784 and 0.460.

Table 1

Polymerization of *n*-triethyl(methyl)silylstyrenes and *n*-triethyl- α -methylstyrene

Experiment no.	Monomer (name and formula)	Pressure, atm.	Temp., °C	Initiator	Yield of precipitated polymer, % of monomer	Appearance of polymer, $[\eta]$, ml/g	Found, % C	Found, % H	Found, % Si
1	<i>n</i> -Triethylsilylstyrene ($(C_2H_5)_3SiC_6H_4CH=CH_2$)	6000	120	PTB	75.4	Colorless glass	77.30	10.20	12.65
2	<i>n</i> -Triethylsilylstyrene	1	120	Same	62.0	Colorless glass	77.40	10.38	12.27
3	<i>n</i> -Triethylsilyl- α -methylstyrene	6000	120	ADN	52.0	Colorless glass	77.24	10.32	12.21

Experiment no.	Monomer (name and formula)	Pressure, atm.	Temp., °C	Initiator	Yield of precipitated polymer, % of monomer	Appearance of polymer, [η], ml/g	Found, % C	Found, % H	Found, % Si
4	<i>n</i> -Triethylsilylstyrene	1	80	Same	47.3	Colorless glass	68.33		
5	<i>n</i> -Trimethylsilylstyrene (CH ₃) ₃ SiC ₆ H ₄ CH=CH ₂	6000	120	PTB	67.0	Colorless glass	75.2475	9.2369	4.2152
6	<i>n</i> -Trimethylsilylstyrene	1	120	Same	60.0	Colorless glass	68.24		
7	<i>n</i> -Triethylsilyl- α -methylstyrene (C ₂ H ₅) ₃ SiC ₆ H ₄ C(CH ₃)=CH ₂	6000	120	Same	49.4	Colorless glass	77.1177	10.5710	1.4685

* Duration of the experiment—6 h.

** The initiator was used in an amount of 1 mol.%; PTB—tert-butyl peroxide, ADN—azobisisobutyronitrile.

The results of the study of the copolymerization of *n*-triethylsilylstyrene with styrene showed that, both under pressure and without the application of pressure, a copolymer is formed with a ratio of *n*-triethylsilylstyrene and styrene units of 1 : 2 and with intrinsic viscosities of 1.515 and 0.818 for the products obtained, respectively, under high and atmospheric pressure.

Table 2

Copolymerization of *n*-triethylsilylstyrene with styrene in the presence of 1 mol.%* tert-butyl peroxide at 120°

Experiment no.	Pressure, atm.	Molar ratio of monomers	Yield of copolymer, wt. % of mixture	Character of copolymer	[η], ml/g	Found, %		Calculated, %		n/m ***		
						C	H	(from Si)	(from Si)			
1	6000	1 : 1	89.1	Colorless glass, difficultly soluble in benzene, readily soluble in butanol	1.5	83.218	4.032	9.367	6.654	4.44	8.98	2
2	1	1 : 1	88.9	Colorless glass, readily soluble in benzene	1.8	84.988	4.881	7.216	4.494	4.44	8.98	2

* Relative to the monomer mixture.

** Duration of the experiment—6 h.

*** n —number of styrene units in the copolymer, m —number of *n*-triethylsilylstyrene units;

Fig. 1

Figure 1: Fig. 1

$$\frac{n}{m} = \frac{\frac{2806}{x} - M_2}{M_1},$$

where M_2 is the molecular weight of *n*-triethylsilylstyrene, M_1 is the molecular weight of styrene, and x is the percentage content of Si in the copolymer.

The products of polymerization and copolymerization were subjected to thermomechanical tests, as a result of which it was found that the polymer

n-triethylsilylstyrene has a higher softening temperature than polystyrene prepared under the same conditions; the polymer of *n*-triethylsilyl- α -methylstyrene has an even higher softening temperature (Fig. 1).

The thermomechanical curves of the polymers and copolymers obtained are presented in Fig. 1.

Fig. 1. Dependence of deformation on temperature for polymer samples. Left: 1—polymer of *n*-triethylsilyl- α -methylstyrene, obtained under pressure with tert-butyl peroxide; 2—polymer of *n*-triethylsilylstyrene under the same conditions; 3—the same polymer, obtained without pressure; 4—polystyrene, obtained without pressure. Center: 1—polymer of *n*-triethylsilylstyrene, obtained under pressure with tert-butyl peroxide; 2—polymer of *n*-triethylsilylstyrene, obtained under pressure with azobis(isobutyric acid) nitrile; 3—polymer of *n*-trimethylsilylstyrene, obtained under pressure; 4—polymer of *n*-trimethylsilylstyrene, obtained without pressure. Right: 1—polymer of *n*-triethylsilylstyrene, obtained under pressure in the presence of tert-butyl peroxide; 2—copolymer of *n*-triethylsilylstyrene with styrene, obtained under the same conditions; 3—copolymer of *n*-triethylsilylstyrene with styrene, obtained without pressure; 4—polystyrene, obtained under pressure.

Experimental Part

n-Trialkylsilylstyrenes were obtained by the method developed by us⁽⁵⁾. The technique for experiments under high pressure has been described by us previously⁽⁶⁾. Experiments without the use of pressure were carried out in sealed glass ampoules. In all cases the monomer to be charged was distilled into the ampoules in a stream of nitrogen immediately before the experiment.

As initiator we used tert-butyl peroxide and azobis(isobutyric acid) nitrile in an amount of 1 mole %. The reactions were carried out for 6 h at 120 and 80°. When tert-butyl peroxide was used as initiator, the polymerization product had the form of a monolithic glassy rod; when azobis(isobutyric acid) nitrile was used, the polymer was obtained in the form of a solidified foam. The polymerization

products were purified by reprecipitation from benzene, and copolymer No. 1 (Table 2) from butanone into methyl alcohol. The reprecipitated polymers and copolymers were colorless powders.

The products were characterized by the viscosity of toluene solutions and by thermomechanical properties. Viscosity was measured in an Ostwald viscometer at 20°. From the data obtained, the intrinsic viscosity was determined graphically. The thermomechanical properties were investigated on a Tsetlin apparatus (7) at a load of 100 g and a punch diameter of 4 mm. The results of the experiments are presented in Tables 1 and 2 and in Fig. 1.

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