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Abstract

Full Text

CHEMISTRY

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INVESTIGATION OF THE POLYMERIZATION OF CYANO-CONTAINING ORGANOSILICON COMPOUNDS

In recent years, the attention of researchers has been attracted by organosilicon compounds containing the CN group in radicals bound to the silicon atom. Polymers obtained from these compounds possess a number of valuable properties ([1]). Cyanoalkyl organosilicon polymers have begun to be used in industry as rubbers and rubber-like pastes ([1,2]). One of us previously ([3]) synthesized a series of silicon-containing nitriles, including α-cyanoisopropoxyalkenylsilanes. The latter are characterized by being fairly stable in the hydrolysis reaction.

The present work is devoted to a study of the ability of cyano-containing alkenylsilanes to polymerize.

Polymerization was carried out both under pressure (6000 atm.) in the presence of radical-type initiators, and without the use of pressure with platinum-on-carbon or chloroplatinic acid as catalyst. The results of the experiments are presented in Table 1.

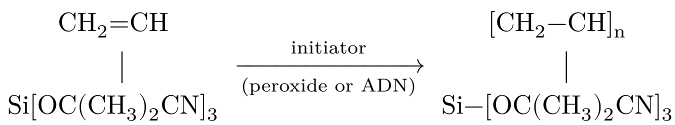
The investigation showed that polymerization of cyanoisopropoxyalkenylsilanes should be carried out at relatively low temperatures; above 120° signs of decomposition of these compounds are observed, for example in their polymerization in the presence of peroxide initiators under pressure. Only in experiments using azodiisobutyric acid dinitrile (ADN) as initiator at 80° were colorless polymers formed. In the remaining cases, polymeric products colored from yellow to brown were obtained. Some experiments ended in explosive polymerization with carbonization of the product.

Most of the polymers obtained, as is seen from the data of Table 1, are distinguished by limited solubility.

We carried out also experiments on the interaction of tetraalkyldihydrodisiloxanes with diallyl cyano-containing silanes (23 and 24). In this case oil-like products were obtained, as previously on treating the same disiloxanes with dialkyldiallylsilanes ([5]).

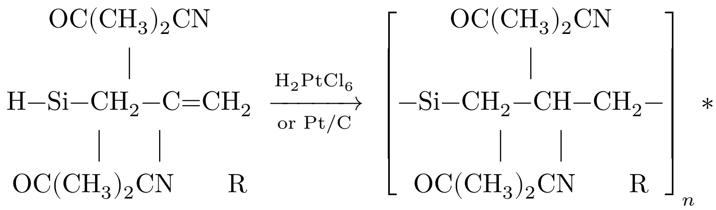
The transformations of the monomers listed in Table 1, in those cases where

explosive polymerization with carbonization of the product did not occur, may be expressed by the following schemes:



(1)

Apparently, the polymerization of di-alkenyl cyano-containing compounds proceeds analogously, through multiple bonds, possibly with the formation of cyclic structures ([6]), since some of the polymers we obtained were soluble



(2)

* As was shown previously on other compounds ([4]).

Table 1

Experiment no.	Monomer	Experimental conditions[1]: pressure (atm.); initiator (mol. %), temp., °C	Appearance of the polymerization product	Yield of purified polymer, wt. %	Mol. wt. or reduced viscosity[3]	Solubility of the polymer
1	$CH_2-CH-Si-[OC(CH_3)_2CN]_2$ CH$_3$	6000; ADN (0.5); 80	Colorless porous rubber-like mass	208060 |	8100.01[2]	In benzene In dimethylformamide
2	Same	Same; ADN (0.35)	Same	72	0.02	Same

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Experiment no.	Monomer	Experimental conditions[1]: pressure (atm.); initiator (mol. %), temp., °C	Appearance of the polymerization product	Yield of purified polymer, wt. %	Mol. wt. or reduced viscosity[3]	Solubility of the polymer
3	» »	Same, without initiator	Does not polymerize			
4	» »	1; ADN (0.35); 80	Colorless thick oil	32	656	In benzene
5	» »	6000; PTB (1); 130	Light-brown gelatinous mass	45		In dimethylformamide
6	» »	6000; PB (0.35); 80	Gel-like yellowish mass	48		Same
7	$CH_2=CH-Si[OC(CH_3)_2CN]_3$	6000; PTB (1); 180	Solid mass			
8	Same	Same, 150°	Same			
9	$CH_2=C(CH_3)-Si[OC(CH_3)_2CN]_3$	6000; PTB (1); 180	Solid mass			Partly in dimethylformamide
10	Same	Same, 120°	Viscous yellow oil	44	544	In benzene
11	$CH_2=CH-CH_2-Si[OC(CH_3)_2CN]_3$	6000; PTB (1); 180	Solid mass			

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Experiment no.	Monomer	Experimental conditions[1]: pressure (atm.); initiator (mol. %), temp., °C	Appearance of the polymerization product	Yield of purified polymer, wt. %	Mol. wt. or reduced viscosity[3]	Solubility of the polymer
12	Same	Same, 120°	Thick mass	14		In dimethylformamide
13	$(CH_2=CHSi(CH_3)_2)_2Si(CH_3)_2$	Same	Yellowish transparent glass	12	Trimer	Insoluble
14	$CH_2=CH-COO-Si(CH_3)_2-OC(CH_3)_2CN$	60°; PTB (1); 150	Dark brown mass	30	0.07	In $(CH_3)_2$ dimethylformamide
15	$(CH_2=CHSi(CH_3)_2O)_2Si(CH_3)_2$	Same	Black	~100		Partly in C_2H_5 dimethylformamide
16	$(CH_2=CH-COOCH_2)_3SiCH_2CH_2CN$	60°; PTB (1); 120	Solid red-brown	25	0.04	In dimethylformamide

No.	Compound	Conditions	Product	Yield, %	η_{sp}/C	Mol. wt.	Solubility
17	$CH_2=CH-COO-Si(CH_3)_2-OC(CH_3)_2CN$	60°; TB (0.37); 80	Yellowish oil	30			In benzene

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No.	Compound	Conditions	Product	Yield, %	η_{sp}/C	Mol. wt.	Solubility
18	$CH_2{=}CH{-}CH_2{-}Si(H)[OC(CH_3)_2CN]_2$	1; 6% platinum on carbon (1.1 g per 1 mole); 180	Dark-brown mass	67			Insoluble in dimethyl-formamide
19	Same	1; 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol (0.005 g); 120	Viscous oil	75		1070	In benzene
20	» »	6000; TB (0.37); 80	Dark-yellow	35	0.05		In dimethyl-formamide
21	$CH_2{=}C(CH_3){-}CH_2{-}Si(H)[OC(CH_3)_2CN]_2$	1; 5% platinum on carbon (1.1 g per 1 mole); 150	Viscous yellow oil	73		1320	In benzene
22	Same	Same, 180°	Dark-brown mass	70			Insoluble in dimethyl-formamide

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No.	Compound	Conditions	Product	Yield, %	η_{sp}/C	Mol. wt.	Solubility
23	$(CH_2{=}CH{-}CH_2)_2Si(OCH_2CH_2CN)_2$	1; 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol (0.005); 120°	Viscous oil	[illegible]	0.18	1018	In benzene
24	$(CH_2{=}CH{-}CH_2)_2Si(OCH_2CH_2CN)_2$	Same	Viscous oil	52	0.13	1030	In benzene

[1] Duration of the experiments: 6 h. ADN —azodiisobutyronitrile; TTB —tert-butyl peroxide; TB —benzoyl peroxide.
[2] Reduced viscosity η_{sp}/C in dimethylformamide, at 20°; $C = 0.4\%$.
[3] Molecular weight was determined by the cryoscopic method in benzene.

$$\mathrm{H{-}Si(R')(R'){-}O{-}Si(R')(R'){-}H + CH_2{=}CH{-}CH_2{-}Si(OCH_2CH_2CN)_2{-}CH_2{-}CH{=}CH_2} \xrightarrow[\mathrm{Pt/C}]{\mathrm{H_2PtCl_6\ or}} \longrightarrow [-\mathrm{Si(R')(R'){-}O{-}Si(R')(R'){-}CH_2{-}CH_2CH_2{-}Si(OCH_2CH_2CN)_2{-}CH_2CH_2CH_2-}]_n \quad (3)$$

Experimental Part

The preparation of the monomers, except for three, the synthesis and properties of which are given below, has been described previously ([7], [8]).

Diallyldi-(β-cyanoethoxy)-silane was obtained by method ([1]) from 0.25 g-mole of diallyldichlorosilane, 0.5 g-mole of β-cyanoethyl ether of allyl alcohol, and 0.6 g-mole of pyridine in 100 ml of dry benzene. The yield of crude product with b.p. 178–181°/10 mm (slight decomposition) was about 40%. After redistillation the substance had the following constants: n_D^{20} 1.4674; d_4^{20} 1.0283; MR_D found 67.60; calculated 67.98.

Found, %:	C 56.95; 56.99;	H 7.83;	H 7.63;	Si 10.03; 9.88
$C_{12}H_{18}SiO_2N_2$. Calculated, %:	C 57.56;	H 7.24;	Si 11.20	

Vinylmethyldi-(β-cyanoethoxy)-silane was obtained with reagent ratios analogous to the preceding ones, with b.p. 165–175°/13 mm and a yield of

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76%; after redistillation b.p. 178°/18 mm; n_D^{20} 1.4475; d_4^{20} 1.0428; MR_D found 53.94; calculated 54.25.

Found, %:	Si 13.20; 13.60
$C_9H_{14}SiO_2N_2$. Calculated, %:	Si 13.30

Vinylmethyldi-(α-cyanoisopropoxy)-silane was obtained with analogous reagent ratios in a yield of 47%; b.p. 120–175°/5 mm. After redistillation b.p. 123–124°/5 mm; n_D^{20} 1.4298; n_D^{20} 0.9729; MR_D found 63.22; calculated 63.30

Found, %:	Si 12.0; 12.1
$C_{11}H_{16}SiO_2N_2$. Calculated, %:	Si 11.8

Polymerization. Polymerization under pressure was carried out in lead ampoules. The experimental technique has been described in previous communications ([9]). Experiments without the use of pressure in the presence of platinum-on-carbon catalysts and chloroplatinic acid were carried out in sealed glass ampoules. The polymers were purified either by distilling off the unreacted monomer, in the case of oil-like products, or by reprecipitation from dimethylformamide. Insoluble polymers were purified by repeated treatment with benzene and dimethylformamide.

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