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Abstract

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POLYMERIZATION OF UNSATURATED ORGANO-GERMANIUM COMPOUNDS

The polymerization of unsaturated organic compounds containing Group IV elements has as yet been little studied. The ability of silicon olefins to polymerize has been investigated most fully, although still inadequately. Earlier ([1–3]) we published the results of a study of the polymerization and copolymerization of alkenylsilanes of various structures.

The present investigation is devoted to the study of the polymerizability of unsaturated germanium compounds. There is no information in the literature on the synthesis and polymerization of unsaturated organo-germanium compounds.

We studied the polymerizability of mono-, di-, and tri-allylgermanes and their copolymerization with methyl methacrylate.

Under the standard conditions described by us in previous papers (under a pressure of 6000 atm at 120°, in the presence of tert-butyl peroxide), 5 monomers of alkylallylgermanes were subjected to polymerization and copolymerization. The results of the investigation, presented in Tables 1 and 2,

Table 1

Monomer: formula	b.p.	n_D^{20}	d_4^{20}	Polymerization reaction products: character of the product obtained	mol. wt. (average)	polym. coefficient	polymer yield, %	Note
$(CH_3)_3GeCH_2CH=CH_2$	140°/760 mm	1.4633	0.9952	colorless oil	560	3.5	34.0	
$(C_2H_5)_3GeCH_2CH=CH_2$	180°/760 mm	1.4594	1.0004	same	782	3.9	64.4	
$(CH_3)_3GeCH_2C(CH_3)=CH_2$	120°/733 mm	1.4416	0.9908	does not polymerize				
$(CH_3)_2Ge(CH_2CH=CH_2)_2$	146°/737 mm	1.4645	1.0337	colorless flexible mass	trimer		~ 100	
$CH_3Ge(CH_2CH=CH_2)_3$	190°/747 mm	1.4867	1.0222	colorless transparent glass	trimer		~ 100	
$CH_3Ge(CH_2CH=CH_2)_3$	190°/747 mm	1.4867	1.0222	colorless viscous oil	780	3.7	38.6	The experiment was carried out without applying pressure

show that, in their ability to polymerize, allyl compounds of germanium differ little from analogous silicon compounds. Trialkylallylgermanes $R_3GeCH_2{-}CH{=}CH_2$, where R = CH_3 and C_2H_5, form oil-like polymers, whereas dimethyldiallylgermane and methyltriallylgermane polymerize into trimers having the form of transparent glasses.

Table 2

Copolymerization of trialkylallyl-(methallyl)germanes with methyl methacrylate

Alkenylgermane monomer (formula)	Ratio of alkenylgermane and MMA,* mol.	Initiator concentration, mol. %	$[\eta]$	C found, %	H found, %	Ge found, %	C calculated by % Ge	H calculated by % Ge	n/m
$(C_2H_5)_3GeCH_2{-}CH{=}CH_2$	1:30	1.30	1.83	58.69	8.38	4.79	59.17	8.33	13
$(C_2H_5)_3GeCH_2{-}CH{=}CH_2$	1:30	1.30	1.74	58.87	8.39	4.69	59.17	8.33	13
$(CH_3)_3GeCH_2{-}CH{=}CH_2$	1:40	1.90	1.54	59.23	7.98	1.40	59.58	8.09	53
$(CH_3)_3GeCH_2{-}CH{=}CH_2$	1:40	1.90	1.54	59.17	7.97	1.26	59.58	8.09	53
$(CH_3)_3GeCH_2{-}C(CH_3){=}CH_2$	1:30	1.90	0.94	55.98	7.62	1.39	59.50	8.11	46
$(CH_3)_3GeCH_2{-}C(CH_3){=}CH_2$	1:30	1.90	0.94	56.01	7.63	1.64	59.50	8.11	46

* MMA —methyl methacrylate.

Triethylallylgermane, like the corresponding alkenylsilanes, shows a somewhat greater tendency toward polymerization than trimethylallylgermane. Trimethylmethallylgermane practically does not polymerize. We also observed a lower tendency toward polymerization for compounds containing methallyl radicals in the case of silicon olefins. Monoallylgermanes are capable of entering into a copolymerization reaction. All the monomers we investigated formed copolymers with methyl methacrylate. From the viscosity measurements $[\eta]$ of solutions of the copolymers it follows (as is seen from Table 2 and Fig. 1) that the introduction of alkenylgermane units into the macromolecule of methyl methacrylate lowers the viscosity and, consequently, the molecular weight. The solution of the copolymer of trimethylmethallylsilane, which is incapable of homopolymerization under these conditions, has the lowest viscosity. Investigation of the thermomechanical compression curves of the polymers obtained showed that the homopolymers of dimethyldi- and methyltriallylgermanes are three-dimensional polymers; like the corresponding silicon olefins, they do not exhibit flow and are thermally stable up to a temperature of 250°.

Fig. 1. Dependence of η_{sp}/c on c for methyl methacrylate and its copolymers with alkenylgermanes: 1 —methyl methacrylate; 2 —copolymer with

$(C_2H_5)_3GeCH_2-CH=CH_2$; 3 –copolymer with $(CH_3)_3GeCH_2-CH=CH_2$; 4 – copolymer with $(CH_3)_3GeCH_2-C(CH_3)=CH_2$.

The copolymers of monoalkenylgermanes with methyl methacrylate, however, are linear polymers; at certain temperatures they pass from a glassy state into a highly elastic state and then into a viscous-flow state.

Experimental Part

The technique for studying polymerization under pressure was described by us earlier (1). In the present study, polymerization was carried out under a pressure of 6000 atm at 120°, in the presence of a polymerization initiator –pere-

tert-butyl peroxide–in an amount of 1 mole % in obtaining homopolymers and 1.8-1.9 mole % in the case of copolymers. The heating time was 6 hours. For comparison, experiments were also carried out without applying pressure.

The liquid reaction products were purified by removing the monomer in vacuo. The solid polymers were reprecipitated from chloroform with methanol. The molecular weight of the liquid (low-molecular-weight) polymers was determined by the cryoscopic method, using benzene as the solvent. In the case of solid polymerization products, the relative viscosity η_r of their solutions in chloroform at 25° was measured in an Ostwald viscometer. From the dependence of η_{sp}/c on c, the values of the intrinsic viscosity ($[\eta]$) were determined graphically (see Fig. 1).

The composition of the copolymers, $\frac{n}{m}$, where n is the number of methyl methacrylate residues and m is the number of alkenylgermane residues, was determined from the germanium content and calculated by the formula given by us earlier ([3]). The data obtained are presented in Tables 1 and 2 and in Fig. 1.

The thermomechanical properties of the polymers were determined in the polymer research laboratory under the direction of G. L. Slonimskii, to whom we express our deep gratitude.

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