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Abstract

Full Text

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ON THE SYNTHESIS OF INFUSIBLE BUT SOLUBLE POLYMERS

Such important properties of polymers as their ability to melt* and to dissolve in organic solvents are usually regarded as interrelated and dependent on the structure of the chains of the polymer molecules. It is known that polymers with a linear molecular structure are soluble in organic solvents and melt on heating, independently of the magnitude of the molecular weight. Branching of the polymer chain of the molecules, i.e., the formation of cross-linked and three-dimensional structures, leads to loss of solubility and fusibility by the polymer.

Such a relation between the structure of the molecular chains, solubility, and melting is observed in all known polymers. Hydrogen bonds exert a considerable influence on the indicated properties of linear polymers (as, for example, the poor solubility of certain representatives of polyamides with a linear structure) or the rigidity of the molecules and the packing density of the chains (as in polytetrafluoroethylene). However, even in these cases the relation between melting, solubility, and the structure of the molecular chains is preserved.

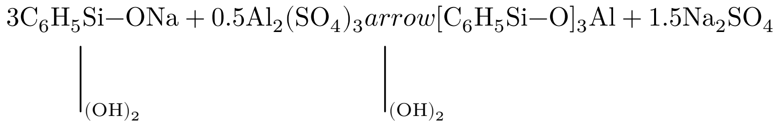
Polymers possessing good solubility in nonpolar or weakly polar solvents but not melting on heating have not been described in the literature. We undertook attempts to synthesize such polymers. In the course of the investigations, the possibility of synthesizing polymers in which there is no such mutual relation between solubility and melting as in the polymers known up to the present time became increasingly clear. After detailed studies among certain classes of polymers, it was found that in preparing cyclic polyorganosiloxanes it is not possible to obtain polymers with the indicated properties. In the hydrolysis of phenyltrichlorosilane in aqueous acidic media it was established that the polymers have the general composition $(C_6H_5SiO_{1.5})_x$.

This composition corresponds to a cyclic molecular structure. However, such polymers dissolve in aromatic solvents and melt on heating. Hydrolysis of fully chlorinated phenyltrichlorosilane leads to products of composition $(C_6Cl_5SiO_{1.5})_6$ and of a more complex cyclic structure, which dissolve well and melt at 210-215°. Hexaethylcyclosiloxane $(C_2H_5SiO_{1.5})_6$ and octaethylcyclosiloxane $(C_2H_5SiO_{1.5})_8$ were isolated (1), but they also melted and dissolved.

Prolonged heating of cyclic polyphenylsiloxanes at a temperature of 250° and above leads to an increase in the melting temperatures, but at the same time the polymer loses solubility. Apparently, growth of the polymer molecule proceeds mainly through opening of the rings and their polymerization with formation of cross-linked structures.

To increase the melting temperature of complex cyclic polyphenylsiloxanes, aluminum was introduced into the polymer molecule. In this case it was believed that it would be possible sharply to increase the rigidity of the polymer chain and thereby—

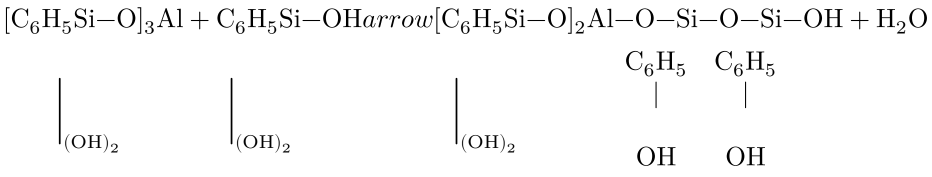
at the same time raise the melting temperature. The synthesis of such a polymer —poly(alumophenylsiloxane)—was carried out according to the following reaction scheme:

1)


$$3C_6H_5\underset{(OH)_2}{Si}{-}ONa + 0.5Al_2(SO_4)_3 arrow [C_6H_5\underset{(OH)_2}{Si}{-}O]_3Al + 1.5Na_2SO_4$$

$$2)\quad C_6H_5Si(OH)_2ONa \overset{H_2O}{\rightleftharpoons} C_6H_5Si(OH)_3 + NaOH.$$

Alumosiloxane reacts with phenyltrihydroxysilane, with liberation of water:

3)


$$[C_6H_5\underset{(OH)_2}{Si}{-}O]_3Al + C_6H_5\underset{(OH)_2}{Si}{-}OH arrow [C_6H_5\underset{(OH)_2}{Si}{-}O]_2Al{-}O{-}\underset{OH}{\overset{C_6H_5}{Si}}{-}O{-}\underset{OH}{\overset{C_6H_5}{Si}}{-}OH + H_2O$$

Then further condensation proceeds at the expense of hydroxyl groups, with formation of a polymer with an average molecular weight of 5990, a hydroxyl-group content of 5.5%, and a silicon-to-aluminum ratio of 4.1.

Fig. 1. Change in poly(alumophenylsiloxane) (*I*) and poly(alumoethylsiloxane) (*II*) upon heating: *1*—initial resin; *2*-*5*—tested substances: *2*—200°, 10 h; *3*—300°, 15 min; *4*—400°, 15 min; *5*—500°, 15 min.

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* Polymers do not melt at a strictly definite temperature, but over a certain temperature interval.

The poly(alumophenylsiloxane) obtained by this scheme is a colorless, brittle, glassy product which does not melt upon heating.

It is evident from Fig. 1 that pulverized poly(alumophenylsiloxane) does not melt and does not sinter at temperatures up to 500°. It dissolved well in benzene, toluene, acetone, ethyl alcohol, chlorobenzene, and carbon tetrachloride, but did not dissolve in petroleum ether or white spirit. After evaporation of the solvent, the polymer forms films which readily redissolve in the same solvents if they have not been heated at high temperature.

A study of the solubility of the polymer showed that it does not lose its solubility after being heated at 150° for 10 h (Table 1), although the content of OH groups in it decreases during this time from 5.53 to 2.7%.

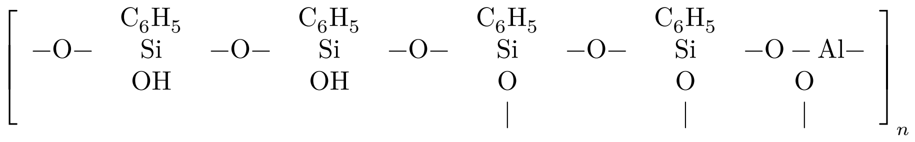
When poly(alumophenylsiloxane is heated at 200° for 4 h, it retains its solubility in acetone; after exposure to 300° for 15 min, it dissolves to the extent of 85%. With longer heating at 200° and heating for 15 min at 400 and 500°, the polymer completely loses its solubility. Chemical analysis of poly(alumophenylsiloxane and investigation of the molecular weight (?) showed that the elemental—

Table 1

Solubility of polyalumophenyl- and ethylsiloxane (in percent)

Solvent	100°10 h	150°10 h	200°2 h	200°4 h	200°10 h	300°0.25 h	400°0.25 h	500°0.25 h
Polyalumophenylsiloxane								
Toluene	100	100	11	4	insoluble	2	insoluble	insoluble
Ethanol	100	100	100	91	insoluble	31	2	insoluble
Acetone	100	100	100	100	2	85	3	insoluble
Chlorobenzene	100	100	47	7	insoluble	5	insoluble	insoluble
Polyalumoethylsiloxane								
Ethanol	100	90	3	insoluble	insoluble	7	insoluble	insoluble
Acetone	100	100	4	insoluble	insoluble	10	insoluble	insoluble

elemental composition, in %: C 49.18; 49.35; H 4.28; 4.18; Si 18.88; 18.15; Al 4.14—4.39; hydroxyl groups 5.53. This corresponds to Si/Al = 4.1; C/Si = 6.19 and H/C = 1.0. The molecular weight of the infusible polyalumophenylsiloxane is 5990. Fractionation of it from carbon tetrachloride by precipitation with petroleum ether showed that the fractions had a minimum molecular weight of 2770 and a maximum of 11800.* The formation reaction and the chemical composition of the polymer correspond, for a chain unit, to the following empirical formula:



$$\left[-O- \underset{OH}{\overset{C_6H_5}{Si}} -O- \underset{OH}{\overset{C_6H_5}{Si}} -O- \underset{\underset{|}{O}}{\overset{C_6H_5}{Si}} -O- \underset{\underset{|}{O}}{\overset{C_6H_5}{Si}} -O- \underset{\underset{|}{O}}{Al}- \right]_n$$

It is easy to see that such a unit of the molecular chain is a constituent part of a complex cyclic or three-dimensional polymer molecule. The solubility and the low molecular weight of the polymer rule out the supposition of a three-dimensional structure of the molecule. The cyclic structure of the polymer molecule makes it possible to explain readily the good solubility of the polymer in ordinary organic solvents. By the same reaction scheme, from ethylsodium oxydihydroxysilane and potassium alum, polyalumoethylsiloxane was obtained; like polyalumophenylsiloxane, it was colorless, brittle, and glass-like. Polyalumoethylsiloxane had the same properties as polyalumophenylsiloxane; it did not melt on heating (Fig. 1), but dissolved in carbon tetrachloride, chlorobenzene, acetone, ethyl alcohol, benzene, and toluene.

Table 1 gives the solubility of polyalumoethylsiloxane in ethyl alcohol and acetone after heating it at various temperatures.

Polyalumoethylsiloxane loses its solubility more rapidly than polyalumophenylsiloxane. This is probably explained by the fact that in the present case the conversion of the polymer into an insoluble product proceeds more rapidly than in polyalumophenylsiloxane, owing to cleavage of the ethyl radical at the silicon atom and formation of a siloxane bond.

Thus, by the exchange-decomposition reaction, polyalumoethylsiloxane and polyalumophenylsiloxane have been synthesized; they dissolve well in organic nonpolar or weakly polar solvents and do not melt at various temperatures up to 500°.

Polyalumoethylsiloxane and polyalumophenylsiloxane have a complex cyclic molecular structure. Unlike known polymers, which have a linear or cross-linked and three-dimensional molecular structure, they have no interrelation between solubility and melting. These polymers dissolve well in organic solvents, but their melting temperature lies above the decomposition temperature, as in infusible polymers with a spatial molecular structure.

Experimental Part

The following were used in the work: phenyltrichlorosilane with a chlorine content of 50.0% (50.31%), ethyltrichlorosilane with a chlorine content of 65.1%

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* The molecular weight of polyalumophenylsiloxane was determined by S. R. Rafikov and I. I. Tverdokhlebova.

(65.08%), caustic soda of chemically pure grade, GOST 4328-48, sulfuric-acid aluminum of chemically pure grade, GOST 3758-47, and alumopotassium alum of chemically pure grade, GOST 4329-48.

Hydrolysis of phenyltrichlorosilane. Into a glass hydrolyzer having double walls for water circulation and equipped with a mechanical stirrer, dropping funnel, and thermometer, phenyltrichlorosilane was introduced into water with vigorous stirring. The temperature in the hydrolyzer was 20-25°. After all the phenyltrichlorosilane had been added, stirring was continued for complete reaction for another 30 min. The polyphenylsiloxane thus obtained was washed to a neutral reaction according to Congo.

Polyalumophenylsiloxane. The reaction was carried out in a glass three-necked round-bottom flask equipped with a dropping funnel, a mechanical stirrer with an oil seal, a reflux condenser, and a thermometer. At 20° there were placed in the flask 25.8 g of polyphenylsiloxane and 8 g (0.2 mole) of a 20% aqueous solution of caustic soda. The temperature of the reaction medium thereby rose to 28°. The reaction mass was then heated to 70–75°, and 16.63 g (0.025 mole) of a 20% aqueous solution of sulfuric-acid aluminum was introduced into it in a thin stream. After addition of the sulfuric-acid aluminum, the contents of the flask were heated at 70–75° for 2 hours. The reaction was carried out in an aromatic hydrocarbon—water medium. After completion of the reaction, the organic layer was separated from the aqueous layer and washed with water to remove the SO_4'' ion, according to barium chloride. The excess solvent was distilled off at a temperature of 35–40° and a residual pressure of 20–25 mm Hg. The polymer was finally dried from the solvent at 15 mm Hg and 110° for 1.5 hours. The yield of polyalumophenylsiloxane was 80% of theory.

Found, %: C 49.18; 49.35; H 4.28; 4.18; Si 18.88; 18.15; Al 4.39; 4.14; OH 5.53 $[C_{24}H_{22}Si_4AlO_{8,5}]_n$. Calculated, %: C 49.25; H 3.76; Si 19.15; Al 4.6; OH 5.81

M (ebullioscopically in benzene) 5990. For $C_{24}H_{22}Si_4AlO_{8,5}$, M was calculated as 585, and consequently the coefficient n is equal to 10.

Polyalumoethylsiloxane. Synthesized analogously from 25 g of polyethylsiloxane, 12.3 g (0.31 mole) of caustic soda, and 29.2 g (0.062 mole) of alumopotassium alum. The yield of polyalumoethylsiloxane was 76% of theory.

Found, %: Si 28.15; 27.61; Al 5.6; 5.92.
$[C_{10}H_{27}Si_5AlO_{10}]_n$. Calculated, %: Si 29.5; Al 5.7;

M (cryoscopically in benzene) 1020. For $C_{10}H_{27}Si_5AlO_{10}$, M was calculated as 474, and n is equal to 2.

Dissolution of polymers. Dissolution of the starting polymers and of those preliminarily heat-treated at various temperatures was carried out as follows: in all cases, 0.5 g of polymer and 9.5 g of solvent were taken (calculated to give a 5% solution). Dissolution was carried out in flasks with ground-glass stoppers. The polymers were in contact with the solvent for 24 hours at 20°. During this time the flasks were shaken three times: a) at the beginning of the experiment,

b) after 19 hours from the beginning of the experiment, c) after 24 hours from the beginning of the experiment. After this, the amount of polymer (in %) that had passed into the solvent was determined.

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