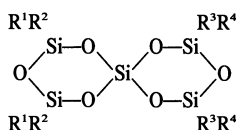


ANIONIC POLYMERIZATION OF METHYLPHENYLSPIROBICYCLOSILOXANES

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Abstract—The polymerization of spirobicyclosiloxanes containing methyl and phenyl side-chain groups in different ratio:



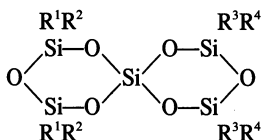
- I. $R^1 = R^2 = \text{Me}$
 $R^3 = R^4 = \text{Ph}$
- II. $R^1 = R^3 = \text{Me}$
 $R^2 = R^4 = \text{Ph}$
- III. $R^1 = R^2 = R^3 = \text{Ph}$
 $R^4 = \text{Me}$
- IV. $R^{1-4} = \text{Ph}$
- V. $R^{1-4} = \text{Me}$

has been investigated. These compounds polymerize in presence of base catalyst to yield polymer networks together with soluble products. The content of cross-linked structures depends upon the relationship between the rates of intra- and intermolecular interaction. It has been shown in many cases, that gel can be transformed into soluble state when equilibrated. Under specific conditions it is possible to obtain linear polymers, containing rings in the main chain. Some thermo-mechanical properties of these polymers have been studied.

Catalytic polymerization of organo-cyclosiloxanes under the effect of bases has at present been investigated quite fundamentally and is now the primary method of obtaining high-molecular polyorgano-siloxanes with linear structure of macromolecules. Catalytic polymerization of polycyclic compounds of the siloxane series is a process, in many respects similar to the polymerization of organo-cyclosiloxanes, but its mechanism is more complex. It is obvious that spiranic compounds containing, along with D-units, tetrafunctional units (Q) are, in principle, capable of forming branched macromolecules. The final result of the uncontrolled and non-specific polymerization of polyfunctional siloxane monomers (as well as other polyfunctional compounds) is a spatially cross-linked disordered structure/gel. At greater dilutions polymerization can produce microgels—soluble, irregularly linked, highly polydispersed products with low intrinsic viscosity.

It should, however, be taken into account that steric interactions of side groups prevent, in a number of cases, the formation of polymer chain branches. Such interactions result in the increasing role of intramolecular cyclization, during the reconstruction of siloxane chains under the effect of initiator, which leads to polycyclic structures being formed.

There are no data in literature on the polymerization of organo-spirosiloxanes. In the present work anionic polymerization has been studied as exemplified by organo-spiropentasiloxane with the following structure:



- I 2,2,4,4-tetramethyl-8,8,10,10-tetraphenyl spiro[5,5]pentasiloxane
- II 2,4,8,10-tetramethyl-2,4,8,10-tetraphenyl spiro[5,5]pentasiloxane
- III 2,4-dimethyl-2,4,8,8,10,10-hexaphenyl spiro[5,5]pentasiloxane
- IV 2,2,4,4,8,8,10,10-octaphenyl [5,5]pentasiloxane
- V 2,2,4,4,8,8,10,10-octamethyl [5,5]pentasiloxane

Investigations of the polymerization of methyl-phenyl spirobicyclosiloxanes (Table 1) have shown that, with the exception of octaphenyl spiro[5,5]pentasiloxane, they polymerize with the formation of a spatially cross-linked structure. Polymerization was conducted in block at 150° in the presence of a homogeneous nucleophilic initiator—dipotassium salt of octamethyl cyclotetrasiloxane: $\text{K}_2\text{O}[\text{SiMe}_2\text{O}]_4\text{K}$. In these conditions, practically the entire octamethyl spiro[5,5]pentasiloxane is converted into gel. When some of the methyl groups in the bicyclic molecule are substituted by phenyl groups, together with the formation of a space lattice a soluble polymer is also obtained, the content of gel fraction in the polymerization products decreasing as of methyl groups are substituted by phenyl. The product of octaphenyl spiro[5,5]pentasiloxane polymerization is a fully soluble polymer product with intrinsic viscosity $[\eta] 0.1 \text{ dl/g}$, containing, from the data of i.r. spectra, neither six-membered cyclosiloxane fragments nor functional groups.

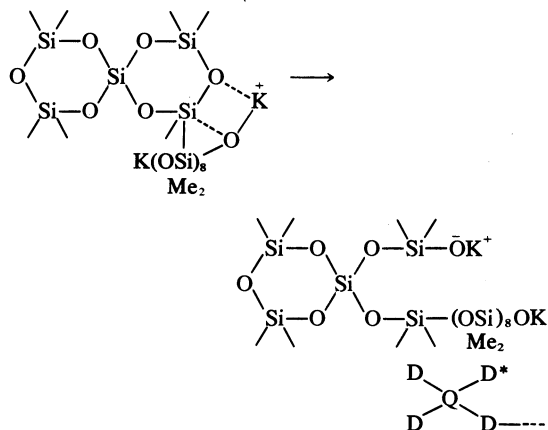
In the polymerization of spiranic compounds the growing polymer chain can apparently enter two competing reactions. In these conditions both the addition of another monomer unit to the polymer chain, which results in branching, and the formation of a ring are possible. The polymerization of organo-spirobicyclosiloxanes can be

Table 1. Polymerization of organo-spirocyclosiloxanes in block (initiator— $\text{KO}[\text{SiMe}_2\text{O}]_n\text{K}$)

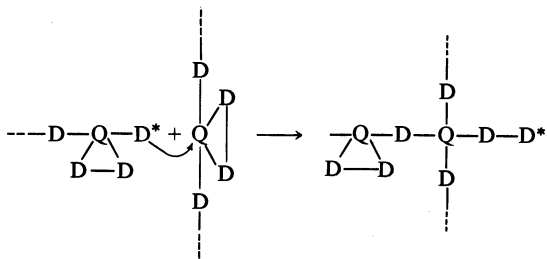
Compound number 1	Formula of monomer 2	M.p. of monomer °C 3	Limiting content of gel fraction % 4	Elemental composition			T_c of polymer (°C) 7	Notes 8		
				Monomer		Polymer				
				C 5	H 6	Si 7				
I		70	56.5	55.3	5.3	23.2	46.3	5.8	26.2	22
II		151	64	55.6	5.3	23.1	55.2	5.4	23.2	5
III		114	28	62.6	5.0	19.3	63.1	5.2	18.3	100
IV		252	0	67.6	4.7	16.5	67.5	4.4	16.9	
V		121	96	26.9	6.6	39.3	26.0	6.1	38.8	

schematically presented as follows:

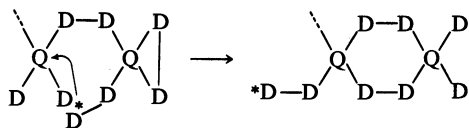
Initiation:



Interaction of chains:



Intrachain cyclization:



The polymerization process can, thus, be considered to develop in two directions and to be of equilibrium nature (Fig. 1).

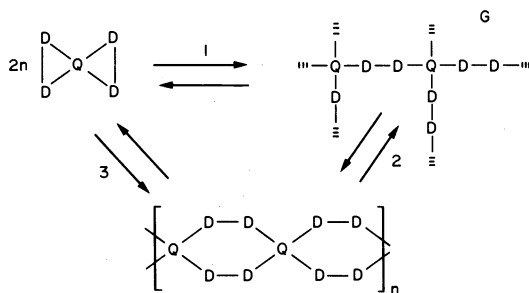


Fig. 1. Scheme of organospirobicyclic siloxanes polymerization.

The state of equilibrium in such a system must be characterized by a minimum of free energy. Since the free energy of a system is related to thermodynamic parameters by the well known relationship,

$$\Delta F = \Delta H - T\Delta S$$

where F —free energy ($v = \text{const}$)
 H —enthalpy
 S —entropy,

it is of interest to consider the effect exerted on the polymerization process by both the structural factors and the conditions in which the process is conducted. Enthalpy variation should be, mainly, affected by structural factors: strain energy in the ring, interaction of side groups etc. The entropy term is, first of all, influenced by the temperature of the process.

The free energy decrease with the polymerization of spiro[5,5]pentasiloxanes, which are strained rings, is mainly connected with the enthalpy drop during their decyclization. The opening of the rings is accompanied with the growth of entropy, whereas the formation of a spatially cross-linked polymer (Fig. 1) proceeds with the decrease of entropy. For this process one can assume the existence of a certain limiting temperature of gel formation, $T_G = (\Delta H/\Delta S)$, above which the formation of a cross-linked polymer is thermodynamically impossible. At temperatures below this limiting temperature, on the other hand, the cross-linked polymer will be stable. The transformation of the spatially cross-linked structure into

the spirocyclic structure (process 2) is, on the contrary, accompanied with the growth of entropy due to the growing freedom of translational motion of the molecules, and the increase of the temperature will, therefore, result in accelerating this process. Enthalpy variation in process 2 is, probably, insignificant.

The initial cyclic structures must also be in equilibrium with the spirocyclic structures (process 3), though this equilibrium will, apparently, be shifted towards the formation of strained structures.

The study of the polymerization of spiro-siloxanes with a differing ratio between the methyl and the phenyl side groups at different temperatures makes it possible to assess the effect of steric factors, created by the phenyl groups, and of the temperature on the nature of equilibrium and to explain the predominant formation of a polymer with a certain structure depending on the process conditions and the initial ring structure.

Thus, the polymerization of octamethyl spiro[5,5]pentasiloxane, in which steric interactions of the methyl groups are insignificantly small, proceeds with the opening of both siloxane rings in the molecule and results in the formation of a three-dimensional lattice. The free energy gain in this process is close to maximal, since in the course of the molecular interaction process there is no increase of enthalpy when side groups are brought closer together. The limiting temperature of gel formation in this case is very high.

Introduction of binary phenyl substituents into the bicyclic molecule will lead to the overall value of ΔH becoming the result of the enthalpy decrease due to the opening of strained rings and of its simultaneous growth caused by the increase of the steric repulsion of phenyl substituents during the transition from the initial rings to the cross-linked polymer. As a result of this, the overall value of ΔH can remain negative, but its absolute value will decrease, which will result in a corresponding decrease of the limiting gel formation temperature. With complete substitution of methyl groups by those of phenyl it is possible that no enthalpy decrease at all is taking place during the inter-chain polymerization and, hence, the formation of a cross-linked structure is ruled out.

In addition to that, steric interactions between the side groups in a cross-linked polymer can lead to the decrease of rotary entropy, which, in its turn, will assist even more in lowering the limiting temperature.

Studying the polymerization of 2,2,4,4-tetramethyl-8,8,10,10-tetraphenyl spiro[5,5]pentasiloxane (I) and 2,4,8,10-tetramethyl-2,4,8,10-tetraphenyl spiro[5,5]pentasiloxane (II), with the ratio between ethyl and phenyl groups equal to 1:1, has shown that, at temperatures below the limiting value (full transformation into polycyclic oligomers takes place at a temperature of about 320°), there is a build-up of the gel fraction in the process of polymerization reaching a certain equilibrium value for the given conditions. At 150° (0.02% of initiator evaluated with respect to KOH) polymerization (I) results in the formation of 56% and (II)—64% of gel fraction in equilibrium with the soluble portion.

The rate of gel forming and the equilibrium content of the gel fraction increase when the initial concentration of initiator is increased (Fig. 2).

The polymerization of 2,4-dimethyl-2,4,8,8,10,10-hexaphenyl spiro[5,5]pentasiloxane (III) (1:3 ratio between the methyl and the phenyl groups) was studied at various temperatures. The presence of considerable amounts of phenylic substituents in this ring results in the

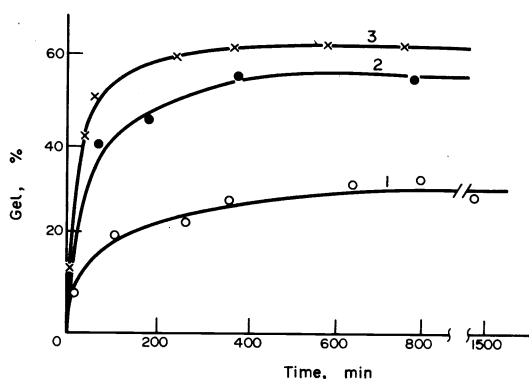
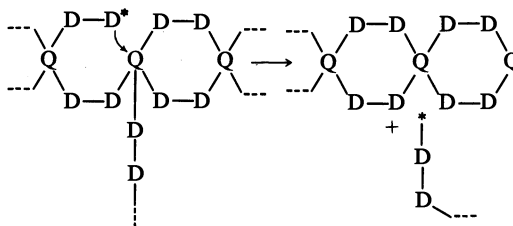


Fig. 2. Relationship between the gel-fraction yield and initiator concentration: (1) 0.075 g KOH/mol; (2) 0.150 g KOH/mol; (3) 3.0225 g KOH/mol.

limiting temperature of gel forming decreasing to values commensurate with the usual temperature of polarization by alkalis. This made it possible to assess the effect of kinetic factors on the polymerization process and to observe the successively proceeding stages (1) and (2) (Fig. 1).

From Fig. 3 it is seen that at polymerization temperatures of 120 and 130°C there is a build-up of the gel fraction content to equilibrium values corresponding to these temperatures, the equilibrium value of the gel fraction content decreasing with the growth of polymerization temperature, though the initial rate of the process, in this case, increases. At polymerization temperature of 150° the kinetic curve of the gel fraction accumulation is characterized by an extreme value—it passes the maximum of cross-linked polymer formation. At this and higher temperatures the cross-linked polymer is thermodynamically unstable and it undergoes an irreversible rearrangement into oligomers with a spiro-polycyclic structure. The process passing through a non-equilibrium stage of cross-linked polymer formation at temperatures above the limiting values appears to result from the general effect of the differences in the reactivities of intermediate structures in the process of attaining the true equilibrium. Until this equilibrium is reached, the ratio between the cross-linked and the polycyclic products seems to be determined by the ratio between the rates of intra- and inter-chain reactions taking place in these conditions.

Viscosity of the soluble polymerization products of 2,4-dimethyl-2,4,8,8,10,10-hexaphenyl spiro[5,5]pentasiloxane (III) decreased with increased polymerization temperature. At high temperatures the process of rearrangement becomes, formally, similar to depolymerization. The tendency to depolymerization at high temperatures appears to be connected with the growth of translational entropy during the rearrangements which are accompanied with the opening of the main chains:



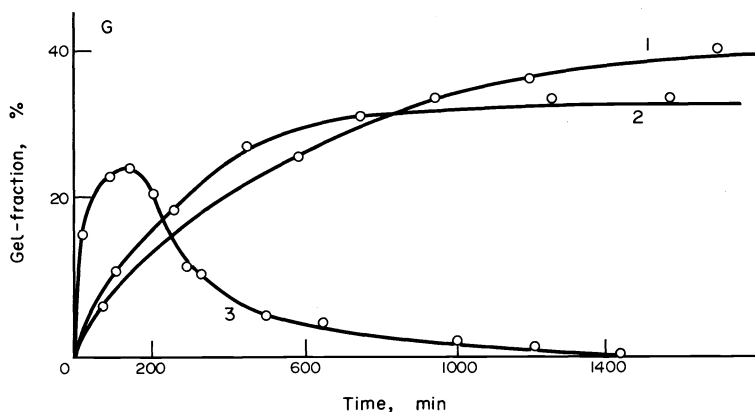


Fig. 3. Relationship between the yield of gel-fraction (for block polymerization of III) and temperature: (1) 120°; (2) 130°; (3) 150°.

That rearrangements are taking place in the siloxane skeleton with the opening of main chains is attested by the fact that the elemental composition of the polymer obtained from 2,2,4,4-tetramethyl-8,8,10,10-tetraphenyl spiro[5,5]pentasiloxane is observed to differ from that of the initial dicycle. This can be explained by the polymerization of a ring simultaneously containing dimethyl- and diphenyl siloxane units with markedly different steric interaction, such polymerization resulting in the redistribution of elementary units between the cross-linked and the soluble structures. According to the data of elemental analysis (Table 2), the content of diphenyl siloxane units in the non-soluble polymerization products is 15% lower than in the initial dicycle. The conclusion to be drawn is that in this case an equilibrium is established corresponding to a minimum of steric interactions between side groups. Such distribution of siloxane units is only possible with profound rearrangement of siloxane chains.

In the case of 2,4-dimethyl-2,4,8,8,10,10-hexaphenyl spiro[5,5]pentasiloxane polymerization (III) the elemental composition of the ring and the cross-linked polymer coincide. From this it follows that, with the low limiting temperature for this compound, no such rearrangements are observed. Spirocycles with homogeneous units and the polymers obtained from them have the same elemental composition. This can only indicate the absence, in any appreciable degree, of reactions associated with the splitting-off of organic groups.

The polymerization of spirobicyclosiloxanes in solution proceeds slower, which made it possible to draw some conclusions with respect to their reactivity. Polymerization of I, II and III was studied in the presence of $\text{Me}_4\text{N}-\text{O}(\text{SiMe}_2\text{O})\text{NMe}_4$ initiator, where $n = 26$.

This polymerization was studied in diluted toluene solutions (7.5 wt.%) at the temperature of 34°. In this case

all the polymerization products remained soluble and consisted of spirocyclic oligomers with specific viscosity of 1% benzene solution not exceeding 0.04 (at 20°). Variation of monomer concentration was recorded with the help of PMR spectra (Fig. 4). In these conditions polymerization results in the complete consumption of initial rings. The study, in these same conditions, of the temporal dependence of heat-evolution rate in the process of polymerization made it possible to arrive at an assumption of the existence of some differences in the character of polymerization I and IV. Figures 5 and 6 show the kinetic curves (differential and integral) of the thermal effect of polymerization vs time. Comparing these characteristics with the curves in Fig. 6 one can see that, in the case of ring polymerization I, heat evolution comes to an end within approximately the same time as it takes for the monomer to be completely exhausted. During polymerization III only half the total amount of heat is evolved within the time corresponding to the full conversion of the initial dicycle. Since the thermal effect of spirobicyclosiloxane polymerization in solution is only determined by the enthalpy decrease due to the dissolution of strained six-membered rings (steric strains in initial

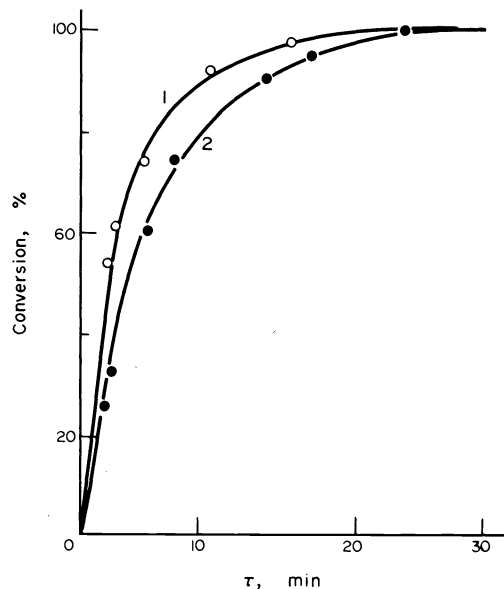


Fig. 4. Kinetic curves for polymerization in solution: (1) for I; (2) for III.

Table 2

Temperature of polymerization (°C)	Maximum yield of gel fraction (%)	Specific viscosity of soluble portion (1% benz. sol.)
120	37	0.16
130	30	0.14
150	28	0.11
180	5	0.06
200	0	0.03

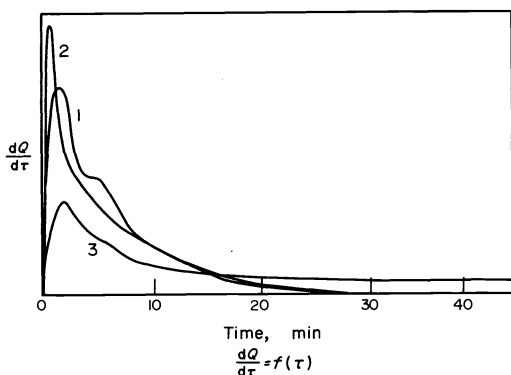


Fig. 5. (1) I; (2) II; (3) III.

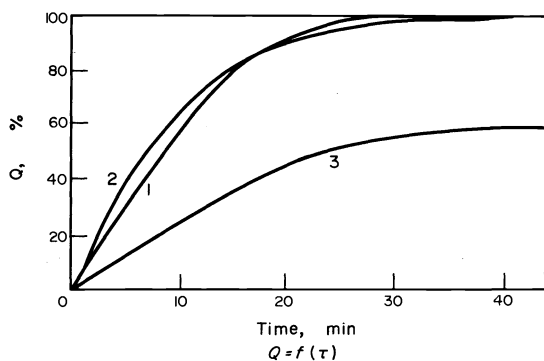


Fig. 6. (1) I; (2) II; (3) III.

and final products can be considered as approximately equal), a conclusion can be drawn that, in polymerization I, for complete monomer transformation there is also a corresponding complete decyclization of all the six-membered rings. On the contrary, in the process of polymerization III, six-membered cyclic fragments are preserved at full conversion of the monomer. Besides this, calculations showed the polymerization reaction to be of the first order as estimated from the heat evolved. And this is quite understandable if we take into account that the amount of evolved heat is proportional to the number of opened six-membered rings.

Polymerization I in more concentrated solutions (50–60%) resulted in structurization (Fig. 7), whereas in III, in these conditions, there was a transformation into a

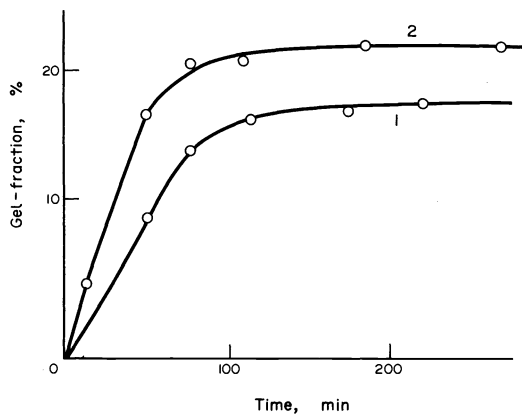
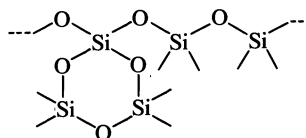


Fig. 7. Relationship between the yield of gel-fraction and temperature (polymerization I in toluene solution): (1) 50°; (2) 100°.

soluble polymer with specific viscosity 0.2 (after reprecipitation, at 20°). I.R. spectra showed (Fig. 8) that, alongside with the appearance of an absorption band of 1090 cm characteristic of the open siloxane chain, these spectra also preserve the absorption band with two maxima of 1025 and 1040 cm⁻¹ which is characteristic of the initial dicycle. This is indicative of the presence of six-membered cyclic fragments in the polymer structure:



Figures 9–11 show the thermomechanical curves of the polymer and oligomer products obtained.

Soluble products of the polymerization of octaphenyl- and dimethyl hexaphenyl spiro[5,5]pentasiloxane at room temperature are in vitreous state, vitrification temperature rising with the increase of the content of diphenyl siloxane units in the initial compound molecule (Fig. 9). Figure 10 shows the thermomechanical curves of the polymerization products of dimethyl hexaphenyl spiro[5,5]pentasiloxane III at various temperatures. Insoluble samples were extracted with the help of benzene to which trimethyl chlorosilane had been added to bind the residual silanolate groups. Spatially cross-linked polymers (Curves 1 and 2) obtained at 120 and 150°, respectively, have different vitrification temperatures. With the

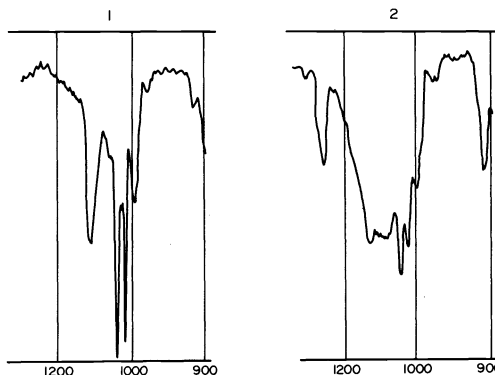


Fig. 8. I.R.-spectra: (1) for cycle III; (2) polymer from III.

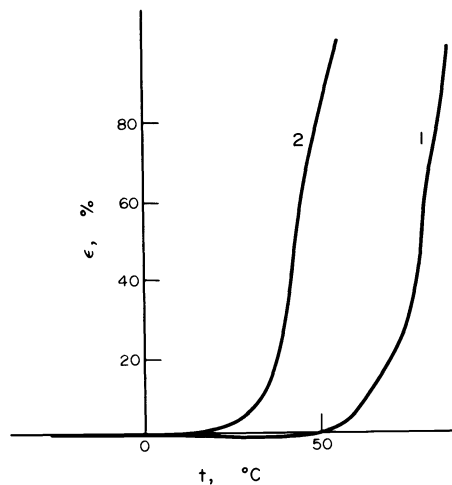


Fig. 9. Thermomechanical curves of polycyclic block-polymerization products: (1) from IV; (2) from III.

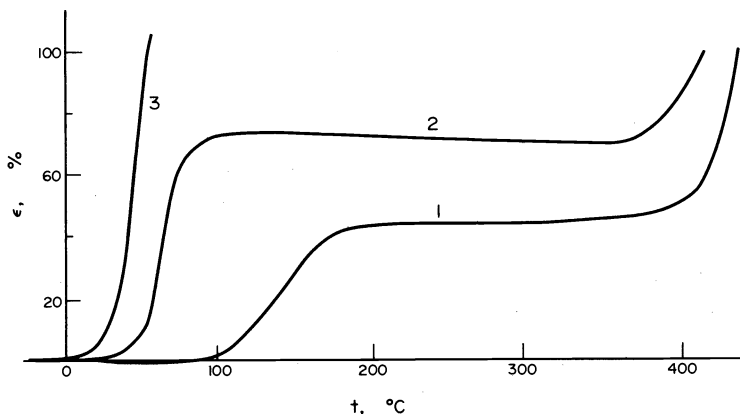


Fig. 10. Thermomechanical curves of block-polymerization product from III at different temperatures: (1) at 130°; (2) at 150°; (3) at 200°.

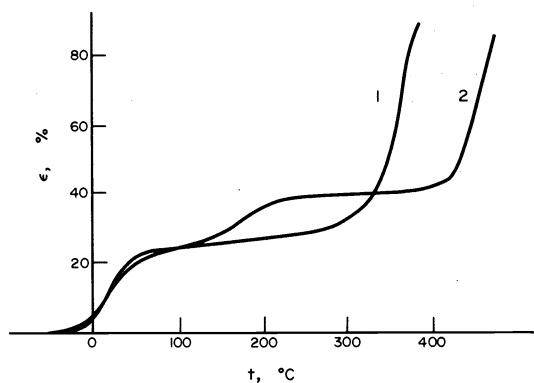


Fig. 11. Thermomechanical curves of block-polymerization product (I).

increase of polymerization temperature both the vitrification temperature and the degree of polymer chain cross-linkage decrease. The portion of highly elastic state, for the polymer obtained at 150° (Curve 2), corresponds to a greater value of highly elastic deformation, as compared to that of the polymer obtained at 120° (Curve 1). During polymerization at 200° the only polymer formed is a soluble polymer with a high molecular weight (Curve 3). A similar picture is displayed by the samples of the spatially cross-linked polymer obtained by polymerizing 2,2,4,4-

tetramethyl-8,8,10,10-tetraphenyl spiro[5,5]pentasiloxane I (Fig. 11). The flow of samples, which is observed at high temperatures, is caused by the process of thermocatalytic destruction taking place and is associated with the transformation into soluble spirocyclic structures. Such transformation occurs at a lower temperature, if there are active initiator centres present in the sample (Curve 1), as compared with the extracted sample (Curve 2).

CONCLUSIONS

1. Anionic polymerization of spirobicyclosiloxanes containing methyl and phenyl side groups in varying combinations has been investigated. Polymerization has been shown to proceed as a complex process resulting in the simultaneous formation of both spatially cross-linked and soluble polycyclic polymer structures.
2. The effect of the ratio between methyl and phenyl groups in the initial spirocycle molecule, as well as of temperature and initiator concentration, on the polymerization process has been studied. It has been shown possible for spatially cross-linked structures to be transformed into spirocyclic ones, as well as for linear polymers containing cyclic fragments in their chains to be synthesized.
3. The physico-mechanical properties of the polymerization products have been investigated.