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Preparation and Properties of Some Polyaluminum Organosiloxanes with Cyclonetwork Structures

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SUMMARY

Polycondensation of aluminum butoxide with α,ω-dihydroxydimethylsiloxanes having varied polymerization coefficients has been studied. Some kinetic dependencies in the generation of cyclonetwork poly(aluminum dimethylsiloxanes) have been investigated and the rate constants of cross-linking reaction, depending on the chain length of initial α,ω-dihydroxypolydimethylsiloxanes, have been calculated.

The relaxation properties of cross-linked polyaluminum dimethylsiloxanes have been tested. The curves of relaxation described by the Kohlrausch equation were shown to provide an estimation of equilibrium stress in specimens after completion of the relaxation process.

The existence of quantitative correlation between equilibrium stress and size of structural cell was established for poly(aluminum dimethylsiloxanes). It was also shown that these data are in good accord with those on the kinetic study of polycondensation of cross-linked poly(aluminum dimethylsiloxanes).

Recently a number of methods have been described for the preparation of polyorganosiloxanes and polyorganometallic siloxanes by polycondensation of tri- and tetrafunctional oligomers containing terminal monofunctional groups in the branches [1-4]. Such reactions provide cross-linked structures containing the atoms of polyfunctional elements in the knots.

The investigation of cross-linking process for polyorganometallic siloxanes is an extremely difficult problem. Regular methods may be used until the polymer retains its solubility during the polycondensation. But the content of cyclonetwork structure is insignificant in the last stage of reaction.

After initiation of the gelation process, the elucidation of the structure becomes much troublesome, since a loss of solubility expels any investigation in solution.

Indirect semiquantitative information on a polymer may be obtained by investigation of thermomechanical properties, but the latter do not always unequivocally correlate with the structure, and the conclusions to be drawn may in a number of cases be only of a qualitative nature.

In the present paper an attempt was made to elucidate the structures of insoluble polymers from the data on their mechanical properties. In our opinion, to quantitatively state the dependency between the structure and properties of the polymer essentially allows expansion of the investigation of cross-linked structures.

Polycondensation of aluminum butoxide with α, ω-dihydroxypolydimethylsiloxanes, in which the length of siloxane chain varies, has led to the polymers of cyclonetwork structures containing aluminum atoms in the knots. The molar ratio of reagents applied was 1 : 3.

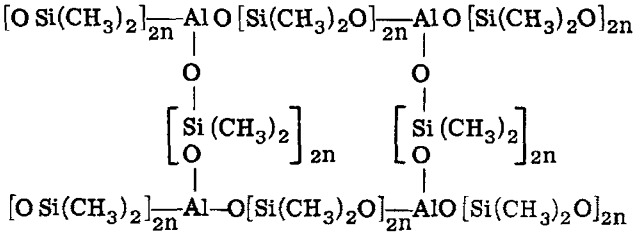
The process proceeds according to the following scheme.

$$Al(OC_4H_9)_3 + 3HO\ [Si(CH_3)_2O]_nH \rightarrow$$

$$Al\{O[Si(CH_3)_2O]_nH\}_3 + 3\,C_4H_9OH$$

$$2\ Al\ \{O\,[Si(CH_3)_2O]H\}_3 \rightarrow$$

$$\{H\,[O\,Si(CH_3)_2]_nO\}\ Al\ O\,[Si(CH_3)_2O]_{2n}\ Al\{O\,[Si(CH_3)_2O]_nH\}_2 \rightarrow$$



$$\begin{array}{l} [O\,Si(CH_3)_2]_{2n}\text{—}\underset{|}{Al}\,O\,[Si(CH_3)_2O]_{2n}\text{—}\underset{|}{Al}\,O\,[Si(CH_3)_2O]_{2n} \\ \qquad\qquad O \qquad\qquad\qquad\quad O \\ \qquad\quad \left[\begin{array}{l} Si(CH_3)_2 \\ O \end{array}\right]_{2n} \qquad \left[\begin{array}{l} Si(CH_3)_2 \\ O \end{array}\right]_{2n} \\ [O\,Si(CH_3)_2]_{2n}\text{—}\overset{|}{Al}\text{—}O[Si(CH_3)_2O]_{2n}\text{—}\overset{|}{Al}O\,[Si(CH_3)_2O]_{2n} \end{array}$$

The mean value of polymerization coefficient (n) characterizing the starting α, ω-dihydroxypolydimethylsiloxane defines a distance between aluminum atoms which is of 2n order of magnitude because in the polycondensation process a siloxane bond is generated due to the linking of two branches having n silicon atoms in each.

Figure 1 shows the dependency of specific viscosity of 1% benzene solutions of the polymers on the duration of polycondensation with aluminum butoxide. The specific viscosity of oligomers with lower n (curve 1, n = 20) increased slower than the viscosity of those with high n (curves 2, 3, and 4; n = 61, 99, and 177). Since hydroxy groups in olygomer are equivalent in reactivity, we explain these results by the fact that under the same conditions each elementary reaction of a hydroxy group in oligomer of high n leads to polymer of higher molecular weight and higher specific viscosity.

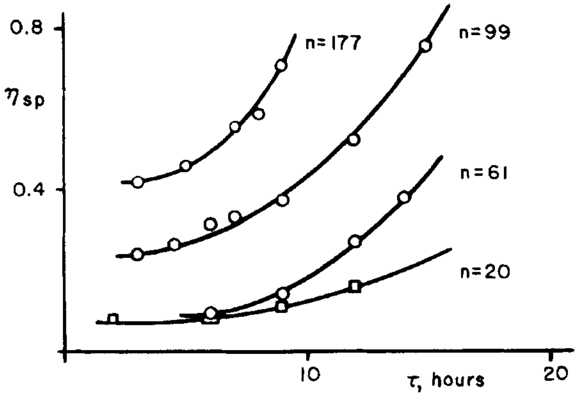


Fig. 1. Specific viscosity of 1% benzene solutions of the polymer vs. polycondensation time with aluminum butoxide.

Determination of the latter makes it possible to describe only the stages when the polymer remains completely soluble, i.e., when the cyclonetwork structure is still not expanded enough. This made us investigate also the yield-time dependency for a gel fraction in the reaction of polycondensation at 200°C in order to estimate the kinetics of cyclonetwork-structure generation.

Figure 2 shows the content of insoluble gel fraction versus time of polycondensation of aluminum alkoxide with α, ω-dihydroxypolydimethylsiloxanes having different chain lengths.

As seen from these data, yield of gel fraction naturally increases with time.

It may be accepted that when the gelation process starts, the molecules of branched poly(aluminum organosiloxane) approach such dimensions that each elementary reaction gives either the molecule of insoluble polymer or the closure of the branch ends within the same molecule. In this case no gel is formed.

If C_i is the per cent concentration of gel fraction and C_s is the concentration of soluble phase, then the latter decreases with time proportionally to the concentration of soluble phase at a given moment.

$$\frac{dC_s}{d\tau} = kC_s \qquad \text{or} \qquad \lg C_s = 2 - k\tau$$

where τ is the time and k the rate constant of gelation.

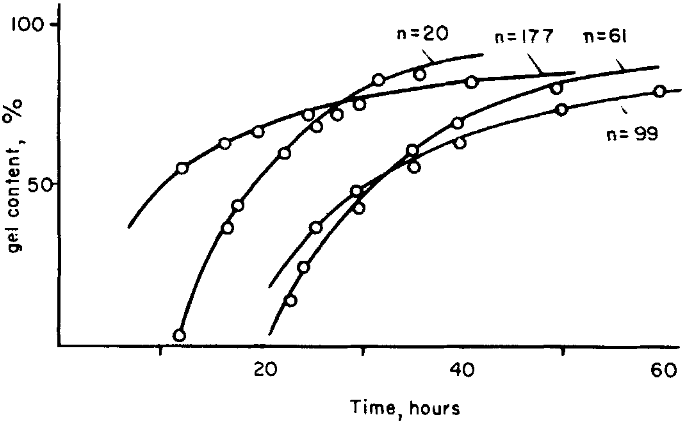


Fig. 2. Content of insoluble gel fraction vs. polycondensation time of α,ω-dihydroxypolydimethylsiloxane with aluminum alkoxide.

Figure 3 shows the dependency of logarithmic concentration of soluble phase on the time of polycondensation of α,ω-dihydroxypolydimethylsiloxanes having different chain lengths. These data exhibit a linear plot. The rate constants of the gelation reaction observed for oligomers of different n's are listed in Table 1.

In the previous paper [5] we advanced the globular structure for solidized poly(aluminum organosilaxanes) and suggested an effect

Table 1. Rate Constants of Gelation Reaction vs. Chain Length of α,ω-Dihydroxydimethylsiloxane.

n	k
20	0.037
40	0.039
61	0.022
99	0.016
177	0.014

of this submolecular structure on the properties of poly(aluminum organosiloxanes). This led us to the idea of elucidating the influence of the degree of cross-linking on some mechanical properties of the forming polymers and correlating these properties with the above kinetic data.

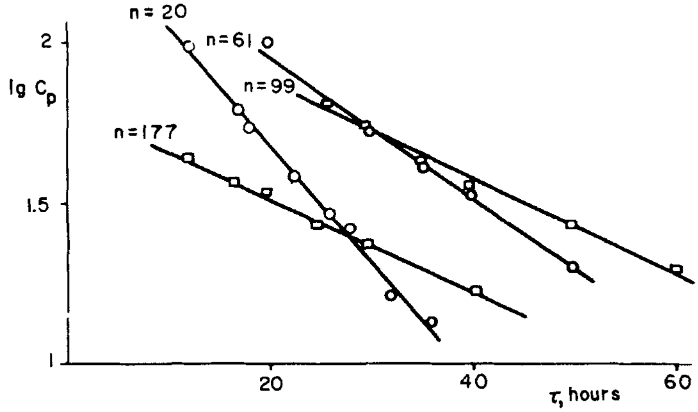


Fig. 3. Logarithmic concentration of the soluble phase vs. polycondensation time of α, ω-dihydroxypolydimethylsiloxanes having varied chain lengths.

The investigation of stress relaxation using Polani's relaxometer was chosen as an example. We have studied the relaxation properties of poly(aluminum organosiloxanes) vs. the n value and curing time. The curves of stress relaxation for poly(aluminum organosiloxanes) at the varied curing time and n = 12, 15, 30, and 80 are shown in Fig. 4(a), (b), (c), and (d), respectively. When the above polymers have the same N, the magnitude of stress grows with the curing either when the strain propagation completes or after 1 hr of relaxation. Moreover, after a certain period of cross-linking the curves practically impose.

To investigate the equilibrium and kinetic properties vs. the time of cross-linking in more detail we have calculated stress relaxation curves which may be satisfactorily described by the well-known Kohlrausch equation [6]:

$$\delta = \delta_\infty + \delta_0 e^{-at^k}$$

where δ = stress in the specimen at the moment t

δ_0 = maximal value of relaxation part in stress

δ_∞ = equilibrium stress in the specimen at the end of the relaxation process

a and k = constants characterizing the material of a specimen.

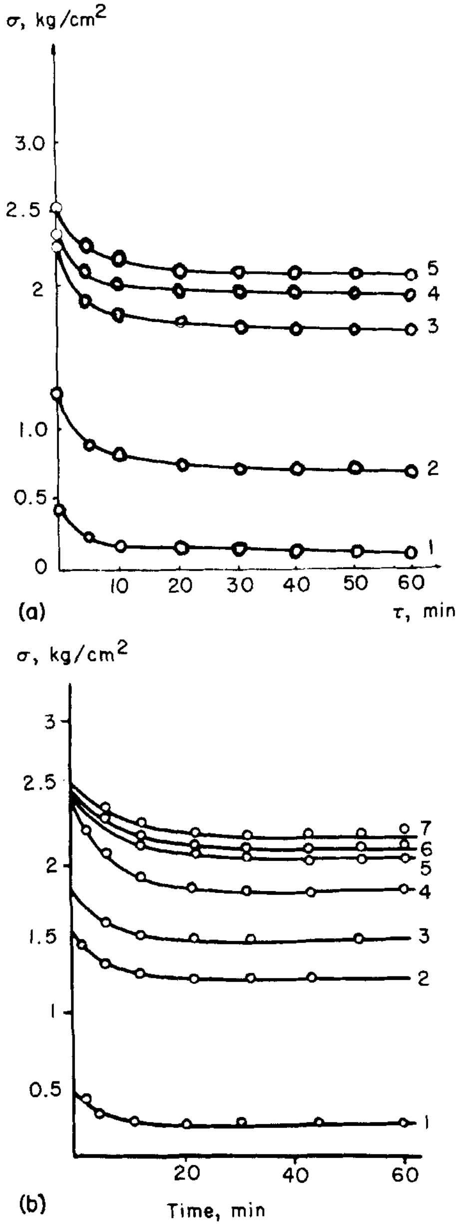


Fig. 4. Tension relaxation curves of poly(aluminum organosiloxanes): (a) n = 12, (b) n = 15, (c) n = 30, (d) n = 80.

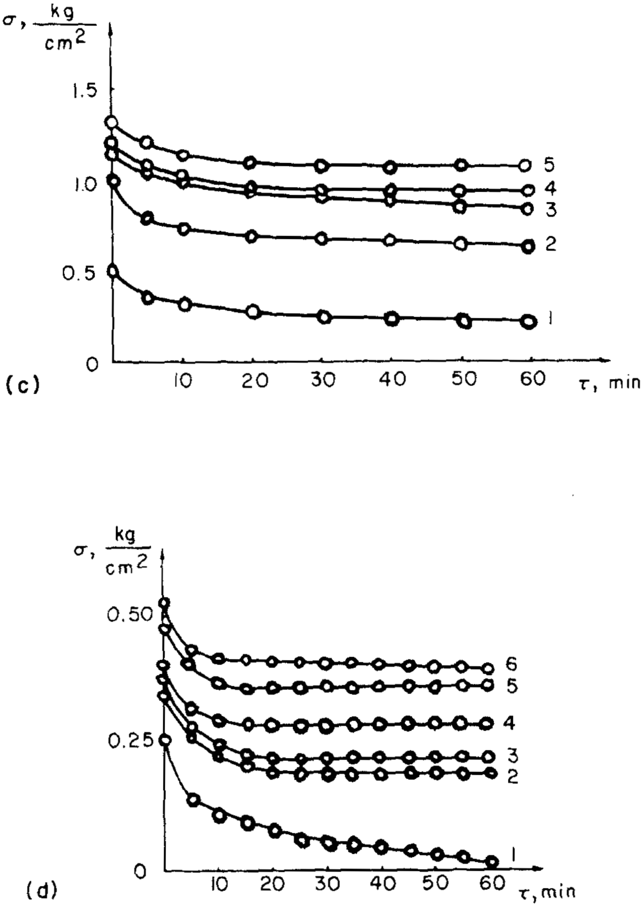


Fig. 4 (continued)

Figure 5 shows the dependency of equilibrium stress δ_∞ on the time of thermostatting for poly(aluminum organosiloxanes) having varied n. As seen from this figure, a decrease in n causes an increase in time of achieving gelation point. An attention should be paid to the fact that the δ_∞ value after attaining the gelation point grows more rapidly than that for polymers with small n.

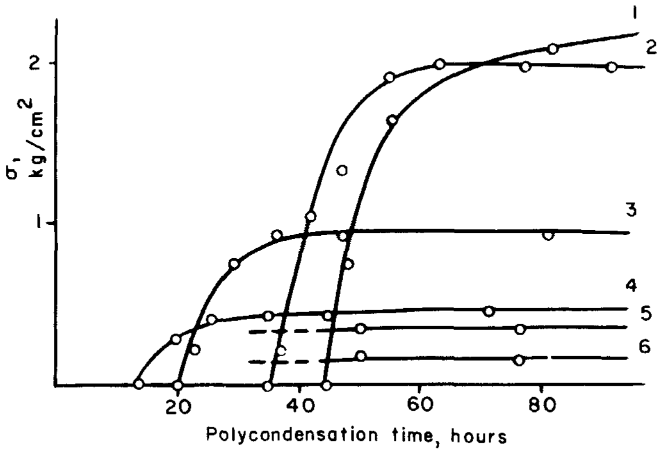


Fig. 5. Equilibrium stress vs. thermostatting time for poly(aluminum dimethylsiloxanes) having varied n.

At a certain thermostatting time δ_∞ arrives at the constant δ_∞^{equil}. The above data indicate a complete correlation between results on kinetics of gelation and those concerning the mechanical properties of the polymers. (The reverse dependency between the n value and the time of achieving the gelation point was observed and the gelation rate was proportional to n.)

It is known that in case of high-elastic polymers the equilibrium elasticity modulus and therefore the equilibrium stress unequivocally testify to the extent of cross-linking in polymer, which according to the modern kinetic theory of high elasticity is equivalent to the number of knots in spatial macromolecular network per 1 cm^3. The data obtained unequivocally manifest the clear distinction of mechanical properties of poly(aluminum siloxanes) having varied n. It is likely that in the case of small global generations linked by chemical and physical bonds, the content of the latter per 1 cm^3 is higher; i.e., poly(aluminum dimethylsiloxanes) having small n's possess all the properties responsible for a high degree of cross-linking.

Figure 6 represents the dependency of δ_∞^{equil} on n. The estimation of this data shows that the mechanical properties of poly-

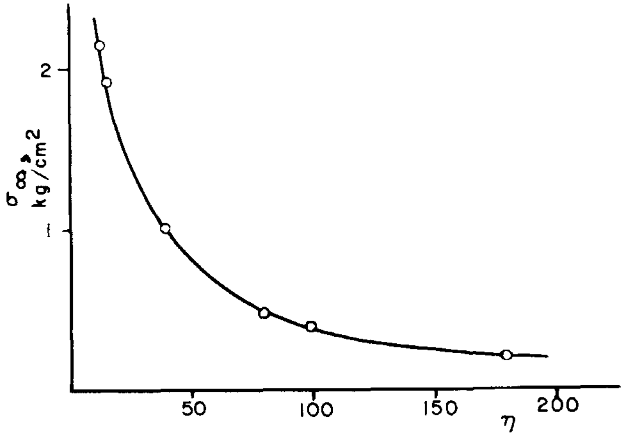


Fig. 6. δ_∞^{equil} vs. n.

(aluminum dimethylsiloxanes) most of all vary for n from 12 to 80. For higher n's these changes are negligible.

Figure 7 shows the dependency of lg δ_∞^{equil} on lg n. The line produced may be expressed by

$$\lg \delta_\infty^{equil} = A - B \lg n$$

Thus a direct quantitative correlation was discovered between δ_∞^{equil} and n for poly(aluminum dimethylsiloxanes). Such a correlation may be obtained for any particular state of the polymer.

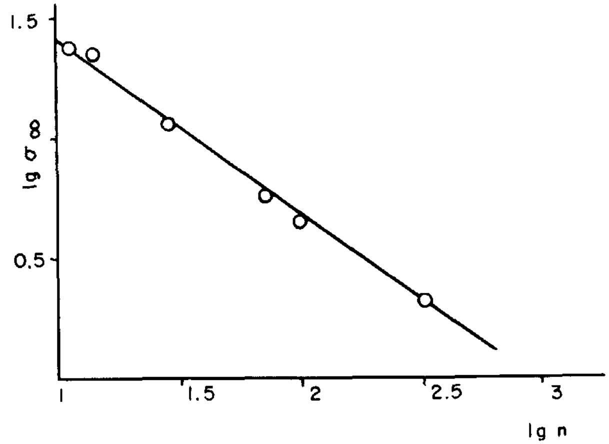


Fig. 7. lg δ_∞^{equil} vs. lg n.

The relaxation curves also permit quantitative estimation of the effect of curing temperature on the rate of cross-linking. Poly(aluminum dimethylsiloxane) (n = 15) kept at 200°C for 30 hr was thermostatted at different temperatures for 10 hr. The relaxation curves for specimens kept at various temperatures are shown in Fig. 8. Thus at 150°C no notable cross-linking was observed after 10 hr and the stress in the specimen relaxed down to zero. Increase in temperature causes a sharp increase in the rate of cross-linking, slowing at 200°C.

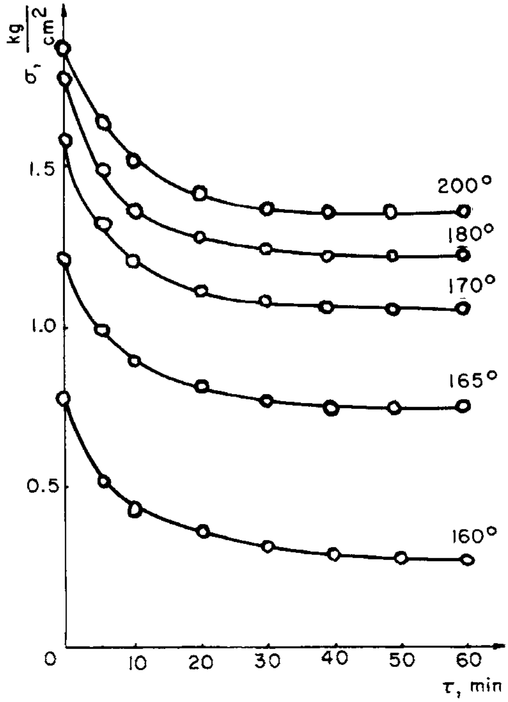


Fig. 8 Stress relaxation curves at various temperatures.

EXPERIMENTAL

α, ω-Dihydroxydimethylsiloxanes have been prepared by telomerization reaction of octamethylcyclotetrasiloxane in the presence of dimethyldichlorosilane using the procedure described in [7].

α, ω-dichloropolydimethylsiloxanes obtained were hydrolyzed by aqueous sodium bicarbonate in the presence of benzene or acetone [8]. Characteristics of the α, ω-dichloro and α, ω-dihydroxypolydimethylsiloxanes obtained are given in Table 2.

Table 2. Characteristics of α,ω-Dihydroxypolydimethylsiloxanes (I) Applied

	Molar ratio of $(CH_3)_2SiO_4$ to $(CH_3)_2SiCl_4$ in telomerization reaction	Cl content in the polymer obtained, %	Chain length of telogen (Si atoms) calculated on Cl content	OH percentage in I	Inherent viscosity of I	Chain length of I calculated from its viscosity
1	2.5:1	5.87	14.6	2.57	0.021	20
2	6.25:1	3.17	28.4	1.36	0.039	40
3	10:1	2.02	45.6	—	0.051	61
4	17.5:1	1.13	82.9	—	0.070	99
5	25:1	0.94	100.0	—	0.102	177

Table 3. Characteristics of Applied Poly(aluminum dimethylsiloxanes)

Involved in reaction, g/mole			Analysis of the polymers					
			C		H		Si	
Oligomer	n	Butanol obtained, g/mole	Found	Calc.	Found	Calc.	Found	Calc.
54. 03 (0. 036)	20	2. 96 (0. 012)	31. 87 32. 01	31. 66	8. 04 7. 93	7. 97	36. 95 37. 45	37. 04
58. 60 (0. 018)	40	1. 41 (0. 019)	32. 39 32. 48	32. 02	8. 17 8. 18	8. 06	37. 45 37. 55	37. 45
54. 33 (0. 012)	61	0. 91 (0. 012)	32. 53 32. 32	32. 15	8. 29 8. 21	8. 10	38. 80 38. 39	37. 60
66. 10 (0. 009)	99	Traces	32. 17 32. 21	32. 24	8. 02 7. 98	8. 12	37. 55 37. 45	37. 71
55. 09 (0. 0042)	177	Traces	33. 34 33. 12	32. 31	8. 39 8. 27	8. 13	37. 18 37. 55	37. 78

Aluminum butoxide was prepared by reaction of aluminum with butanol. Freshly distilled reagent was used in the reaction. The reaction between aluminum butoxide and α,ω-dihydroxypolydimethylsiloxanes was carried out in a three-necked flask provided with a stirrer, reflux condenser, and nitrogen-introducing tube. The mixture was heated in the thermostatted oil bath at a constant temperature (200°C). After the temperature of the mixture reached 200°C, a weak stream of nitrogen was allowed to pass through, to facilitate the remove of butanol and water generated. Characteristics of the process and compositions of the polymers obtained are shown in Table 3.

For determination of specific viscosity and the content of gel fraction the tests were withdrawn periodically (1 g) and extracted with benzene (30 hr). After drying the material until constant weight, the content of insoluble fraction was calculated. The results are listed in Tables 4 and 5.

Table 4. Specific Viscosity of Polymer Solutions vs. Polycondensation Time

Polycondensation time at 200°C, hr	Specific viscosity of 1% benzene solutions of the polymers prepared from α,ω-dihydroxydimethylsiloxanes having varied degrees of polymerization			
	n = 20	n = 40	n = 99	n = 177
2.0	0.08	0.06	—	—
3.0	—	—	0.24	0.42
4.5	—	—	0.26	—
5.0	—	—	—	0.46
6.0	0.08	0.09	0.31	—
7.0	—	—	0.33	—
8.0	—	—	—	0.59
9.0	0.11	0.14	0.37	0.71
12.0	0.16	—	0.52	—
14.0	—	0.88	—	—
15.0	—	—	0.75	—
20.0	0.18	—	—	—

Table 5. Yield of Gel vs. Polycondensation Time[a]

n = 20	n = 40	n = 61	n = 99	n = 177
1.46 (12)	0.42 (20.5)	0.31 (20)	36.54 (26)	56.81 (12)
38.35 (17)	13.44 (23)	47.42 (30)	45.13 (30)	63.90 (17)
45.58 (18)	25.03 (24)	59.83 (35)	57.25 (35)	65.75 (20)
61.61 (22.5)	64.22 (34)	66.68 (40)	64.21 (40)	73.11 (25)
70.34 (26)	69.76 (36)	80.18 (50)	73.26 (50)	76.38 (30)
73.58 (28)	—	—	80.32 (60)	83.39 (41)
83.81 (32)	—	—	—	—
86.56 (36)	—	—	—	—

[a] The yield of gel (%) for the polymers prepared from dihydroxypolydimethylsiloxanes having various n's. The time matched from the start of polycondensation is indicated in parentheses.

For the investigation of mechanical properties, the preparation of polymers was carried out in specially prepared Teflon casts at 200°C. After a certain period a specimen was withdrawn and the film of required size cut out. The thickness of a specimen was measured by a micrometer with an accuracy of 50 μk (5% of the thickness). The relaxation stress was measured at constant strain (70%) attained after 10 sec. A fixed rate of strain was governed by some methodical reasons.

In the ideal case the strain should master instantly. In fact, however, this is impossible, and stress in the specimen partially relaxes when the strain attains its master value.

In the calculation of relaxation curves this methodical trouble may be solved by the proper choice of time t, which should exceed by 10 times the time of master strain. In our experiment the lower clutch of the dynamometer* translated at the highest speed of 0.66 mm/sec for which the time of master strain was 1 sec, which greatly decreases the accuracy of mastering the strain. There seems to be no reason to master the strain higher than chosen above, since the specimens have small breaking elongations.

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*The test was performed using a hard string provided with a stress data unit of extremely high sensitivity to any small stress required to maintain the strain mastered.

These ideas have formulated the basis for the choice of experimental conditions. After mastering the strain, the stress by which the strain was maintained was scanned continuously for 1 hr by means of an X recorder.

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