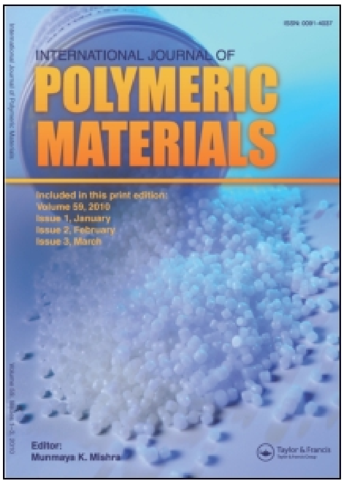


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Carbosiloxane Copolymers with Cyclosiloxane Fragments in the Chain

Omari V. Mukbaniani[a]; Lotari V. Khananashvili[a]; Nelli A. Koyava[a]; Guram V. Porchkhidze[a]; Yuri I. Tolchinski[a]
[a] I. Javakhishvili Tbilisi State University, Tbilisi, Republic of Georgia

**To cite this Article** Mukbaniani, Omari V. , Khananashvili, Lotari V. , Koyava, Nelli A. , Porchkhidze, Guram V. and Tolchinski, Yuri I.(1992) 'Carbosiloxane Copolymers with Cyclosiloxane Fragments in the Chain', International Journal of Polymeric Materials, 17: 3, 113 — 119

**To link to this Article: DOI:** 10.1080/00914039208041106

**URL:** http://dx.doi.org/10.1080/00914039208041106

*Intern. J. Polymeric Mater.*, 1992, Vol. 17, pp. 113–119
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

# Carbosiloxane Copolymers with Cyclosiloxane Fragments in the Chain

OMARI V. MUKBANIANI, LOTARI V. KHANANASHVILI, NELLI A. KOYAVA,
GURAM V. PORCHKHIDZE and YURI I. TOLCHINSKI

*I. Javakhishvili Tbilisi State University, 3 Chavchavadze ave., Tbilisi 380028, Republic of Georgia*

*(Received November 7, 1991)*

The reaction of hybrid polyaddition of dihydroorganocyclotetra (penta, hexa)siloxanes to divinylorganocyclopenta(hexa)siloxanes in the presence of 0.01 M $H_2PtCl_6 \cdot 6H_2O$ solution in tetrahydrofuran has been investigated. The rate constant and activation energy of the polyaddition reaction were calculated. It was established that with an increase in cycle volume, the rate of polyaddition decreases. Thermomechanical and X-ray analyses of amorphous copolymers were conducted as well as thermogravimetric investigations were performed with simultaneous analysis of gaseous products of the reaction. It was shown that with an increase in the volume of cyclic fragments, thermal stability of copolymers decreases.

KEY WORDS Carbosiloxane copolymers, cyclosiloxane.

## INTRODUCTION

Synthesis of carboorganosiloxane oligomers and polymers is based on the reaction of hybrid polyaddition of organohydrosiloxanes to organoalkenylsiloxanes.[1] Not only carboorganosiloxane oligomers and polymers of linear structure were obtained by this method,[2–7] but also polymers of cyclolinear structure with eight-membered fragments in the polymer chain.[8]

By means of the reaction of self-polyaddition of 1-hydrid-3-vinylhexamethylcyclotetrasiloxane, polycarbosiloxanes with methylcyclotetrasiloxane ethylene-bridged links were obtained.[9]

The polymers with 1,5-arrangement of cyclotetrasiloxane fragments in the chain were synthesized by the reaction of hydrid polyaddition of 1,5-dihydroorganocyclotetrasiloxane to 1,5-divinylorganocyclotetrasiloxanes.[10]

Compared to polyorganosiloxane analogs, the polymers with disilyethylenic groups have smaller-thermal-oxidative stability, but larger thermal stability in the absence of oxygen.[11,12]

## EXPERIMENTAL PART

The starting materials for synthesis of carbosiloxane copolymers with cyclosiloxane fragments in the chain were 1,5-divinyl(dihydrid)-1,5-dimethyltetraphenylcyclotetrasiloxanes, 1,5-divinyl(dihydrid)-1,5-dimethylhexanphenylcyclopentaxanes and 1,7-divinyl(dihydrid)-1,7-dimethyloctaphenylcyclohexasiloxanes, obtained by the methods outlined in References 8, 12, and 13.

The purity of the starting compounds was controlled by a gas-liquid chromatograph "Cvet-4" or "LHM-8MD," the phase SRTP—100 (10%)—on a chromosorb NAW, carrier gas helium—on a 2M column. The PMR spectra were taken on a R-32 "Perkin Elmer" instrument at an operating frequency of 90 MHz in a $CCl_4$ or dioxane solution with the internal standard HMDS or TMS.

For the polymer synthesis, 0.01m solution of platinochlorohydric acid in tetrahydrofuran ($9 \times 10^{-5}$ g per 1 g of the starting substance) was used as a catalyst. The polyaddition reaction was run in the Ar atmosphere in a 1:1 mole ratio of the starting substances in the absence of a solvent at temperatures of 75, 95 and 115°C.

The reaction proceeded in dry Ar ambient for 6–7 h. Then the reaction mixture was diluted in toluene, filtered off and reprecipitated by methyl alcohol.

The IR spectra were taken on an UR-20 instrument in a NaCl dish 0.16 in thick. Thermomechanical curves were taken on a custom-made equipment. The test conditions were: $\nu = 5$ deg/min, $\sigma = 0.1$ kgf/cm$^2$.

Thermogravimetric investigations were performed on an electronic thermal balance of the firm "Seteram," model B-60, in Ar atmosphere (heating rate being 5 deg/min) with simultaneous sampling and analysis of gaseous products of the destruction.

Diffractograms were taken on a "DRON-2.0" instrument. A—Cu was measured without a filter, the angular velocity was $\omega = 2$ deg/min.

## RESULTS AND DISCUSSION

The present paper deals with synthesis and studies of the properties of carbosiloxane copolymers contained in the chain, along with organocyclopentasiloxane fragments, organocyclotetra- and organocyclohexasiloxane fragments. There are no data on the polymers of the above mentioned structure in the literature.

The polymer synthesis was carried out at temperatures not exceeding 115°C, so that in the polyaddition conditions, cycloxane opening did not take place.

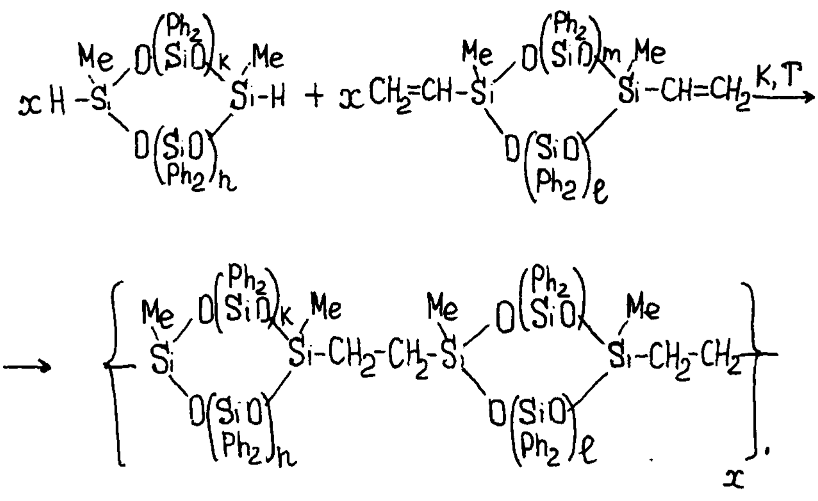
In the literature it was reported that the platinum group catalysts in the amount of 0.01–1%, when heated with siloxanes, can tear off a methyl or phenyl group.[14,16]

Preliminary heating of organocyclosiloxanes in the temperature range 75–115°C for 10 h in the presence of platinochlorohydric acid ($9 \times 10^{-5}$ g per 1 g of substance) as a catalyst showed that in this case polymerization of the starting cycles does not occur.

Therefore, the reaction of hydrid polyaddition under the conditions selected by us proceeds according to the Scheme.

As a result of the reaction, polymers are obtained with $\eta_{spec} = 0.13–0.18$, which are vitreous light-yellow transparent products soluble in usual organic solvents. Some physico-chemical properties, elementary composition and yield of synthesized copolymers are presented in Table.

The course of the reaction was watched by an increase in viscosity of the 10%



K=n=1, m=1, l=2(I); K=n=1, m=l=2 (II);
K=1, n=2, m=1, l=2(III); K=1, n=m=l=2(IV);
K=n=m=l=2(V),

SCHEME

TABLE

Elementary analysis, some physico-chemical properties and yield of copolymers

| Copolymer | $T_{react}$ °C | $\eta_{spec}$[a] | $T_{soft}$ °C | $d_1$, Å | Elementary composition[b] C | H | Si | Yield | $M.10^{3}$[c] |
|---|---|---|---|---|---|---|---|---|---|
| I | 95 | 0.15 | 48–50 | 9.4 | 63.91 | 5.03 | 19.20 | 93.7 | 97 |
| | | | | | 63.65 | 5.46 | 19.66 | | |
| | 115 | 0.18 | | | | | | | |
| II | 115 | 0.16 | 43–46 | 9.5 | 64.71 | 5.13 | 18.36 | 90.6 | — |
| | | | | | 64.86 | 5.40 | 18.92 | | |
| III | 75 | 0.11 | | 9.5 | 64.13 | 5.07 | 18.71 | 89.1 | |
| | | | | | 64.86 | 5.40 | 18.92 | | |
| | 95 | 0.14 | | | | | | | |
| | 115 | 0.18 | 45–48 | | | | | | 87 |
| IV | 95 | 0.10 | 42–44 | — | 65.91 | 4.91 | 18.09 | 92.1 | — |
| | | | | | 65.79 | 5.36 | 18.36 | | |
| V | 115 | 0.11 | 39–41 | 9.7 | 66.13 | 4.98 | 17.32 | 87.5 | 51 |
| | | | | | 66.52 | 5.33 | 17.91 | | |

[a] In toluene at 25°C.

[b] In denominator, found values; in numerator, calculated values.

[c] Molecular masses are found by light diffusion.

toluene solution (Figure 1). It was established that with temperature rise with 95°–115°C, the rate of viscosity increase rises. Figure 1 also shows that with an increase in the cycle $v$ volume this viscosity rise decreases.

The dependence of the Si—H bond optical density on time was studied on the

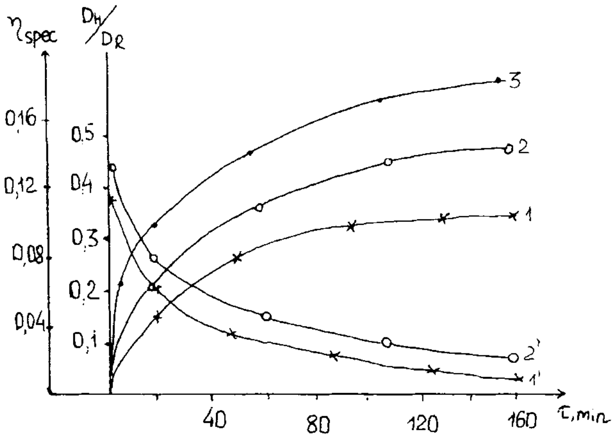


FIGURE 1 Change in optical velocity of the Si—H bond and specific viscosity with time: curves 1, 1' are for copolymer IV; 2,2' are for copolymer I at 95°C; 3 are for copolymer I at 115°C.

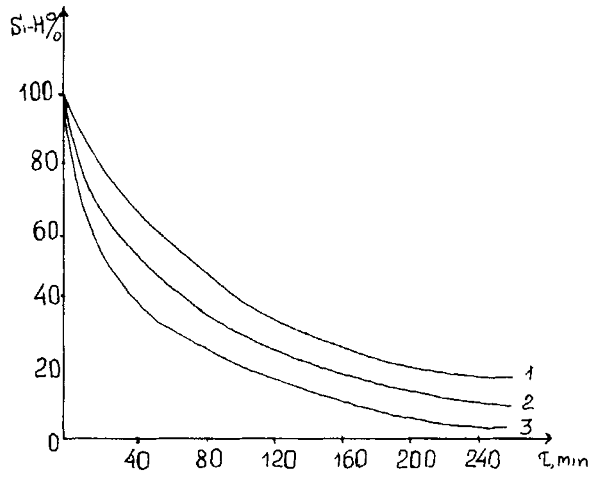


FIGURE 2 Change in Si—H(%) with time upon polyaddition of dihydroorganocyclopentasiloxane to divinylorganocyclopentasiloxane, where curve 1 is for temperature 75°C; curve 2 is for 95°C; curve 3 is for 115°C.

IR spectra in the region 2160 $cm^{-1}$ (Figure 1) over the temperature range 95–115°C. The reaction order was found to be equal to 2.

Figures 2 and 3 show the Si—H(%) concentration decrease with temperature as well as the reverse concentration (%) dependence on time, respectively. Proceeding from the data of Figure 3, the rate constants were calculated: $k_{75^\circ C} = 1.44 \times 10^{-2}$, $k_{95^\circ C} = 2.33 \times 10^{-2}$ and $k_{115^\circ C} = 3.20 \times 10^{-2}$.

Figure 4 shows the dependence of *lgk* on reverse temperature as well as the calculated activation energy of the polyaddition reaction which is equal to 24.7 kJ/mol.

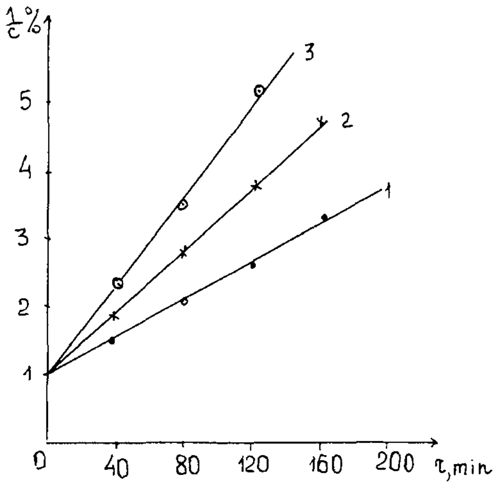


FIGURE 3 Dependence of reverse concentration on time. Curve 1 is for 75°C; curve 2 is for 95°C; curve 3 is for 115°C.

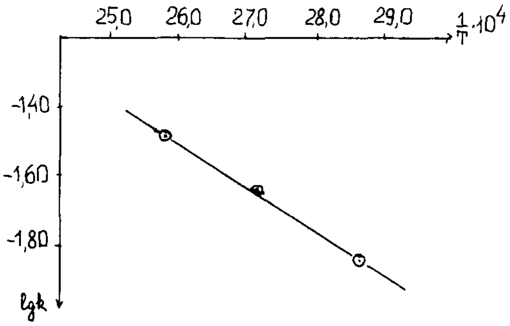


FIGURE 4 Dependence of reverse temperature on the logarithm of the rate constant of the polyaddition reaction.

The examination of the IR spectra of the copolymers obtained has revealed that the absorption bands characteristic of the Si—H bond in the range 2160–2170 $cm^{-1}$ do not vanish completely. At the same time new absorption bands occur in the spectra at 1150 $cm^{-1}$, typical for fan-shaped oscillations of the $CH_2$ groups, as well as absorption bands in the range 2900–2950 $cm^{-1}$ typical for valence oscillations of the CH bonds in the $CH_2$ groups of the ethylenic bridges.

It has been established by the NMR-$H^1$ spectra that addition proceeds mainly by the Farmer rule with formation of dimethylenic bridges between cyclic fragments. Thus, in the NMR-$H^1$ spectrum of compound **1** there appears a complex multiplet in the range 6.9–7.8 ppm, characteristic of phenyl group protons in silicon atoms, while the signal with the centre at 0.28 ppm corresponds to methyl groups. Also, there appears a signal for the grouping —$CH_2$—$CH_2$— with the chemical shift 0.36 ppm. Integral relations of these signals correspond to the copolymer formula. Besides, in the spectrum there are proton signals of unreacted vinyl groups (a complex multiplet in the range 5.6–6.1 ppm) and Si—H groups at 4.8 ppm. In the spectrum of copolymer I one can observe a double signal with the chemical shift centre at 1.05 ppm, which, as in Reference 10, can be assigned to methyl protons in the grouping $=\mathrm{CH}\text{—}\mathrm{CH}_3$, whose amount does not exceed 8%.

Thermogravimetric investigations of copolymers were carried out, and the influence of introduction of volume cyclic fragments into macrochains on their thermal stability was studied.

These investigations have shown (Figure 5) that the initial mass losses take place at 280–300°C depending on the volume of the cyclic fragments in the chain. In the temperature range 350–400°C one can observe hydrogen and methane release, which is caused by breaking of the Si—C and C—H bonds resulting in suturing for methyl and phenyl groups. A similar phenomenon was mentioned upon thermal destruction of both carbosiloxane[16] and organosiloxane copolymers.[17] The destruction process proceeds according to the radical mechanism with formation of oligomeric products.[18,19]

Above 600°C the curves reflect the level where mass losses reach their limit. The finite mass losses in the Ar atmosphere are equal to 34–38%.

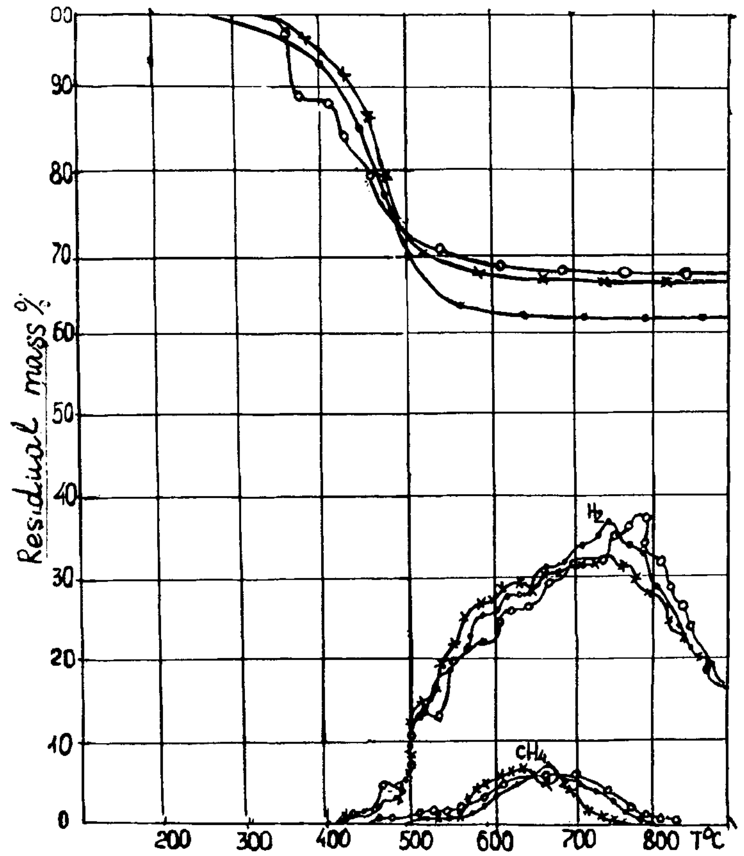


FIGURE 5 Thermogravimetric analysis of cyclolinear carbosiloxane copolymers, where for copolymer III —•—; for copolymer IV —o—; for copolymer II — x —.

As to thermal stability, the synthesized cyclolinear copolymers give way to the carbosiloxane copolymers containing only cyclotetrasiloxane fragments in the chain.[9,10]

Thermomechanical studies of the obtained copolymers were carried out and it was established that vitrification temperature of the copolymers lowers with an increase in the volume of the cyclosiloxane ring in the chain. The data on $T_{soft}$ are presented in the Table.

X-ray investigations of the copolymers showed that unlike previously synthesized copolymers,[10] they are amorphous systems. As is seen from the table, an increase in the cyclic fragment volume results in a slight increase of the interchain distance.

Thus, for the first time by means of the reaction of hybrid polyaddition we have managed to obtain and to study the properties of carbosiloxane copolymers of the cyclolinear structure, which, along with organocyclopentasiloxane, contain organocyclotetra- and organocyclohexasiloxane fragments in the chain.

## References

1. K. A. Andrianov, I. Souchek and L. M. Khananashvili,*Uspekhi Khimii,* **48,** 233 (1979).
2. A. D. Petrov and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk,* 939 (1959); *Chem. Abstr.,* **54,** 265b (1960).
3. G. Greber and L. Metzinger, *Macromol. Chem.,* **39,** 189 (1960).
4. G. Greber and R. Reese, *Macromol. Chem.,* **77,** 13 (1964).
5. K. A. Andrianov, L. A. Radrokova and E. F. Rodionova, *Vysokomol. Soedin., Ser.* **A937,** 13 (1971); *Chem. Abstr.,* **75,** 49817j (1971).
6. I. Souchek, K. A. Andrianov, L. M. Khananashvili and V. M. Myasina, *Dokl. Akad. Nauk SSSR,* **222,** 128 (1975); *Chem. Abstr.,* 78060c (1975).
7. K. A. Andrianov, I. Souchek, L. M. Khananashvili and L. Ambruz, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 606 (1975); *Chem. Abstr.,* **82,** 199690d (1975).
8. A. A. Zhdanov, K. A. Andrianov and A. P. Malykhin, *Dokl. Akad. Nauk SSSR,* **211,** 1104 (1974).
9. K. A. Andrianov, V. I. Sidorov, M. G. Zaitseva and L. M. Khananashvili, *Khim. Geterots. Soedin.,* 32 (1967); *Chem. Abstr.,* **67,** 73940z (1967).
10. A. A. Zhdanov, V. V. Severnii, E. Yu. Gutsait and K. A. Andrianov, *Plast. Massy,* 23 (1966); *Chem. Abstr.,* **64,** 16065h (1966).
11. V. V. Severnii, V. Yu. Flaks, A. A. Zhdanov, V. A. Vlasova, K. A. Andrianov and F. N. Vyshnevski, *Vysokomol. Soedin., Ser.* **A16,** 419 (1974); *Chem. Abstr.,* **81,** 26417p (1974).
12. A. A. Zhdanov and T. V. Astapova, *Vysokomol. Soedin., Ser.* **A23,** 626 (1981); *Chem. Abstr.,* **94,** 209261w (1981).
13. N. A. Koyava, O. V. Mukbaniani and L. M. Khananashvili, *Zhurn. Obshch. Khimii,* **51,** 130 (1981); *Chem. Abstr.,* **97,** 6886t (1982).
14. I. S. Akhrem, N. I. Chistovalova, E. I. Mysov and M. E. Vol'pin, *Zhurn, Obshch. Khimii,* **42,** 1868 (1972); *Chem. Abstr.,* **78,** 29883m (1973).
15. I. S. Akhrem, N. I. Chistovalova, E. I. Mysov and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser., Khimich.,* 2069 (1976).
16. M. R. Stober, M. C. Musole and J. L. Speier, *J. Org. Chem. Soc.,* **30,** 1651 (1965).
17. S. M. Meladze and O. V. Mukbaniani, *Zhurn. Obshch. Khim.,* **51,** 1624 (1981); *Chem. Abstr.,* **95,** 220087k (1981).
18. M. V. Sobolevski, I. I. Skorokhodov, V. E. Ditsent, L. V. Sobolevskaya and V. M. Efimova, *Vysokomol. Soedin., Ser.* **A11,** 1109 (1969); *Chem. Abstr.,* **71,** 30802w (1969).
19. K. A. Andrianov, S.-S. A. Pavlova, I. V. Zhuravleva, Yu. I. Tolchinski and B. A. Astapov, *Vysokomol. Soedin., Ser.* **A19,** 895 (1977); *Chem. Abstr.,* **86,** 190625D (1977).
20. K. A. Andrianov, S.-S. A. Pavlova, I. V. Zhuravleva, Yu. I. Tolchinski, N. N. Makarova and O. V. Mukbaniani, *Vysokomol. Soedin., Ser.* **A19,** 1387 (1977); *Chem. Abstr.,* **87,** 85456x (1977).
21. W. Pathnode and D. F. Wilcock, *J. Am. Chem. Soc.,* **68,** 358 (1946).
22. K. A. Andrianov, V. C. Papkov, A. A. Zhdanov and S. E. Yakushkina, *Vysokomol. Soed., Ser.* **A11,** 2030 (1969).