Ladder Polyphenylsiloxanes with Single and Double Stranded Fragments in the Chain

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The reaction of heterofunctional polycondensation (HFC) of ladder polyphenylsiloxanes with hydroxyl groups at the ends with α, ω-dichlorodimethylsiloxanes in a solution in the presence of an acceptor, HCl-pyridine, and with α, ω-bis(dimethylamino)dimethylsiloxanes in a melt in a mole ratio 1:1 and 1:2 of the starting components, respectively, has been studied. Block copolymers completely soluble in organic solvents are synthesized. Thermogravimetric, thermomechanical and X-ray analyses of polymers obtained werre carried out. The thermomechanical and X-ray analyses have made it possible to establish that at certain lengths of the phenylsiloxane and dimethylsiloxane links phase separation is observed, which points to block copolymer formation.

KEY WORDS Ladder polyphenylsiloxanes.

INTRODUCTION

It is known[1] that polyphenylsiloxane (PPS) molecules, obtained as a result of anionic polymerization of the products of phenyltrichlorosiloxane hydrolysis, include two different configurations: cis-syndiotactic and cis-anti-cis-tactic ones, in which the cis-syndiotactic structure prevails. The said configurations can be constructed by using the fragment 1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane (tetrol, T_4) as a repeated chain fragment:

trans-T_4-chair   cis-syndiotactic configuration

cis-T_4-bath   cis-anti-cis-tactic configuration

cis-isotactic configuration
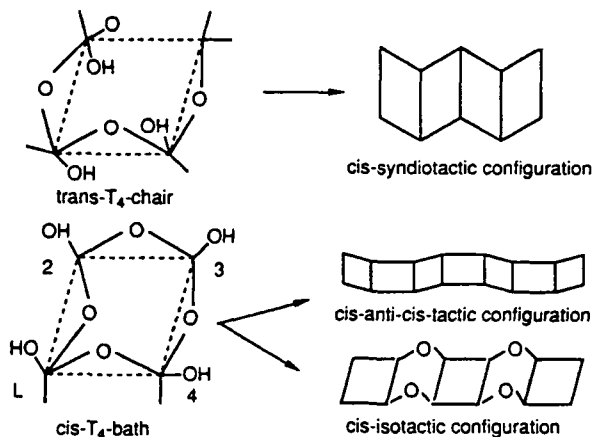
During homofunctional polycondensation of cis-tetrol in a solution or melt, PPS with the cis-anti-cis-tactic molecule configuration are formed. In this case it is not excluded that along with molecules having cis-anti-cis-tactic structure, molecules with cis-syndiotactic structures can be formed. Realization of the latter configuration, however, is connected with a number of steric difficulties, and, hence, such molecules are obtained in small amount and are characterized by a short chain.

The difference in the PPS structure, obtained by thermal condensation of cis-tetrol and anionic polymerization of phenytrichlorosilane hydrolysis products is also seen upon comparison of their IR spectra. Thus, for PPS, obtained by thermal condensation of tetrol in the toluene solution,[2] for asymmetric valence oscillations of the Si—O—Si bonds in the range $1000-1200$ cm^{-1} one can observe a wide absorption band with a well defined single maximum at 1145 cm^{-1}, while for PPS, obtained by anionic polymerization of phenyltrichlorosilane hydrolysis products, one can always observe bifurcation with the maxima at $\nu_{as} = 1045$ cm^{-1} and $\nu_{as} = 1145$ cm^{-1}.[2]
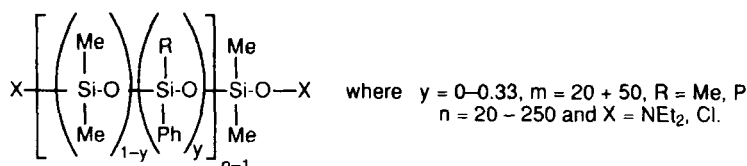
We have studied the HPC reaction between the PPS, obtained by anionic polymerization of phenyltrichlorosilane hydrolysis products with the general formula:

$$
\mathrm{HO}\!\!\left[\begin{array}{c} \mathrm{Ph} \\ | \\ \mathrm{Si-O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{Si-O} \\ | \\ \mathrm{Ph} \end{array}\right]_{m}\!\!\mathrm{H} \qquad (3)
$$
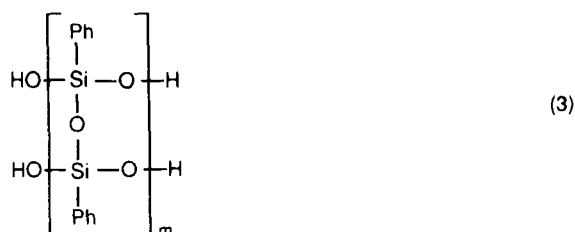
and α, ω-bis(diethylamino)- or α, ω-dichlorodiorganosiloxanes:

$$
\mathrm{X}\!\!\left[\left(\begin{array}{c}\mathrm{Me}\\|\\\mathrm{Si-O}\\|\\\mathrm{Me}\end{array}\right)_{1-y}\!\!\left(\begin{array}{c}\mathrm{R}\\|\\\mathrm{Si-O}\\|\\\mathrm{Ph}\end{array}\right)_{y}\begin{array}{c}\mathrm{Me}\\|\\\mathrm{Si-O}\\|\\\mathrm{Me}\end{array}\right]_{n-1}\!\!\!\mathrm{X}
$$

where $y = 0-0.33$, $m = 20 + 50$, R = Me, P
$n = 20 - 250$ and X = NEt_2, Cl.

The reaction was run with mole ratios of the starting components from 1:1 to 1:1.3, respectively. At certain stages of conversion, gel formation was observed. It was established that maximum tend to gel formation takes place at a 1:2 mole ratio of PPS to α, ω-bis(diethylamino)diorganosiloxane, respectively. It is also found that the gel formation time is reduced with an increase in the degree of polymerization (η) in linear organosiloxane.

In the literature[4] there is some information on soluble copolymers containing ladder polyphenylsiloxane and single strained dimethylsiloxane fragments in the chain with different arrangement of polyphenylsiloxane blocks. To synthesize the above copolymers, first partial blocking of the end hydroxyl groups and starting

PPS synthesized by thermal condensation of cis-tetrol in the toluene solution was carried out according to the scheme:
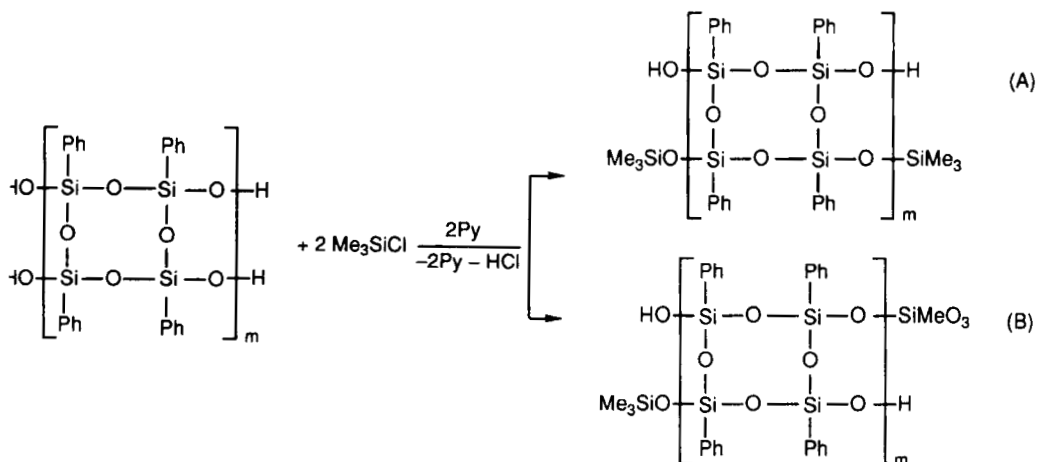
In the course of the reaction the authors do not exclude the possibility of formation of a mixture of products A and B and consider formation of a product with the structure:
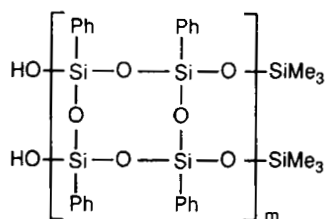
not probable because of a strong screening effect of the neighbouring trimethylsiloxy groups.

By means of the HFC reaction of partially blocked PPS with α, ω-dichlorodimethylsiloxanes in the presence of pyridine, block copolymers were obtained including two different structures in the chain:

and
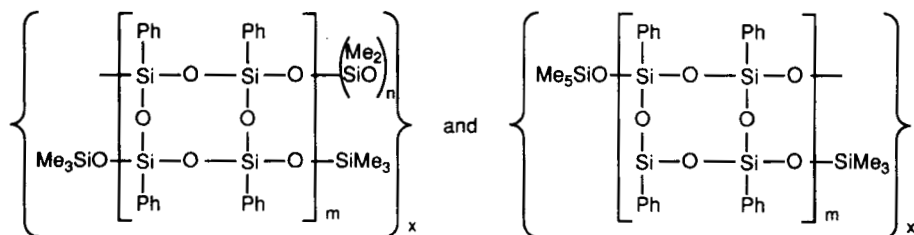
$m = 3 - 20$, $n = 2 - 35$,

while by the HFC reaction of PPS partially blocked by 1,3-dichlorotetramethyl-disiloxane with α,ω-dichlorodimethylsiloxanes in the presence of pyridine block copolymers were obtained having the following structure:

$$
\left\{
\begin{array}{c}
\overbrace{}^{\displaystyle \qquad \quad \left(\!\!\begin{array}{c}Me_2\\ SiO\end{array}\!\!\right)_{\!n}\!\!-} \\
\text{Ph}-\!\overset{|}{\underset{|}{Si}}\!-O-\overset{|}{\underset{|}{Si}}\!-\text{Ph} \\
\;\;O \qquad\qquad O \\
\text{Ph}-\!\overset{|}{\underset{|}{Si}}\!-O-\overset{|}{\underset{|}{Si}}\!-\text{Ph} \\
\;\;O \qquad\qquad O \\
Me_2Si-O-SiMe_2
\end{array}
\right\}_{x}
$$

$$n = 2 - 35$$

The investigations of thermal-oxidative stability and thermo-mechanical properties of block copolymers have shown that arrangement of ladder pol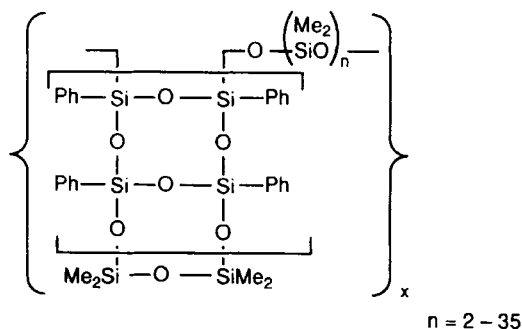ycyclic fragments of the same length in the dimethylsiloxane chain does not exert a substantial effect on thermal stability of the mentioned copolymers. It is also established that the length of the polycyclic fragments in the dimethylsiloxane chain, starting from $m = 3$ at a constant value of n, only slightly exceeds thermal stability and vitrification temperature (T_{vit}) of block copolymers. Thus, an increase in the length of the ladder polyphenylsiloxane fragment (m) from 3 to 20 results in an increase in T_{vit} only by 15–20°C.

In the literature there is no information on soluble copolymers containing ladder polyphenylsiloxane fragments with residual hydroxyl end groups and single stranded dimethylsiloxane links in the chain as well as ladder polyphenylsiloxane and double stranded dimethylsiloxane fragments in the chain.

EXPERIMENTAL

The organic solvents and pyridine used in the synthesis were purified by drying and distillation.

The starting PPS, synthesized by thermal condensation of cis-tetrol produced by the method outlined in Reference 5 in the toluene solution[4] were reprecipitated from the toluene solution by methanol, and the degree of their polymerization as well as the degree of polymerization of α, ω-dichloro- and α, ω-bis(dimethylamino)dimethylsiloxanes obtained by the methods[6,7] were determined from the percentage of the functional (Cl and Me_2N) groups in them and from molecular mass found by the abulliometric method.

The IR spectra were measured on an UR-20 instrument. The diffractograms were taken on a "IIPOH-2" instrument, A-Cu_α was measured without a filter; the angular velocity of the meter ω = 2 deg/min.

Thermomechanical curves were taken on a custom-made installation. The test conditions were: v = 5 deg/min, δ = 0.1 kgf/cm².

Thermogravimetric investigations were carried out on a MOM-102 Paulic-Paulic-Erdey derivator. The test conditions were: temperature rise rate = 5 deg/min, weight 100 g.

HFC of PPS with Dimethylchlorosilane and α, ω-Dimethylchlorosiloxanes Cl-(SiMe$_2$O)$_{n-1}$SiMe$_2$Cl, n = 1-9

Into a reaction flask equipped with a stirrer and a reflux condenser with a chlorocalcium tube, 0.2240 g (1.1 × 10^{-3} mol) of 1,3-dichlorotetramethylsiloxane in 0.5 ml of anhydrous toluene was placed, and 2.8876 g (1.1 × 10^{-3} mol) of the PPS solution with m = 5 in the 0.1744 g (2.2 × 10^{-3} mol) of the pyridine solution and 1.5 ml of anhydrous toluene was added drop-by-drop into it. The mixture was stirred and heated up to the solvent boiling point for 4–5 h, then the reaction mixture was diluted with 10 ml of toluene, washed with water to remove salt-acidic pyridine, dried with sodium sulfate, filtered off and reprecipitated from the toluene solution by methanol. 2.67 g (85.8%) of copolymer was obtained.
Anal. Calcd, %: C 54.52, H 4.14, Si 22.57
Found, %: C 54.13, H 4.32, Si 22.12

HFC of PPS with m = 5 and 10 with dimethylchlorosilane and with the rest α, ω-dichlorodimethylsiloxanes was carried out similarly by the above mentioned method. Also, the HFC reaction of PPS with dimethyldichlorosilane and α, ω-dichlorodimethylsiloxanes with a 1:2 mole ratio of the starting components was run.

HFC of PPS with α, ω-Bis(dimethylamino)dimethylsiloxanes Me$_2$N-(SiMe$_2$O)$_{n-1}$SiMe$_2$Cl, n = 21-66

2.7488 g (1.05 × 10^{-3} mol) of PPS with m = 5, 1.7085 g (1.05 × 10^{-3} mol) of α, ω-bis(dimethylamino)dimethylsiloxane with n = 21 were put into a reaction flask with a sealed stirrer, two (inlet and outlet) tubes, and 2–3 drops of anhydrous toluene to form a homogeneous mixture which was stirred and heated up in the Ar flow up to 80–100°C and at the final stage—vacuum treated at 120–150°C and at pressure of 1 mm Hg until a constant value of viscosity was reached. It was diluted with 10 ml of toluene, washed with water to neutral reaction, dried with sodium sulfate, filtered off and reprecipitated from the toluene solution by methanol. 3.90 g (87.5%) of copolymer was obtained.
Anal. Calcd., %: C 47.01, H 5.49, Si 27.76
Found: C 47.68, H 5.16, Si 27.31

HFC of PPS with m = 5 and 10 with the rest of α, ω-bis(dimethylamino)dimethylsiloxanes was run similarly by the above mentioned method. HFC of PPS with α, ω-bis(dimethylamino)dimethylsiloxanes in a 1:2 mole ratio of the starting components, respectively, was realized in the same manner.

RESULTS AND DISCUSSION

In the present work we have investigated the HFC reaction between PPS, obtained by thermal polycondensation of cis-tetrol in the toluene solution and, therefore,

with cis-anti-cis-tactic structure of the molecules and α, ω-dichloro- or α, ω-bis(dimethylamino)dimethylsiloxanes in 1:1 and 1:2 mole ratios of the starting components, respectively. The reaction proceeds according to the general scheme:
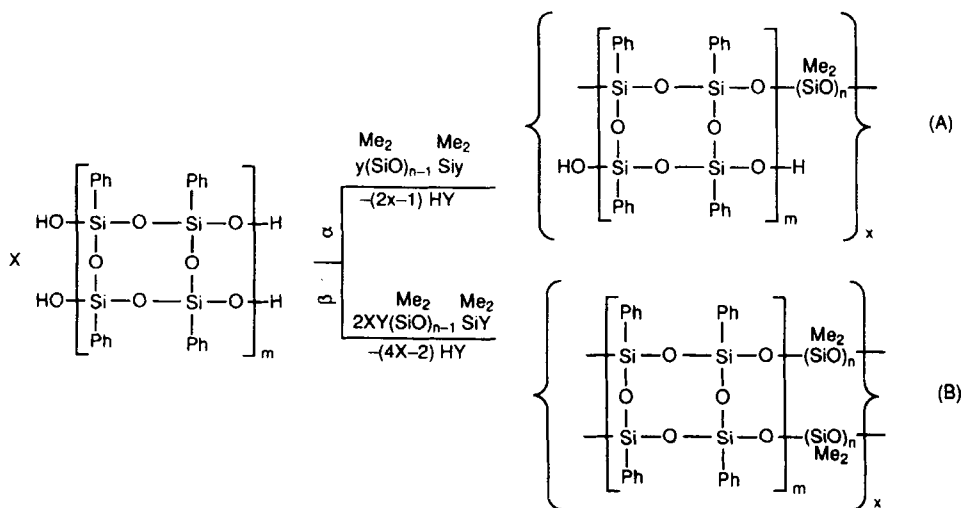
where y = Cl, Me_2N

a) m = 5: n = 1(I), 2(II), 9(III), 21(IV), 32(V), 38(VI), 66(VII)

    m = 15: n = 1(VIII), 2(IX), 9(X), 21(XI), 32(XII), 38(XIII), 66(XIV)

b) m = 5: n = 1(XV), 2(XVI), 9(XVII), 21(XVIII), 32(XIX), 38(XX), 66(XXI)

    m = 15: n = 1(XXII), 2(XXIII), 9(XXIV), 21(XXV), 32(XXVI), 38(XXVII), 66(XXVIII).

For y = Cl, the HFC reaction was run in the 60% solution of anhydrous toluene and in the presence of HCl-pyridine as an acceptor. At the final stage the reaction mixture was heated up to the boiling point of the solvent. But for y = Me_2N, the HFC reaction was realized in a block. To the starting mixture a small amount of anhydrous toluene was added (to obtain a homogeneous mixture) and at 80–100°C the reaction mixture was stirred, an inert gas being simultaneously passed over it. At the final stage the mixture was vacuum-treated at 120–150°C and 1 mm Hg. It should be noted that viscosity of the copolymers obtained in the block is somewhat higher than that of the copolymers obtained in the solution. After being washed with water and reprecipitated from the toluene solution by methanol, the obtained copolymers are solid or viscous (depending on the value of n) substances, which are completely soluble in organic solvents with $\eta_{spec.}$ = 0.11–0.32.

When constructing a polymer chain in the conditions of the HFC reaction according to scheme a, besides the above mentioned structure, other variations of macromolecule construction are also possible: along the diagonal (B) and ridge (C).

$$
\mathrm{HO}\!-\!\left[\begin{array}{cc}
\overset{\text{Ph}}{\underset{\text{O}}{\mathrm{Si}}}\!-\!\mathrm{O}\!-\!\overset{\text{Ph}}{\underset{\text{O}}{\mathrm{Si}}}\!-\!\mathrm{O} \\
\underset{\text{Ph}}{\mathrm{Si}}\!-\!\mathrm{O}\!-\!\underset{\text{Ph}}{\mathrm{Si}}\!-\!\mathrm{O}
\end{array}\right.\!\!\overset{\mathrm{Me_2}}{\underset{}{\text{—(SiO)}_n\text{—}}}\!\!\left.\begin{array}{c}\\ \\ \text{—H}\end{array}\right]_m
$$
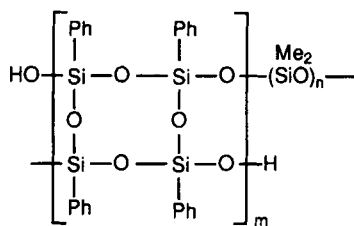
(B)
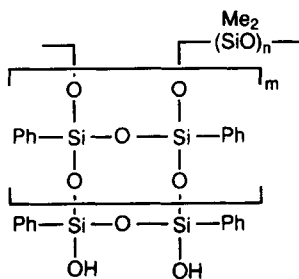
(C)

However, as was mentioned in Reference 4, the arrangement of the polycyclic fragment does not exert a substantial effect on thermomechanical properties and thermal-oxidative stability of such copolymers.

The fact that the above mentioned reaction, unlike Reference 3, does not proceed with gel formation, must be caused by the cis-anti-cis-tactic configuration of starting PPS.

According to the data of References 3, in which cis-syndiotactic configuration in the starting PPS is prevalent, there, probably, exists a defect structure containing unreacted hydroxyl groups in the chain. The arrangement of these as well as end hydroxyl groups seems to favour the reaction of gel formation, which is evidenced by the HFC reaction conducted by us between the PPS obtained from mother tetrol and α, ω-dichloro- or α, ω-bis(dimethylamino)dimethylsiloxanes. It is established that as soon as equimolar relationship of the starting components is violated towards an increase in dimethylsiloxanes, gel formation takes place. Besides, the diethylamine released in the course of the reaction is characterized by more basic properties, than dimethylamine, which, in its turn, can have an effect on gel formation.

The yield and η_{spec} of the synthesized copolymers are presented in Table I.

TABLE I

Yield and η_{spec} of the synthesized copolymers

Copolymer No.	I	II	III	IV	V	VI	VII	VIII	IX
Yield, %	85.6	85.8	86.8	87.5	88.3	88.7	89.6	86.2	86.7
η_{spec} of 1% solution in toluene at 25°C	0.12	0.12	0.13	0.18	0.22	0.23	0.29	0.12	0.13

TABLE I (continued)

Copolymer No.	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII
Yield, %	87.4	87.6	89.4	89.8	91.2	84.8	85.8	86.1	87.3
η_{spec} of 1% solution in toluene at 25°C	0.16	0.19	0.23	0.26	0.30	0.11	0.13	0.19	0.24

Copolymer No.	XIX	XX	XXI	XXII	XXIII	XXIV	XXV	XVI	XVII	XXVIII
Yield, %	87.9	88.6	89.7	86.3	86.5	87.6	88.5	88.7	89.3	89.8
η_{spec} of 1% solution in toluene at 25°C	0.26	0.27	0.31	0.13	0.14	0.17	0.23	0.27	0.27	0.32

TABLE II

Yield, η_{spec} and elementary analysis of copolymers X and its fractions

| Copolymer No.	X	X^1	X^2	X^3	X^4	X^5
Yield, %	87.4	14.0	18.1	20.2	23.1	24.6
η_{spec} of 1% solution in toluene at 25°C	0.16	0.24	0.21	0.18	0.14	0.08
C 53.96		54.23	54.39	54.54	54.20	53.65	53.50
H 4.22		4.09	4.02	4.41	4.29	4.64	4.19
Si 22.98		22.29	22.67	23.26	23.16	22.41	22.53

TABLE III

Yield, η_{spec} and elementary analysis of copolymer XVII and its fractions

Copolymer No.	XVII	$XVII^1$	$XVII^2$	$XVII^3$	$XVII^4$	$XVII^5$
Yield, %	86.1	18.2	20.1	22.0	24.8	14.8
η_{spec} of 1% solution in toluene at 25°C	0.19	0.26	0.23	0.21	0.16	0.09
Calculated				real		
C 47.85		48.18	47.21	47.60	47.31	47.53	47.40
H 5.32		5.51	5.19	5.21	5.61	5.53	5.48
Si 27.20		27.39	27.54	27.61	27.04	27.46	27.11

Fractionation of products X and XVII was made and five fractions of each product were released (X^1-X^5 and $XVII^1-XVII^5$). As is seen from Tables II and III, in both cases the elementary analysis of the fractions shows little difference between them, between the calculated and found values and between the synthesized and starting copolymers. This means that during the HFC reaction copolymers are formed, rather than a mixture of homofunctional polycondensation products.

In the IR spectra of all the synthesized copolymers, as in the starting PPS, one broad absorption band is conserved in the region of 1145 cm^{-1} for asymmetric valence oscillations of the Si—O—Si bonds, which in its turn, is indicative of conservation of the cis-anti-cis-tactic structure of the polycyclic blocks in the copolymers obtained. Therefore, dimethylamine released in the course of the reaction does not result in rearrangement of separate parts of the macromolecular chain. In the IR spectra one can also see absorption bands for the Si—Ph and Si—Me bonds at 1435 and 1275 cm^{-1}, respectively. A weak band in the interval 3400–3600 cm^{-1} for the associated Si—OH bonds points to the presence of both end and unreacted groups not only in copolymers I–XIV, but, probably, also in copolymers XV–XXVII in the case of presence of defects of the structure in the chain:
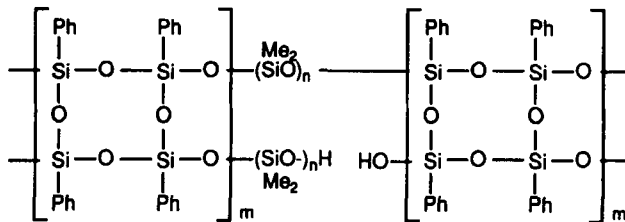
The intensity of the mentioned absorption band for copolymers I–XIV is larger, than that for copolymers XV–XXVIII.

At one and the same values of m of the polycyclic block, an increase in the length of dimethylsiloxane (both single and double stranded) fragment (n) results in enhancement of the absorption band intensity, characteristic of the Si—Me bond. And at a constant value of m and n the enhancement in double stranded copolymers is larger, than in single stranded copolymers.

Thermogravimetric analysis of the synthesized copolymers was made. Table IV presents the results of the investigation, from which it is seen that the obtained copolymers with single and double stranded dimethylsiloxane fragments in the chain have approximately equal thermal-oxidative stability. The same thermal-oxidative stability is characteristic of the copolymers reported in Reference 4. It also follows from the Table that an increase in length (m) of the polycyclic block at one end and the same length (n) of the dimethylsiloxane (both single and double stranded) link results in an insignificant rise of thermal-oxidative stability of the copolymers

TABLE IV

Temperature of 5% mass losses of some synthesized copolymers in air at a heating rate of 5°C/min

Copolymer No.	I / XV	II / XVI	III / XVII	VI / XX	VIII / XXII	IX / XXIII	X / XXV	XIII / XXVII
	5	5	5	5	15	15	15	15
	1	2	9	38	1	2	9	38
T°C of 5% mass losses	520 / 510	445 / 430	415 / 400	360 / 335	535 / 525	470 / 455	450 / 435	410 / 380

obtained. However, an increase in the length (n) of the dimethylsiloxane fragment at a constant length (m) of the polycyclic block is accompanied by a decrease in thermal-oxidative stability.

The main destruction process proceeds in the interval 550–700°C, while in the interval 700–750°C the thermographic curves reflect the level where mass losses reach their limit.

Figure 1 shows thermomechanical curves of some synthesized copolymers, from which it follows that there is only a slight difference between T_{vit} of single and double stranded copolymers. The copolymers are characterized by elevated T_{vit} at small lengths of the dimethylsiloxane link ($n = 1$–9). The maximum value of T_{vit} is reached at the minimum length of the dimethylsiloxane link ($n = 1$) and it equals ~250°C(XV). As can be seen from the data of the figure, an increase in the length (m) of the polycyclic block, at a constant length of the dimethylsiloxane link (n) (both in single and double stranded copolymers) results in a small increase of T_{vit}. Thus, for the single stranded copolymer with $m = 5$ and $n = 9$(III), $T_{vit} \approx 150°C$, while for the same copolymer with $m = 15$ and $n = 9$(X), $T_{vit} \approx 165°C$. The difference in T_{vit} between double stranded copolymers with $m = 15, n = 9$(XXIV) and with $m = 5, n = 9$(XXVII) is $\approx 30°C$.

With an increase in lengths (n) of the dimethylsiloxane fragment, T_{vit} decreases, and starting from $n \geqslant 32$ (Figure 2), on thermomechanical curves one can observe several phase transitions, which characterizes a two-phase system and points to block copolymers formation.

The copolymers described in Reference 4 have comparable T_{vit} at small lengths of dimethylsiloxane link, and starting with $n \geqslant 35$, on thermomechanical curves one can also observe phase separation, characteristic of block copolymers.

X-ray analysis of the synthesized copolymers has been carried out. It is established that at small lengths of the dimethylsiloxane link ($n = 2$–9), irrespective of the length (m) of the rigid polycyclic block, on diffractograms two diffraction maxima
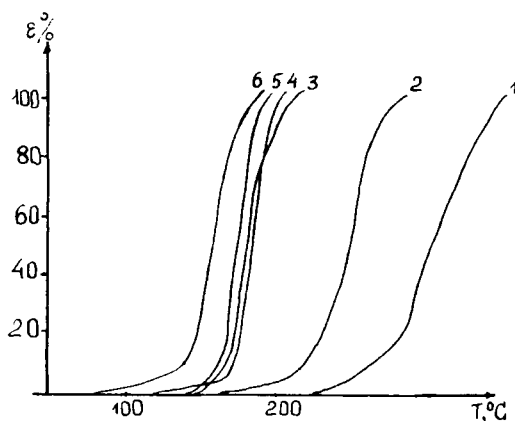

FIGURE 1   Thermomechanical curves of the copolymers, where curve 1 is for copolymer XV, curve 2 is for copolymer XVI, curve 3 is for copolymer XXIV, curve 4 is for copolymer X, curve 5 is for copolymer III, curve 6 is for copolymer XVII ($v = 5$ deg/min, $\delta = 0.1$ kgf/cm^2).
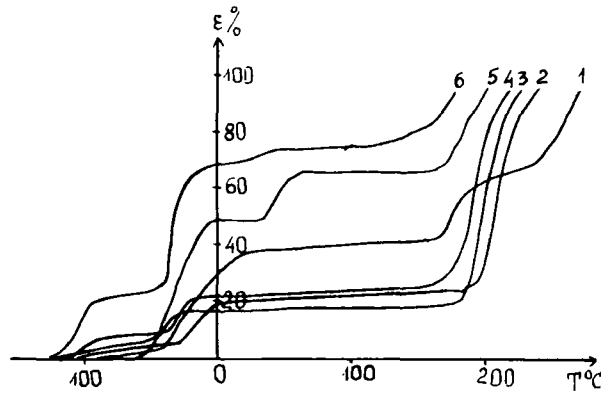
FIGURE 2 Thermomechanical curves for the copolymers, where curve 1 is for copolymer V, curve 2 is for copolymer XII, curve 3 is for copolymer XIII, curve 4 is for copolymer XXVI, curve 5 is for copolymer XXVII, curve 6 is for copolymer XIX (v = 5 deg/min, δ = 0.1 kgf/cm²).

are observed: the first one (d_1) characterizes the average interchain distance in an amorphous polymer, while the second one (d_2) is of more complicated nature and corresponds both to intrachain and interchain atomic distances[8]. As is seen from Table V, at a constant value of m and n, d_1 for single and double stranded copolymers are the same. Thus, for copolymers XVII and XXIV (m = 5, n = 9), $d_1 \approx 12.45$ Å. The maximum value of the first diffraction maximum is reached at the minimum length (n = 1) of the dimethylsiloxane link and is equal to 12.63 Å.

The absence of the diffraction maximum corresponding to the linear dimethylsiloxane component suggests that in the region of the lengths under consideration (n = 1–9), within the accuracy of the X-ray method, phase separation takes place. The observed phenomenon can be explained, if we assume that in case of small values of n, when phase separation does not occur, the presence of linear dimethylsiloxane fragments, which do not release to a single phase, results in equivalent presence of defects in the chains, and hence their regular packing becomes difficult.

With an increase in the length of the dimethylsiloxane link (n), irrespective of the length of the polycyclic block (m), the value of the first diffraction maximum decreases, and starting from $n \geqslant 21$, on the diffractograms in the region 7.2–7.4 Å there appears a third diffraction maximum (d_1^t) corresponding to the interchain distance of the flexible dimethylsiloxane link (Table V, Figures 3 and 4). Probably, at high values of n the linear dimethylsiloxane fragments form an individual phase and do not hinder packing of chains in the ladder polyphenylsiloxane phase.

The value of the second diffraction maximum d_2 changes only slightly, being in the range 4.31–4.50 Å.

TABLE V

Interchain distances d_1 and d_1^1 in (Å) for some synthesized copolymers

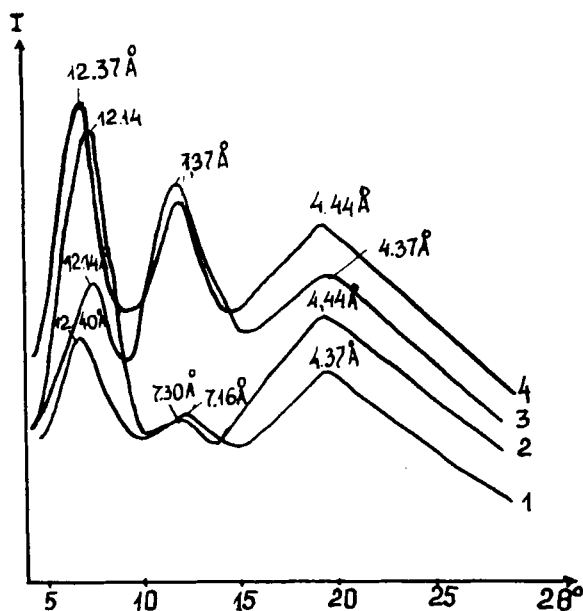| No.	I	II	XVI	III	XVII	XXIV	V	XIII	XXVII
m	5	5	5	5	5	15	5	15	15
n	1	2	2	9	9	9	32	38	38
d_1	12.63	12.60	12.60	12.45	12.45	12.45	12.23	12.21	12.20
d_1^1							7.35	7.36	7.36

FIGURE 3   Diffractograms of the copolymers, where curve 1 is for copolymer XI, curve 2 is for copolymer XIV, curve 3 is for copolymer VII, curve 4 is for copolymer IV.
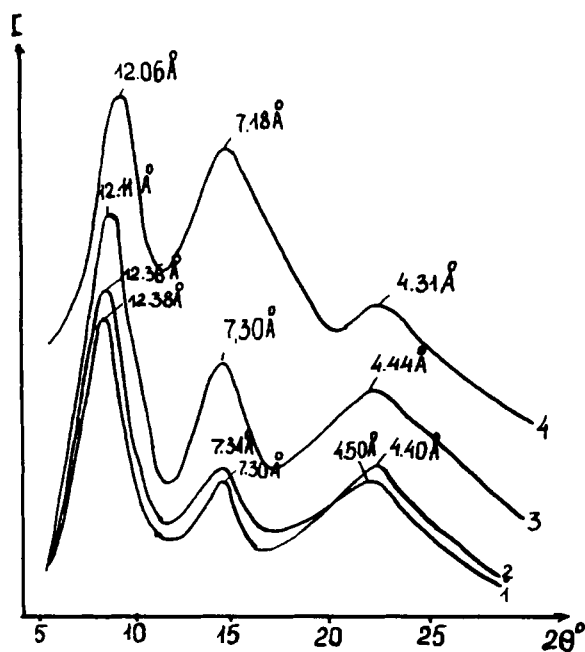

FIGURE 4   Diffractograms for the copolymers where curve 1 is for copolymer XVIII, curve 2 is for copolymer XXIV, curve 3 is for copolymer XXVIII, curve 4 is for copolymer XXI.

Thus, appearance of the third diffraction maximum d_2 on the diffractogrms in the region 7.2–7.4 Å (Figures 3 and 4, Table V), corresponding to the distance of a flexible dimethylsiloxane fragment, together with thermomechanical analysis, suggests that at certain lengths of a rigid polycyclic block ($m = 5$–15) and of a flexible (single and double stranded) dimethylsiloxane fragment ($n = 21$–66), a two-phase system occurs which is characteristic of block copolymers.

It should be mentioned that the value of d_1 for such single stranded copolymers[4] at small values of n are also only slightly dependent on the length of the di-methylsiloxane fragment, and at ($n = 2$–8) of the dimethylsiloxane link d_1 has comparable values ($d_2 = 13.0 \div 12.5$ Å). With an increase in the length of the dimethylsiloxane link $n \geqslant 35$ in the range 7.5–8.1 Å, the third diffraction maximum appears d_1^2, whose value rises with an increase in the length (m) of the rigid polycyclic block from 7.5 Å ($m = 3$, $n = 35$) to 8.1 Å ($m = 20$, $n = 35$).

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