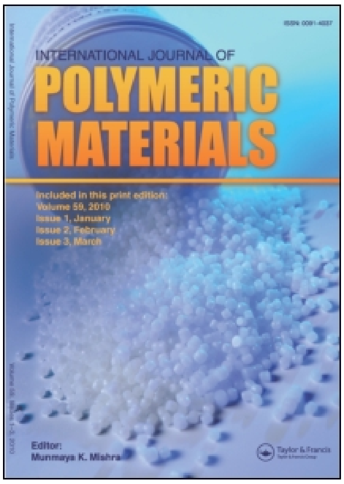

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# Siliconorganic Oligophenylenes on the Base of some Diethynylsilanes and -Siloxanes

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The siliconorganic oligophenylenes have been synthesized. The reaction of polycyclotrimerization of some of diethynylsilanes and siloxanes as well as their co-polycyclotrimerization with phenylacetylene and *p*-diethylnylbenzene in presence of catalysts of the Ziegler-Natta type were investigated. The general regularities of synthesis of the siliconorganic oligophenylenes were studied. The influence of the structure and the ratio of the used monomers on the properties of siliconorganic oligophenylenes was established.

*Keywords:* Co-polycyclotrimerization; diethynylsilane; oligophenylene; thermostability; brenching; fluidity

## INTRODUCTION

The siliconorganic polymers, obtained by the introduction of silicon containing fragments into the oligophenylenes chain during the process of their synthesis from diethynyldiphenylsilane and their mixture with phenylacetylene are described in the literature [1, 2]. The investigation of the other method of incorporation of siliconorganic fragments into the oligophenylenes chain *via* the reaction of

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*Corresponding author.

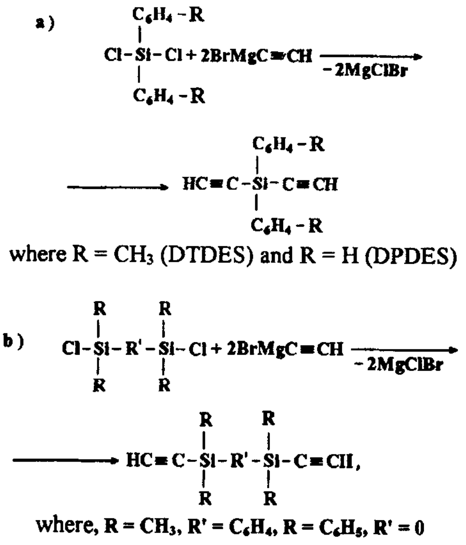
hydrosilylation has also been carried out. This reaction is not very convenient because the oligomers must contain a sufficient number of active multiple bonds capable of addition of hydridsilanes and hydridsiloxanes. The method based on the reaction of polyaddition of $\alpha,\omega$-dihydridsiloxanes to acetylene groups of oligophenylenic chain is more interesting and leads to chemical modification of the above mentioned oligomers [3]. The method of co-polycyclotrimerization of diethynylsilanes seems to be more technological [4], but the data about the synthesis and the general regularities of the formation of these polymers and their properties are extremely restricted.

## RESULTS AND DISCUSSION

The present work is dedicated to the study of the reaction of polycyclotrimerization of silanes and -siloxanes, containing the acetylene groups at silicon atoms, their co-polycyclotrimerization with phenylacetylene (PA) and *para*-diethynylbenzene (P-DEB) as well as of the properties of the obtained siliconorganic oligophenylenes (SOOP).

For the initial siliconorganic monomers we used ditolyldiethynylsilane (DTDES), diphenyldiethynylsilane (DPDES), 1,4-bis-(dimethylethynylsilyl)benzene (DESB) and 1,3-diethynyltetraphenyldisilioxane (DETPDS). They were obtained *via* the interaction of the Iotsich reactive with corresponding diclorsilanes through the scheme [4, 5, 6]:

The polycyclotrimerization of siliconorganic diethynyl derivatives were carried out in presence of catalyst of the Ziegler-Natta type Al(iso-$C_4H_9)_3$-$TiCl_4$ in the toluene-hexane solution at the temperature of 15 – 20°C in Argon medium. The solid powder-like products were slightly yellow-orange colored. Their yield was between $60 \div 97$ p.c. (Tab. I). The extent of polycylotrimerization was determined by measuring the integral intensities of $\nu_{as}$ (—C≡CH) and $\nu_{as}$ (—$C_6H_5$); their yield and structure depend on the nature of the organic groups at silicon atoms (Scheme 1, Tab. I) and on the structure of the initial siliconorganic diethynyl compound. The high yield and the relatively low unsaturation of the oligophenylenes based on DTDES, are attributed to a high degree of the cyclotrimerization process completion due to the presence of electron-donor aliphatic (*e.g.*, methyl)



where R = $CH_3$ (DTDES) and R = H (DPDES)

where, R = $CH_3$, R' = $C_6H_4$, R = $C_6H_5$, R' = 0

SCHEME 1

TABLE I The properties and the yield of the oligophenylenes based on diethynylsilanes

| *No.* | *The initial diethynyl silanes* | *Yield, %* | *Solubility in benzene toluene and $CHCl_3$* | *Unsaturation* | *The data of the elemental analysis % is found/is calculated* | | |
|---|---|---|---|---|---|---|---|
| | | | | | *C* | *H* | *Si* |
| 1 | DPDES | 60 | part. sol. | 0.081 | 82.12 | 5.53 | 11.67 |
| | | | | | 82.75 | 5.17 | 12.06 |
| 2 | DTDES | 97 | part. sol. | 0.030 | 82.53 | 6.47 | 10.49 |
| | | | | | 83.07 | 6.15 | 10.77 |
| 3 | DESB | 88 | unsoluble | 0.014 | 68.82 | 7.51 | 22.45 |
| | | | | | 69.42 | 7.44 | 23.14 |

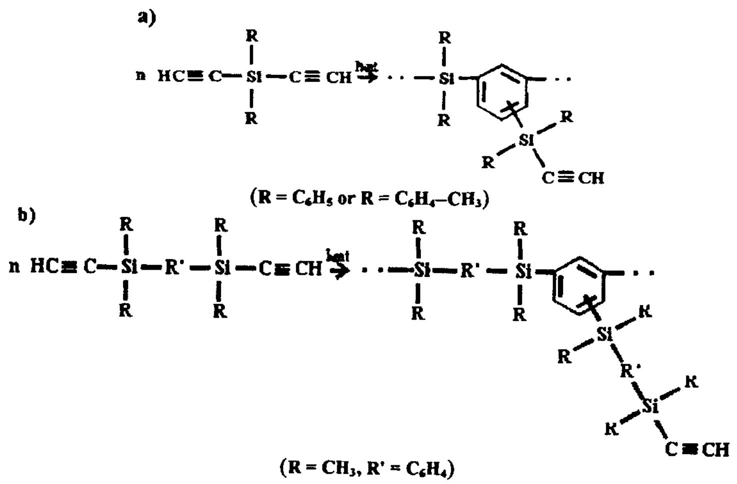
substituents in *para*-position of benzene groups. This leads to the increase of the electronic density on the acetylene groups, the opening of triple (— C≡C —) bonds and thus, facilitates the formation of aromatic cycles [7].

The different situation is observed in the case of monomers with the spatial radicals at the silicon atoms, where the formation of benzene cycles is hindered. Therefore, the reaction products have relatively low yield and are characterized by high unsaturation (Tab. I).

The extent of process of cyclotrimerization and the yield of the obtained siliconorganic oligophenylenes are higher in the case of 1,4-bis(dimethylethynylsilyl)benzene (Tab. I). Note that the values of specific viscosity of products having approximately equal molecular weights, differ from each other. This reflects the formation of the chain of macromolecules with different lengths and degrees of branching. We also established the dependence of solubility of the products of polycyclotrimerization on the structure of the initial monomers (Tab. I).

The structure and the composition of the above-mentioned siliconorganic oligophenylenes were determined from the data of the elemental and IR spectral analyses. The appearance and the increase of the integral intensities of absorption maxima in the region of 812–820 cm$^{-1}$ with the simultaneous decrease of the integral intensities of $\nu_{as}$ of C—H bonds in monosubstituted ethynyl groups ($—C\equiv C—H$, 3300 cm$^{-1}$) manifests the formation of trisubstituted benzene cycles [7, 8].

The obtained results do not allow us to determine with certainty the precise structure of the obtained oligophenylenes, nevertheless it can present the most probable scheme of the polycyclotrimerization:



SCHEME 2

As the data given in Table II reveal, completely soluble polymers are obtained in polycyclotrimerization of DETPDS, while at the same reaction of DEB the process should be carried out in the presence of PA with the PA ratio to DEB not less than 1.5:1.0 [8]. The formation of soluble products of the polycyclotrimerization of DETPDS depends on the probability of the formation of the cyclic fragments due to the presence of flexible siloxanic bonds between ethynylic groups of the initial monomer. This was confirmed by the IR spectra of the obtained polymers. The spectra demonstrate that in the process of polycyclotrimerization the ethynylic groups entirely disappear with the simultaneous indication on the absorption regions of 810 $\text{cm}^{-1}$, characteristic for trisubstituted products of benzene.

The formation of the soluble and fusible products is also confirmed by their thermomechanical curves (Fig. 1).

The light orange and pink products completely insoluble in benzene, toluene and chloroform are obtained (yield 63–90%) *via* the polycyclotrimerization of the above-mentioned diethynylsilanes with phenylacetylene (PA) (Tabs. II and III) [7]. According to Table III in case of cyclotrimerization of DPDES and DTDES with PA, the higher the fraction of PA in initial mixture of the monomers, the lower is the unsaturation of the product of the reaction. Molecular masses (M.M.) of the co-polymers of DTDES with PA are higher than those of the co-polymers on the base of DPDES and PA at the same proportions of the initial monomers (4820 and 3960 at the molar ratio 1:1; 6450 and 4280 at the molar ratio 1:2 correspondingly).

TABLE II The ratio of the initial monomers and some properties of the (co)polymers on the base of DETPDS

| *Polymer No.* | *Molar ratio DETPDS: DEB:PA* | *Yield,* %* | *Solubility in benzene, toluene and chloroform* | *Unsaturation of (co)polymers* | *M.M.*** |
|---|---|---|---|---|---|
| 1 | 1:0:0 | 75.00 | soluble | 0 | 2930 |
| 2 | 1:0.1:0 | 65.09 | part. solub. (93%) | 1:35 | – |
| 3 | 1:0.75:0 | 63.60 | part. solub. (78%) | 1:12.5 | – |
| 4 | 1:0:0.5 | 84.25 | soluble | 0 | – |
| 5 | 1:0.5:0.5 | 53.36 | soluble | 1:13.5 | – |
| 6 | 1:1:1 | 71.80 | soluble | 1:12.5 | – |
| 7 | 1:1:0.5 | 75.97 | soluble | 1:22.9 | 5520 |
| 8 | 0:1:1.5 | 65.0 | soluble | 1:10 | 1440 |

*Determined through the sum of the monomers.
**Determined using ebullioscopy in chloroform.

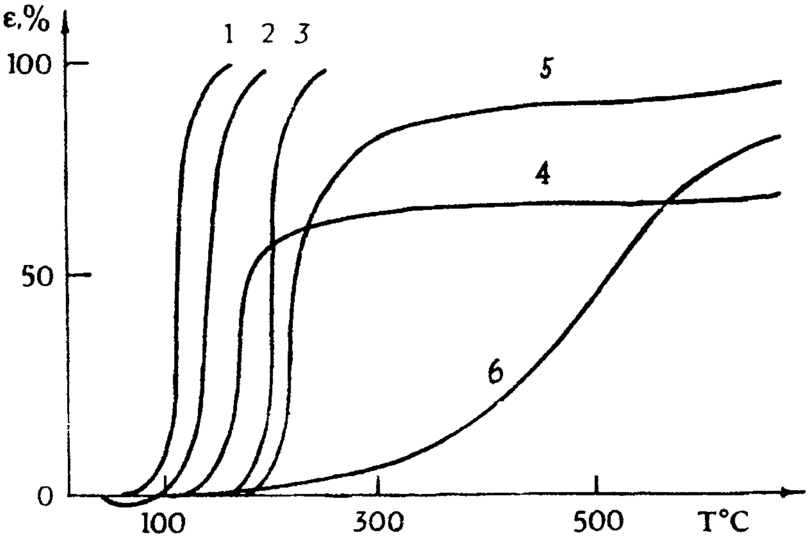


FIGURE 1 Thermomechanical curves of (co)polymers DETPDS:DEB:PA: 1) 1:0:0; 2) 1:0.1:0; 3) 1:0:0.5; 4) 1:1:0.5; 5) 1:1:1; 6) The product of co-polycyclotrimerization DEB:PA (1:1).

TABLE III The ratio of initial monomers and some properties of the co-polymers based on siliconorganic diacetylenes and phenylacetylene

| *No.* | *The mole ratio of initial monomers* | *Yield, %** | *Unsaturation* | *Molec. mass*** | *The data of elemental analysis, % is found/is calculated* | | |
|---|---|---|---|---|---|---|---|
| | | | | | *C* | *H* | *Si* |
| 1 | 1:0.5 (DPDES:PA) | 35.0 | 0.043 | – | 83.37/84.80 | 5.71/5.33 | 10.33/9.89 |
| 2 | 1:1 (DPDES:PA) | 70.0 | 0.041 | 3960 | 84.57/86.22 | 5.75/5.38 | 9.01/8.32 |
| 3 | 1:2 (DPDES:PA) | 55.2 | 0.030 | 4280 | 85.67/88.07 | 5.73/5.58 | 7.61/6.41 |
| 4 | 1:1 (DTDES:PA) | 89.8 | 0.040 | 4820 | 84.54/86.19 | 6.13/6.08 | 6.69/7.73 |
| 5 | 1:2 (DTDES:PA) | 82.5 | 0.0 | 6450 | 86.74/87.17 | 6.57/6.05 | 7.28/6.78 |
| 6 | 1:1 (DESB:PA) | 63.0 | 0.0 | 2150 | 74.24/76.74 | 7.84/6.97 | 17.00/16.27 |
| 7 | 1:1.5 (DESB:PA) | 72.3 | 0.0 | 2380 | 77.62/78.98 | 7.33/6.83 | 14.95/14.17 |

* Determined through the sum of monomers.

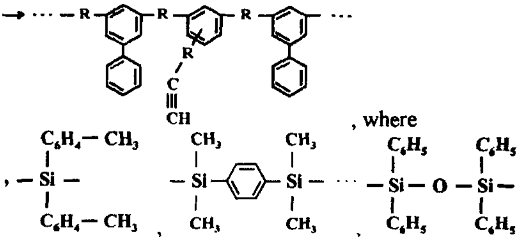
** Determined using ebullioscopy in chloroform.

It should be noted that the co-polymers based on DESB and PA have no unsaturation. This suggests the formation of cyclic fragments during the co-polycyclotrimerization, which are derived by the "hinging" of bonds — C —Si — $C_6H_4$ — Si — C — in initial siliconorganic monomers [7]. This explains the formation of the co-polymers with relatively low-molecular masses (Tab. III).

At the same time the unsaturation of the co-polymer based on DTDES and PA at the proportion of 1:2 is less in comparision with that of the co-polymer of DPDES with PA of the same ratio. This also indicates the high reactivity of DTDES in process of polycyclotrimerization with PA and explains the high extent of this reaction.

The following absorption maxima are found in the IR spectra of the products of co-polycyclotrimerization: 800, 810 and 820 $cm^{-1}$ (mono-, di- and trisubstituted benzene groups), 1260 $cm^{-1}$ ($\nu_{as}$, $Si(CH_3)_2$) and also 1419 $cm^{-1}$($\nu_{as}$, of Si — $C_6H_5$), 2980 $cm^{-1}$ ($\nu_{as}$ CH in alk. group) for co-polymers based on DESB *etc*. The decrease or the complete disappearance of the absorption maxima $\nu_{C-H}$ associated with monosubstituted acetylene groups and the increase of the intensity at 3030 $cm^{-1}$ (H — $C_{ar}$) are also observed.

On the basis of these results the process of the formation of the co-polymers of DES and PA can be expressed with the following general scheme: $n\mathrm{HC} \equiv \mathrm{C} - \mathrm{R} - \mathrm{C} \equiv \mathrm{CH} + m\mathrm{HC} \equiv \mathrm{C} - \mathrm{C_6H_5} \xrightarrow{\text{heat}}$



SCHEME 3

In order to decrease the possibilities of the formation of macrocycles during the co-polymerization and to rise the ability of structuring the siliconorganic oligophenylenes, *para*-diethynyl benzene having a harder structure than DESB was incorporated into the initial mixture. The threefold co-polymerization was carried out at the above described conditions with different proportions of the initial monomers. After precipitation of the soluble products of the reaction in ethanol the yellow colored amorphous products were isolated. The conditions of the synthesis and some of properties of the products of the (co)polycyclotrimerization are given in Tables III and IV. As these data show, the co-polymers with the high yield are obtained by means of these reactions. The solubility of SOOP depends on the molar ratio of the initial monomers. Elevating the fraction of the diethynyl components in the initial mixture the products insoluble in the ordinary organic solvents are formed (exper. 1 and 2, Tab. IV).

On the contrary, the increase of the phenylacetylene fraction in the initial mixture of the monomers leads to the formation of partially or completely soluble products (exper. 3 and 5, Tab. IV). At the same time molecular masses of soluble oligophenylenes determined by ebullioscopy in chloroform are not high (MM ~ 3480).

The thermomechanical properties of the synthesized (co)polymers have been investigated (Kargin scale, $P = 100\,g$). The analysis of thermomechanical curves of SOOP demonstrated that the oligophenylene on the base of DTDES has a well defined region of ductility in the temperature intervale of 150–250°C on the curve achieving the relative deformation ~ 70%. In the temperature region of 220–250°C, the oligophenylene undergo the process of hardening (structuring). At temperatures up to 300°C there are insignificant differences in the characteristics of the thermomechanical curves of SOOP based on DESB. Introduce of disiloxanic fragments into the oligophenylenic chain causes the relative deformation to be increase (Fig. 1).

TABLE IV Yield and some properties of the three-fold co-oligophenylenes on the base of DESB, *p*-DEB and PA

| *No.* | *The molar ratio of the initial monomers DESB: p-DEB: PA* | *Yield, %** | *Solubility in $C_6H_6$, $C_6H_5-CH_3$ and $CHCl_3$* | *Unsaturation* | *Molec. mass*** |
|---|---|---|---|---|---|
| 1 | 1:2:0 | 70 | unsolul. | 0.122 | – |
| 2 | 1:2:1 | 69 | –"– | 0.106 | – |
| 3 | 1:2:2 | 94 | part. sol. | 0.101 | – |
| 4 | 1:1:1 | 70 | part. sol. | 0.080 | – |
| 5 | 1:1:2 | 71 | part. sol. | 0.073 | 3480 |

* Determined though the sum of the monomers.

** Ebullioscopy, in chloroform.

The study of thermomechanical curves of co-polycyclotrimers shows, that they are typical for polymers with the low molecular mass (Fig. 2), which completely melt in the vicinity of 160–165°C.

The co-polymers based on the DTDES and PA melt at lower temperatures ($T_{\mathrm{melt}} = 130°\mathrm{C}$ – curve 4 and $T_{\mathrm{melt}} = 115°\mathrm{C}$ – curve 5, Fig. 2) than in case of co-polymers obtained from DPDES and PA at the same molar ratios of the initial monomers ($T_{\mathrm{melt}} = 120 \div 160°\mathrm{C}$ – curves 2 and 3, Fig. 2). Note that by enhancing the fraction of PA in the initial mixture of monomers the melting temperature of the co-polymers is reduced (Fig. 2, curves 1, 2, 3 for the co-polymers of DPDES: PA and curves 4, 5 for the co-polymers of DTDES: PA correspondingly).

The study of thermoxydative destruction of synthesized SOOP (Figs. 3–5) shows that the thermooxydative stability of co-polymers depends on the structure of the initial siliconorganic diacetylenes and on their molar ratio in the monomer mixture (in case of co-

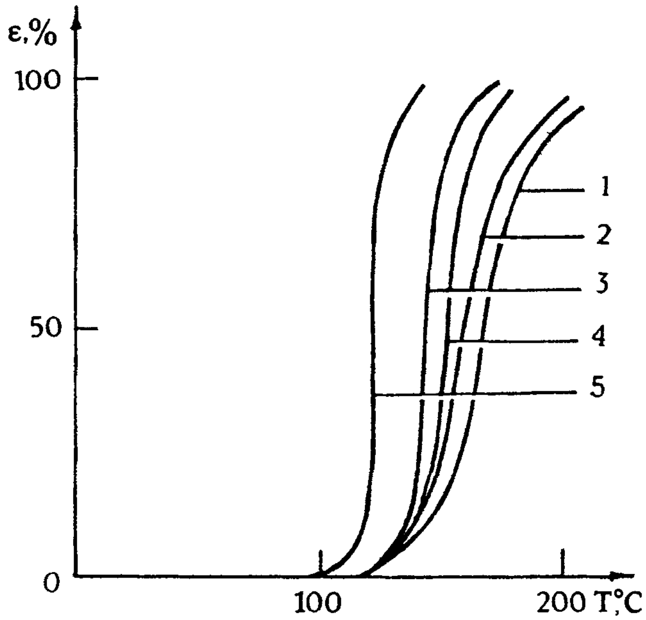


FIGURE 2 Thermomechanical curves of siliconorganic co-oligophenylenes: 1, 2, 3)–DPDES: PA 1) 1:0.5; 2) 1:1; 3) 1:2; 4, 5)–DTDES:PA 4) 1:1; 5) 1:2.

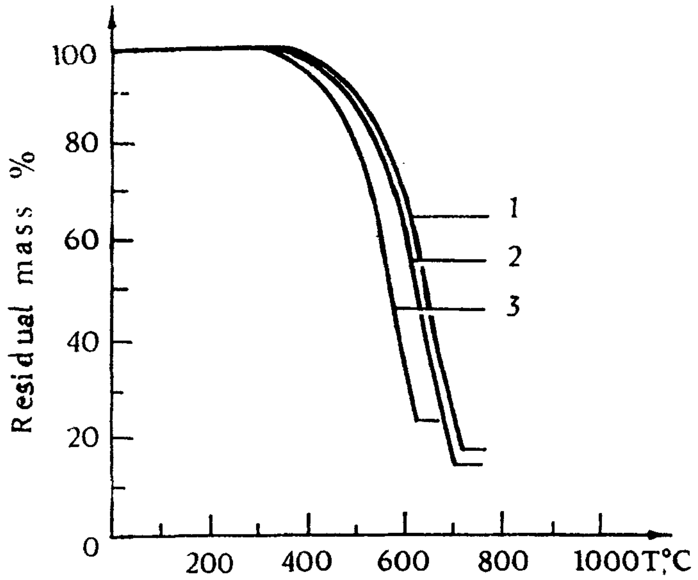


FIGURE 3 The curves of the T.G.A. of siliconorganic co-oligophenylenes based on DTDES and PA at the different molar ratios: 1) 1:2; 2) 1:1; 3) 1:0.5 (in the air).

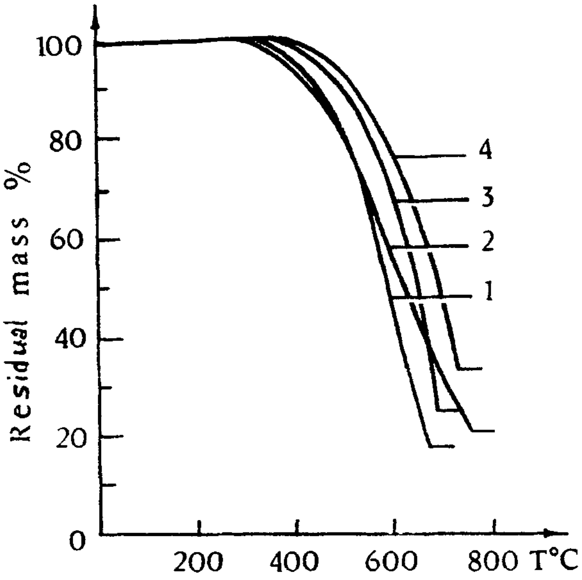


FIGURE 4 The curves of T.G.A. of siliconorganic co-polyphenylenes based on DESB, *p*-DEB and PA at the theirs different molar ratios: 1) 1:0:1; 2) 1:0:1.5; 3) 1:1:1; 4) 1:2:2.

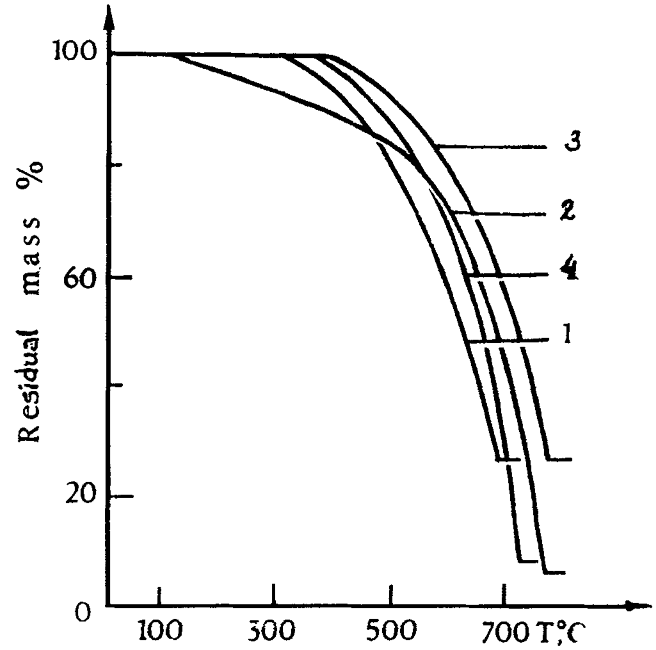


FIGURE 5 The curves of the T.G.A. of (co)polymers based on DETPDS:DEB:PA 1) 1:0:0; 2) 1:1:0.5; 3) 0:1:1.5; 4) DEB:PA (1:1).

polymerization, Figs. 4 and 5). From Figures 4 and 5 we see that the thermooxydative destruction of the polycyclotrimers based on diethynylsilanes and -siloxane starts at 320–325°C, while it takes place at 365°C and 380°C for the double and threefold co-polymers. The highest intensity of mass loss takes place in the region of 430–550°C and 490–620°C for the "double" and "threefold" co-polymers respectively (Figs. 4, 5).

At the same time the temperature intervale of complete destruction depends on the degree of conversion and the level of unsaturation of the products of (co)polycyclotrimerization [10].

In order to estimate the affect of the chemical structure of the co-polymers on their heat-resistance, the efficiency range of the synthesized three-fold co-polymers was determined. Interesting results were obtained for the co-polymers based on DETPDS:DEB:FA. As it is evident from Figure 6, the efficiency range of these co-polymers is higher than that of organic co-polymers based on DEB:PA [9].

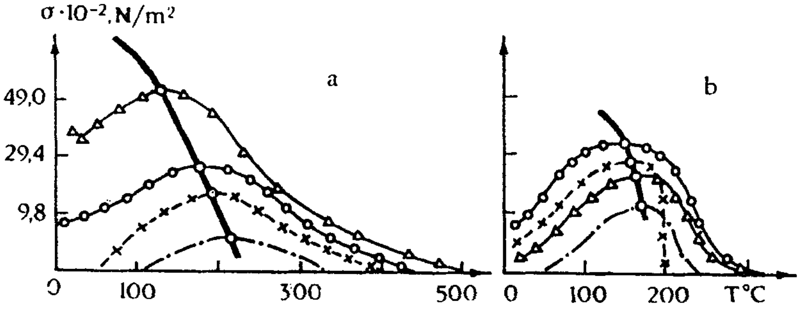


FIGURE 6 Use temperature range of co-oligophenylenes: a) DETPDS:DEB:PA (1:1: 0.5); b) DEB:PA (1:1.5).

The synthesized oligophenylenes can be used for manufacture of thermostable polymeric composites, hardening without evolution of volative compounds.

## *Acknowledgements*

The authors dedicate this work in memory of I. A. Chernomordic who participated in this study.

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