CHEMISTRY

S. B. DOLGOPLOSK, A. L. KLEBANSKII, L. P. FOMINA,

1963

SovietRxiv

Figure 1. UV absorption spectra. 1–$HSi(CH_3)_2C_6H_4Si(CH_3)_2H$, 2–$HOSi(CH_3)_2C_6H_4Si(CH_3)_2OH$, 3–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]$

Figure 1: Figure 1. UV absorption spectra. 1–$HSi(CH_3)_2C_6H_4Si(CH_3)_2H$, 2–$HOSi(CH_3)_2C_6H_4Si(CH_3)_2OH$, 3–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]$

Abstract

Full Text

CHEMISTRY

S. B. DOLGOPLOSK, A. L. KLEBANSKII, L. P. FOMINA,
V. S. FIKHTENGOL' TS, E. Yu. SHVARTS

SILOXANE POLYMERS WITH PHENYLENE UNITS IN THE MAIN CHAIN

(Presented by Academician S. S. Medvedev, October 19, 1962)

The main chain of siloxane elastomers is built up from alternating silicon and oxygen atoms, and the various types of siloxane polymers differ in the nature of the substituents at the silicon atom. The most widespread are polysiloxanes with methyl side groups, as well as polymers of this type containing in the chain a certain number of methylvinylsiloxane and methylphenylsiloxane units. Phenyl units provide a decrease in the crystallizability of the polymer and, correspondingly, increase its frost resistance (^{1}). When introduced in large amounts, they considerably increase the radiation resistance of the polymer (^{2}). The presence of small amounts of vinyl units facilitates the vulcanization process and favorably affects the heat resistance of the vulcanizates (^{3}).

Fig. 1. UV absorption spectra.
1 –$HSi(CH_3)_2C_6H_4Si(CH_3)_2H$,
2 –$HOSi(CH_3)_2C_6H_4Si(CH_3)_2OH$,
3 –$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]$

The introduction of phenyl units into the siloxane chain may be of great interest from the standpoint of increasing the heat resistance and radiation resistance of polymers and the physicomechanical properties of vulcanizates based on them. We have synthesized various types of high-molecular-weight (characteristic viscosity in benzene 1.2–1.9) rubber-like phenyl-containing siloxane polymers, differing in the substituents at the silicon atom and in the nature of the aromatic units:

$$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_x[Si(CH_3)_2O]_y, \tag{I}$$

$$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_x[Si(CH_3)(C_6H_5)O]_y, \qquad (II)$$

$$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_x[Si(C_6H_5)_2O]_y, \qquad (III)$$

$$[Si(CH_3)(R_F)C_6H_4Si(CH_3)(R_F)O]_x[Si(CH_3)(R_F)O]_y, \qquad (IV)$$

$$R_F = CH_2CH_2CF_3,$$

$$[Si(CH_3)_2C_6H_4OC_6H_4Si(CH_3)_2O]_x[Si(CH_3)_2O]_y. \qquad (V)$$

Similar polymers have not been described in the literature up to the present time. In the present communication we set forth the results of a study of the influence of phenylene groups on the properties of siloxane polymers, using as an example copoly-

polymers of group **I**, containing from 50 to 100 mole % of 1-dimethylsilyl-4-dimethylsiloxyphenylene units $[Si(CH_3)_2C_6H_4Si(CH_3)_2O]$ along with tetramethyldisiloxane units $[(CH_3)_2SiOSi(CH_3)_2O]$. The amount of phenylenesiloxane units was determined spectroscopically in the ultraviolet region.

Comparison of the absorption spectra of some model compounds and of the homopolymer $[Si(CH_3)_2C_6H_4(CH_3)_2O]_n$ shows that the spectra are almost identical and that the specific absorption coefficients are practically the same, amounting to 2.3–2.4. This indicates that the optically active group in these compounds is

$$-Si(CH_3)_2C_6H_4Si(CH_3)_2O- .$$

The latter circumstance enabled us to develop a method for the quantitative determination of these groups in copolymers with tetramethyldisiloxane units. A polymer sample (n) of about 0.1 g, weighed on an analytical balance, is dissolved in 10 ml of chloroform; the optical density of the solution is measured in a cuvette with a layer thickness of 0.5 mm on an SF-4 spectrophotometer at a wavelength of 269 mμ (D_{269}). The molar content of 1-dimethylsilyl-4-dimethylsiloxyphenylene units in the copolymers is calculated from the formula:

$$\frac{148}{\dfrac{208n}{(D_{269}-a)/2.4\,d} - 0.6},$$

where d is the thickness of the cuvette layer (according to the passport), and a is the difference in optical densities (cm) of cuvettes filled with chloroform at 269 mμ.

Fig. 2. X-ray spectra.
I–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_n$,
II–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{70n} \cdot [Si(CH_3)_2OSi(CH_3)_2O]_{30n}$,
III–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{60n} \cdot [Si(CH_3)_2OSi(CH_3)_2O]_{40n}$.

Physical properties of the polymers

The homopolymer $[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_n$ is a crystalline product. The copolymer containing 70 mole % of 1-dimethylsilyl-4-dimethylsiloxyphenylene units is a rubber-like product with limited elasticity at room temperature. Copolymers containing 60 and 50% phenylenesiloxane units are rubber-like at ordinary temperatures. For some of the synthesized polymers, X-ray spectra were recorded and thermomechanical properties were studied on Kargin balances (^{4}).

The X-ray pattern of the homopolymer $[(CH_3)_2SiC_6H_4Si(CH_3)_2O]_n$ shows a picture typical of a crystalline polymer, whereas the X-ray pattern of the copolymer containing 60 mole % of these units reveals the absence of a crystalline phase and a complete transition to the amorphous state. The X-ray pattern of the copolymer, containing 70 mol. % phenylenesiloxane units shows that the content of the crystalline phase is still fairly considerable. The X-ray diffraction data correlate with the results of determining the thermomechanical properties on Kargin balances.

Fig. 3. Thermomechanical curves.
I–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_n$,
II–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{70n} \cdot [Si(CH_3)_2OSi(CH_3)_2O]_{30n}$,
III–$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{60n} \cdot [Si(CH_3)_2OSi(CH_3)_2O]_{40n}$,
IV–$[Si(CH_3)_2O]_n$.

The form of the thermomechanical curves resembles those for low-molecular-weight polymers. It is possible that, owing to the structural features of siloxane polymers, which even at very considerable molecular weights (10^6) are "liquids," "pseudopolymers," the region of high-elastic deformation is pronounced. As can be seen from the data presented in Fig. 3, homopolymer I becomes fluid at a temperature of about 25°, which apparently is the melting temperature of the corresponding crystalline phase.

Fig. 4. Plot of the dependence of glass-transition temperature on polymer composition

Copolymer II, with disturbed crystallinity, becomes fluid at 60°, whereas copolymer III, containing 60 mol. % units $[Si(CH_3)_2C_6H_4Si(CH_3)_2O]$, becomes fluid

Fig. 4. Plot of the dependence of glass-transition temperature on polymer composition

Figure 2: Fig. 4. Plot of the dependence of glass-transition temperature on polymer composition

on passing through the glass-transition temperature. Dimethylsiloxane rubber flows at a temperature of −50°, which corresponds to known data on the melting temperature of this polymer (5).

The glass-transition temperature of the polymers obtained, determined by the method for crystallizing polymers, is given in Table 1.

Table 1

Polymer composition	Glass-transition temperature, °C
$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_n$	−23
$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{50n}$ $[(CH_3)_2SiOSi(CH_3)_2O]_{50n}$	−73
$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{60n}$ $[(CH_3)_2SiOSi(CH_3)_2O]_{40n}$	−63
$[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_{70n}$ $[(CH_3)_2SiOSi(CH_3)_2O]_{30n}$	−53

Thus, the relationship between the polymer composition and the glass-transition temperature is linear in character.

On the basis of graphical determination, the glass-transition temperature of dimethylsiloxane rubber is −123°, which corresponds to known data (6).

For polymers of the type $[Si(CH_3)_2C_6H_4Si(CH_3)_2O]_x$ $[(CH_3)_2SiOSi(CH_3)_2O]_y$, the influence of phenylene units on some properties of the polymeric siloxane chain as a function of polymer composition has been studied.

Received
10 X 1962

References

1. K. E. Polmanteer, M. I. Hunter, *J. Appl. Polym. Sci.*, **1**, 1, 3 (1959).

2. L. M. Epstein, *Rubber Age*, **82**, 6, 825 (1958).

3. S. N. Borisov, I. K. Stavitskii, *Kauchuk i rezina*, **17**, No. 2, 1 (1958).

4. T. I. Sogolova, V. A. Kargin, *ZhFKh*, **23**, 530 (1949).

5. M. Ohlberg, L. E. Alexander, E. L. Warrick, *J. Polym. Sci.*, **27**, 115, 1 (1958).

6. C. E. Weir, W. H. Leser, L. A. Wood, *Nat. Bur. Standards*, **44**, 367 (1950).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.