A. M. POLYAKOVA and N. A. CHUMAEVSKII

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Abstract

Full Text

A. M. POLYAKOVA and N. A. CHUMAEVSKII

ON THE INTERACTION OF TETRAALKYLDIHYDRIDODISILOXANES WITH DIFUNCTIONAL UNSATURATED COMPOUNDS

(Presented by Academician I. V. Obreimov, 3 IX 1959)

As was shown earlier ([1]), tetraalkyldihydridodisiloxanes

$$\begin{array}{c} \mathrm{R} \quad\quad \mathrm{R} \\ | \quad\quad | \\ \mathrm{H-Si-O-Si-H;} \quad \mathrm{R=CH_3,\ C_2H_5,} \\ | \quad\quad | \\ \mathrm{R} \quad\quad \mathrm{R} \end{array}$$

in the presence of a catalyst—platinic hydrochloric acid—react with difunctional unsaturated compounds of the type:

$$\mathrm{CH_2=CH(R)M(R)CH=CH_2}$$

and

$$\mathrm{CH_2=CH-CH_2(R)M(R)CH_2-CH=CH_2}$$

where M = Si and Ge; R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_6H_5}$, with formation of polymeric products consisting of units

$$\left[\begin{array}{c} | \quad\quad | \quad\quad | \\ \mathrm{-Si-O-Si-(CH_2)_2-M-(CH_2)_2-} \\ | \quad\quad | \quad\quad | \end{array}\right]$$

or, respectively,

$$\left[\begin{array}{c} | \quad\quad | \quad\quad | \\ \mathrm{-Si-O-Si-(CH_2)_3-M-(CH_2)_3-} \\ | \quad\quad | \quad\quad | \end{array}\right].$$

The aim of the present work is to study the structure of the polymeric products obtained by the method of infrared spectroscopy.

The infrared absorption spectra of the polymers obtained by us make it possible to judge their structure (for comparison, spectra of the starting components were also recorded; Figs. 1, 2, 3, 4).

The reaction of disiloxanes with dialkenes may proceed with formation of linear or cyclic polymers. This can be detected from the corresponding characteristic frequencies of the infrared absorption bands of the terminal groups Si–H and C=C. For linear polymers formed at an equimolecular ratio of the components, the presence of a Si–H bond may be expected at one end of the macromolecular chain, and of a C=C bond at the other.

With an excess of disiloxane in the reaction mixture, Si–H bonds may be expected at the ends of the macromolecular chain, and with an excess of dialkene, C=C bonds. In the case of a cyclic structure these bonds should be absent. The IR absorption bands of the stretching vibrations of the Si–H group lie in the frequency region 2100-2300 cm^{-1} ([2]); they are intense and are readily detected when present in a compound. For the tetraalkyldihydridodisiloxanes investigated by us, the Si–H group corresponds to a frequency of 2125-2130 cm^{-1} (Fig. 1, Table 1).

The stretching vibrations of the C=C bond correspond to IR absorption bands at 1600-1680 cm^{-1}. For the divinyl compounds investigated, the frequency of the C=C bond has the value 1595 cm^{-1}, and for the diallyl compounds, 1630 cm^{-1} (Fig. 2, Table 2). The intensity of the absorption bands of the double bond is weak and depends to a considerable extent on the symmetry of the molecule; this may complicate their detection in polymers, especially if one also takes into account the circumstance that the intensity of these bands will also decrease with increasing molecular···

molecular weights of the polymers, since the number of double bonds per unit volume will decrease as the size of the molecules increases.

The IR absorption spectra of polymers obtained by the interaction of divinyl monomers with disiloxanes, such as the reaction products from the interaction of diethyldivinylsilane, respectively, with all three disiloxanes ($n = 5, 6$), and the reaction product from the interaction of phenylmethyldivinylsilane with dimethyldiethyldisiloxane ($n = 4$) (with an equimolecular ratio of the components), indicate the absence of the Si–H bond. At the same time, the spectra of polymer samples formed in the interaction of diallyl monomers with disiloxanes, such as the product of the interaction of diethyldiallylsilane with tetraethyldisiloxane ($n = 4$), and the products of the interaction of dimethyldiallylgermane with dimethyldiethyldisiloxane ($n = 6$) and with tetraethyldisiloxane ($n = 2$) under the same conditions, indicate its presence (Fig. 3). In the spectra of these same products, reprecipitated with alcohol, the band of the Si–H bond is absent.

Table 1

Frequencies of tetraalkyldihydridedisiloxanes (in cm^{-1})*

Tetramethyldisiloxane	Dimethyldiethyldisiloxane	Tetraethyldisiloxane	Tetramethyldisiloxane	Dimethyldiethyldisiloxane	Tetraethyldisiloxane
2959	29582935	29522935	1252	12541235	–1240
–	29092875	29052865	1060	10601008	10651010
2898			–		
2125	2125	2130	907	962	970
–	1462	1465	880	885	–
1422	1410	1415	835	850	830
1395	1380	1380	776	767	{ 725{ 702
			700	710	

* Frequencies in the region 680–1300 cm^{-1} are given for solutions in carbon tetrachloride.

With an excess of disiloxane in the reaction mixture with the divinyl monomer (tetraethyldisiloxane and phenylmethyldivinylsilane), a band of the Si–H bond is found in the IR spectrum. The same is also observed in the spectrum of the polymer obtained by the interaction of tetraethyldisiloxane with diallyl–

Table 2

Frequencies of dialkenes (in cm^{-1})

Phenylmethyldivinylsilane	Diethyldivinylsilane	Dimethyldiallylsilane	Diallyl	Phenylmethyldiallylsilane	Diethyldivinylsilane	Dimethyldiallylsilane	Diallyl
3065	–	3079	3083	1255	–	–	–
3052	3050	3058	–	–	1235	1240	1245
3006	3003	2989	3000	1108	–	1195	1210
{ 2959	2950	2950	2980	1005	1007	1153	1120
{ 2940	–	–	2920	955	952	1067	1045
2895	2902	2902	–	870	740	1035	992
–	2865	2868	2840	840		1010	912
				800	–	990	695
1595	1595	1630	1630	{ 750	–	960	
1467	1465	1462	1435	{ 740	–	930	
(?)							
1425	–	1415	1410	702	–	895	
1405	1404	1390	1325			{ 800	
1305	–	1300	1295			{ 770	

allyl (Fig. 4). With an excess, respectively, of diethyldiallylsilane and dimethyldiallylsilane in the reaction mixture with tetramethyldisiloxane, the polymers formed contain, in agreement with the assumption, C=C bonds. It should be noted that the frequencies of the groups Si–H (2125–2130 cm^{-1}), Si–O–Si (1060 –1065 cm^{-1}), Si–CH_3 (1250–1255 cm^{-1}), and Si–C_2H_5 (1235–1240 cm^{-1}) are practically the same for monomers and for polymers.

Figure 1. IR absorption spectra of tetraalkyldihydridedisiloxanes

Figure 1: Figure 1. IR absorption spectra of tetraalkyldihydridedisiloxanes

Figure 2. IR absorption spectra of dialkenes

Figure 2: Figure 2. IR absorption spectra of dialkenes

On the basis of the results obtained, the following conclusion may be drawn about the structure of the polymers: the interaction of divinyl monomers

Fig. 1. IR absorption spectra of tetraalkyldihydridedisiloxanes

Fig. 2. IR absorption spectra of dialkenes

with disiloxanes, in an equimolecular ratio, leads to the formation of cyclic polymers, whereas diallyl monomers under the same conditions form linear polymers.

The IR absorption spectra were recorded on double-beam infrared spectrophotometers operating on the principle of the phase comparison method.

with beam intensities* using LiF (2800-3000 cm^{-1}) and NaCl (680-3000 cm^{-1}) prisms. With the LiF prism in the region of 3000 cm^{-1}, the spectral slit width was 6 cm^{-1}, and in the region of 1000 cm^{-1} with the NaCl prism the spectral slit width was 10 cm^{-1}.

The substances were recorded as a layer between two salt windows**, and also in cells of constant thickness (0.016 and 0.05 mm).

Fig. 3. IR absorption spectra of the interaction products (with an equimolar ratio of the components)

In conclusion, we consider it a pleasant duty to thank Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak and Academician I. V. Obreimov for their interest in the work, V. M. Vdovin and V. F. Mironov for carrying out the syntheses, and E. A. Dimitrieva and R. A. Isaev for valuable assistance in recording the IR spectra.

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Fig. 3. IR absorption spectra of the interaction products (with an equimolar ratio of the components)

Figure 3: Fig. 3. IR absorption spectra of the interaction products (with an equimolar ratio of the components)

Fig. 4. IR absorption spectra of the interaction products (with an excess of disiloxane and dialkene)

Figure 4: Fig. 4. IR absorption spectra of the interaction products (with an excess of disiloxane and dialkene)

CITED LITERATURE

1. V. V. Korshak, A. M. Polyakova et al., DAN, **128**, 960 (1959).

2. L. Bellamy, *Infrared Spectra of Molecules.* IL, 1957, p. 394.

Fig. 4. IR absorption spectra of the interaction products (with an excess of disiloxane and dialkene)

* This recording method was developed in the optical laboratory by V. I. Dianov-Klokov.

** Spectra for which the layer thickness is not indicated were recorded between two salt windows.

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