CONDENSATION OF α,ω-DIHYDROXYPOLYDIMETHYLSILOXANE Oligomers with 1,3-DIMETHYL-1,3-DIPHENYL-1,3-DISILOXANEDIOL DIACETATE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 4, pp. 651-654, April, 1963
Original article submitted June 15, 1962

Polymers of the polydimethylsiloxane series have been reported in which some of the methyl groups attached to the chain are replaced by phenyls. Such polymers were prepared by the cohydrolysis of dichloromethylphenylsilane with dichlorodimethylsilane and the subsequent catalytic polymerization of the cyclic monomers obtained with formation of linear polymers. Polymers of analogous structure have been obtained also from heptamethylphenylcyclotetrasiloxane in presence of alkaline and acid catalysts [1, 2]. In the polymers obtained the distribution of the phenyl groups attached to the siloxane chain was not regular.

It was of interest to synthesize linear polymers by the polycondensation of oligomers of the dimethylsiloxane series having terminal hydroxy groups with oligomers containing acetoxy groups, such as 1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol diacetate. In this case it is possible to make sure that dimethylsiloxane blocks will be distributed between methylphenylsiloxane blocks.

For the purpose of the condensation of octamethyl-1,7-tetrasiloxanediol with α,ω-diacetoxypolymethylphenylsiloxanes we synthesized oligomers by the acetylation of pure α,ω-dichloropolymethylphenylsiloxanes with acetic anhydride. Experiment showed that reaction proceeds readily at 130-135° with liberation of acetyl chloride:

By this reaction we obtained α,ω-diacetoxypolymethylphenylsiloxanes for which \( n = 1, 2, \) and 3. All the α,ω-diacetoxypolymethylphenylsiloxanes obtained were liquids at room temperature and were readily soluble in various organic solvents.

Study of the condensation of octamethyl-1,7-tetrasiloxanediol with 1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol diacetate showed that when these reactants were heated together at 125-148° reaction occurred with liberation of acetic acid, and the viscosity of the reaction product rose.

On the basis of the amount of acetic acid liberated and the analysis of the reaction product it may be supposed that reaction was in accordance with the following equation:

Investigation of the condensation of octamethyl-1,7-tetrasiloxanediol with 1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol diacetate showed that the number of acetoxy and hydroxy groups in the reaction mixture fell in proportion to the amount of acetic acid liberated in the reaction and that the viscosity of the polymer rose during the heating process.
Figure 1 presents kinetic data on the condensation of octamethyl-1,7-tetrasiloxanediol with 1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol diacetate.

The average molecular weight of the polymer obtained, determined from the change in viscosity, was about 30,000. The glass point of the polymer (see Fig. 2) was about -55°, i.e., somewhat higher than the glass points of polymers obtained by the cohydrolysis of dichlorodimethylsilane with dichloromethylphenylsilane (glass point -80°) and of polymers obtained by the polymerization of heptamethylphenylcyclotetrasiloxane (glass point -70°). Such differences can probably be explained by different distributions of phenyl groups in the main chains of the polymer molecules.

**EXPERIMENTAL**

The following reactants were used in the work: 1,3-dichloro-1,3-dimethyl-1,3-diphenylsiloxane, b.p. 162-163° (4 mm), chlorine content 21.6%, and \(n_\text{D}^0 1.5317; 1,5\)-dichloro-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane, b.p. 190-193° (1 mm), chlorine content 15.2%, and \(n_\text{D}^0 1.5375; 1,5\)-dichloro-1,3,5,7-tetramethyl-1,3,5,7-tetraphenyltrisiloxane, b.p. 274-275° (8 mm), chlorine content 11.24%, and \(n_\text{D}^0 1.5412; 1,5\)-dichloro-1,3,5,7-tetrasiloxanediol, hydroxyl content 9.45%, mol. wt. 330; acetic anhydride, b.p. 137-140° (760 mm) and \(n_\text{D}^0 1.3900. \alpha,\omega\)-Diichloropolymethylphenylsiloxanes were prepared by the partial hydrolysis of dichloromethylphenylsilane with water in dioxane [3], and octamethyl-1,7-tetrasiloxanediol was prepared by the hydrolysis of 1,7-dichlorooctamethyltrisiloxane with 4% sodium hydroxide solution[4].

**Preparation of \(\alpha,\omega\)-Diacetoxypolymethylphenylsiloxanes**

**Preparation of 1,3-Dimethyl-1,3-diphenyl-1,3-disiloxanediol Diacetate.** A mixture of 84.33 g of 1,3-dichloro-1,3-dimethyl-1,3-diphenylsiloxane and 57.5 g (an excess) of acetic anhydride was prepared in a three-necked flask fitted with a stirrer, a thermometer, and a reflux condenser connected to another condenser set for distillation (for the removal of acetyl chloride). The mixture was stirred for nine hours at 130-135°.

In the course of the reaction 36.77 g (91%) of acetyl chloride separated. When the acetylation was complete, the reaction mixture was vacuum-fractionated, and we obtained 72.8 g (75.9%) of 1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol diacetate; b.p. 194-195.5° (6 mm); \(n_\text{D}^0 1.5082, d_\text{D}^0 1.1273; \text{Found MR } 98.87, \text{calculated MR } 98.77. \text{Found: CH}_3\text{COO } 31.52; \text{C } 57.75; \text{H } 5.76; \text{Si } 14.95%; \text{mol. wt. } 337. \text{Calculated } \text{CH}_3\text{COO } 31.55; \text{C } 57.75; \text{H } 5.88; \text{Si } 14.97%; \text{mol. wt. } 337.

**Preparation of 1,3,5-Trimethyl-1,3,5-triphenyl-1,5-trisiloxanediol Diacetate.** The acetylation was carried out analogously. A mixture of 82.95 g of 1,5-dichloro-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane and 38 g of acetic anhydride was stirred for six hours at 130-135°. In the course of the reaction 15.5 g (55%) of acetyl chloride separated.

By fractionation of the acetylation products we isolated 66.07 g (63.5%) of 1,3,5-trimethyl-1,3,5-triphenyl-1,5-trisiloxanediol diacetate- b.p. 200-204° (1.5 mm); \(n_\text{D}^0 1.5243, d_\text{D}^0 1.1337; \text{Found MR } 136.63, \text{calculated MR } 137.02. \text{Found: CH}_3\text{COO } 22.94; \text{C } 58.70; \text{H } 58.70; \text{Si } 16.88; 16.84%; \text{mol. wt. } 489, 483. \text{Calculated: } \text{CH}_3\text{COO } 23.14; \text{C } 58.82; \text{H } 5.88; \text{Si } 16.47%; \text{mol. wt. } 510.