Chemistry

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Abstract

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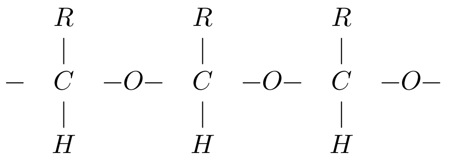
Polymerization of Trichloroacetaldehyde with an Organometallic Catalyst

(Presented by Academician A. V. Topchiev, 24 VIII 1962)

At present, the problem of obtaining polymers possessing low flammability, increased heat resistance, and resistance to abrasion is of great interest. It may be expected that polymers obtained on the basis of chlorinated aldehydes, by analogy with other chlorine-containing polymers, will possess similar properties. In this direction we have undertaken a study of the polymerization of halogen-substituted aldehydes, in particular trichloroacetaldehyde (chloral).

From the literature ($^{1-6}$) it is known that aldehydes readily polymerize on cationic and anionic catalysts. Chlorinated aldehydes are even more reactive compounds in polymerization reactions, since they contain chlorine atoms with a large induction effect. Polymerization readily proceeds through the carbonyl bond, giving a polymer of the following type:



$$-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-O-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-O-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-O-\ ,$$

where R is alkyl or chloro-substituted alkyl.

We are presently studying the polymerization of trichloroacetaldehyde on nucleophilic catalysts at low temperatures.

Experimental Part

As a result of preliminary experiments it was established that triethylaluminum is considerably less active than butyllithium. Therefore the study of the polymerization of trichloroacetaldehyde was carried out by us using the latter as the catalyst.

Preparation of the monomer and solvents. The organic solvents used were purified and dried by the usual methods. The purification and drying of trichloroacetaldehyde presented considerable difficulty, since it is a very reactive substance and readily adds water, forming trichloroacetaldehyde hydrate.

Fig. 1. Influence of catalyst concentration on the yield of crystalline polymer

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Commercial trichloroacetaldehyde was dried over sodium sulfate, distilled at atmospheric pressure, passed through molecular sieves with pore size 4 Å, and fractionated on a rectification column. A fraction with boiling point 97.3—97.5° at 752 mm Hg and n_D^{20} 1.4554 was collected. Literature data: b.p. 97.7° at 760 mm, n_D^{20} 1.4557.

Procedure for polymerization and treatment of the polymer. The polymerization reaction was carried out in an atmosphere of argon purified of oxygen and moisture. A definite amount of solvent–*n*-hexane–and monomer was poured into the reaction vessel. After this the reactor was purged with argon for 15-20 min, and the reaction mixture, with stirring, was cooled to $-78°$ with dry ice and acetone. To the cooled mixture of monomer and solvent, small portions were added over the course of

for 20 min. The catalyst was butyllithium. Polymerization was carried out with cooling and stirring of the reaction mixture for 5-10 h in a stream of dry argon. After completion of the reaction, the catalyst was decomposed with a mixture of *n*-butyl alcohol and acetone. The polymer was filtered off, washed successively with acetone, water, and alcohol, and dried in vacuum at 60°. The amorphous part of the polymer dissolves in acetone; therefore, by washing the polymer with acetone we isolated the crystalline part of polytrichloroacetaldehyde.

Results of the experiments performed. We studied the influence of catalyst concentration, the amount of solvent, and reaction time on the polymer yield (yield in weight percent, calculated on the monomer). The catalyst concentration was varied from 0.0062 mole to 0.0109 mole (see Fig. 1). As can be seen from Fig. 1, at a butyllithium concentration equal to 0.0062 mole, no solid crystalline substance is formed, and only an amorphous polymer was isolated. With a further increase in the catalyst concentration from 0.0073 mole to 0.0109 mole, the yield of crystalline polymer increases from 4.5 to 17.6%.

Fig. 1. Influence of catalyst concentration on the yield of crystalline polymer

An increase in the reaction time also has a sharp effect on the polymer yield. In the polymerization of trichloroacetaldehyde for 5 h, the polymer yield is 10%, whereas increasing the polymerization time to 10 h raises the polymer yield by more than a factor of two (24.5%). The amount of solvent also sharply affects the polymer yield. The polymer yield in the polymerization of trichloroacetaldehyde (25 ml) without solvent for 5 h is only 4%, while the addition of 30 ml of hexane to the reaction mixture increases the polymer yield to 16.2%. Increasing the amount of solvent to 60 ml sharply lowers the polymer yield to 2.9%.

Fig. 2. Infrared absorption spectrum of polytrichloroacetaldehyde (NaCl prism)

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Figure 2: Fig. 2. Infrared absorption spectrum of polytrichloroacetaldehyde (NaCl prism)

Fig. 3. Infrared absorption spectrum of polytrichloroacetaldehyde (lithium fluoride prism)

Figure 3: Fig. 3. Infrared absorption spectrum of polytrichloroacetaldehyde (lithium fluoride prism)

Product characterization. The polymer obtained is a white solid, melting with decomposition above 200°. The X-ray diffraction pattern showed that the polymer is crystalline. At room temperature, polychloral dissolves well only in pyridine and partially in dimethylformamide, acrylonitrile, and methyl ethyl ketone. Neither at room temperature nor on heating to 50° does polychloral dissolve in other organic solvents, for example, dioxane, carbon tetrachloride, hexane, chlorobenzene, tetrahydrofuran, etc.

An elemental analysis was performed for polychloral, which gave the following—

following results:

Found, %: C 17.76; Cl 65.33; H 1.01; O 15.9 (by difference)

Calculated for trichloroacetaldehyde, %: C 16.28; Cl 72.18; H 0.62; O 10.68

The increased content of C, H, O can probably be explained by the attachment of the alkyl radical of the catalyst to the ends of the macromolecular chains and by the presence of terminal hydroxyl groups. All this is confirmed by the infrared absorption spectra. In the infrared absorption spectrum of trichloroacetaldehyde obtained with a NaCl prism (Fig. 2), a number of bands are observed that characterize elements of the polymer structure. The bands at 795, 1070, and 1128 cm^{-1} are characteristic of stretching vibrations of C—Cl in the $C—CCl_3$ group; the band at 664 cm^{-1} is also assigned to $C \cdot Cl$ stretching vibrations, and the bands at 822 and 838 cm^{-1} to the C—C bond in the polymer molecule (4).

Fig. 3. Infrared absorption spectrum of polytrichloroacetaldehyde (lithium fluoride prism)

The intense bands at 963 and 1091 cm^{-1} are assigned respectively to symmetric and antisymmetric stretching vibrations of C—O—C. The bands at 1330 and 1360 cm^{-1} characterize deformation vibrations of C—H. In the infrared absorption spectrum of polychloral obtained with a lithium fluoride prism (Fig. 3), a broad band with its maximum at about 3364 cm^{-1} is observed, assigned to stretching vibrations of —OH groups bonded in complexes by hydrogen bonding. The presence in the structure of polychloral of a very small amount of OH groups, which is clearly seen from the low intensity of the 3364 cm^{-1} band, is apparently explained by the fact that they are located at the ends of large polymer molecules of polytrichloroacetaldehyde.

The stretching vibrations of C–H in CH_3–and CH_2–groups are represented by bands at 2852, 2922, and 2959 cm^{-1}. The presence in the polymer of a small amount of $-CH_3$ and CH_2–groups is probably explained by the fact that the CH_3-CH_2–group formed during the decomposition of butyllithium attaches to the end of the polymer chain.

The spectra presented above for polychloral obtained on butyllithium are in good agreement with the spectra known in the literature (4) for polychloral obtained on acidic and basic catalysts.

At present, further study is being carried out of the polymerization reaction of trichloroacetaldehyde and other chlorine-containing aldehyde derivatives.

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