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Academician A. V. TOPCHIEV, E. A. MUSHINA, A. I. PERELMAN

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Abstract

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Academician A. V. TOPCHIEV, E. A. MUSHINA, A. I. PERELMAN
and B. A. KRENDZEL

SYNTHESIS OF POLYVINYLCYCLOHEXANE

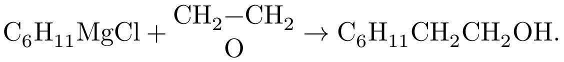
The preparation of new crystalline polymers of stereoregular structure on organometallic and oxide catalysts is attracting ever-increasing attention from researchers throughout the world. This is explained both by the valuable technical properties of the polymers formed and by the interest in studying the mechanism of the polymerization reaction on various catalysts. Recently, a number of reports have appeared in print on the polymerization of various vinyl compounds on organometallic and oxide catalysts. However, there are no data in the literature on the polymerization of vinyl derivatives of cyclohexane. The possibility of obtaining polyvinylcyclohexane and investigating the influence of the nature of the catalyst on the properties of the polymer seemed to us worthy of attention.

Experimental Part

Vinylcyclohexane was obtained from cyclohexylethyl alcohol according to the following scheme ([1]):

$$C_6H_{11}CH_2CH_2OH \xrightarrow{(CH_3CO)_2O} C_6H_{11}CH_2CH_2OCOCH_3 \xrightarrow[500^\circ]{} C_6H_{11}CH{=}CH_2$$

Cyclohexylethyl alcohol was synthesized by two routes: I. By the action of absolutely dry gaseous ethylene oxide on cyclohexylmagnesium chloride (obtained by the Grignard reaction) in an ether solution ([2], [3])



$$C_6H_{11}MgCl + \underset{O}{CH_2{-}CH_2} \rightarrow C_6H_{11}CH_2CH_2OH.$$

II. By hydrogenation of phenylethyl alcohol. The literature contains data on carrying out this process in the presence of nickel on aluminum oxide ([4]) or on the hydrogenation of phenylethyl alcohol according to Sabatier ([5]). For the reduction of phenylethyl alcohol we used Raney nickel catalyst at a temperature of 160° and a pressure of 100 atm; the yield of cyclohexylethyl alcohol was ~50%.

Figure: microstructure of investigated alloys

Figure 1: Figure: microstructure of investigated alloys

Figure: X-ray diffraction patterns

Figure 2: Figure: X-ray diffraction patterns

By acetylation of cyclohexylethyl alcohol and pyrolysis of the acetate (^{1}) we obtained vinylcyclohexane with the following constants: b.p. 83–85°/15 mm (lit. (^{1}) 125/740), n_D^{20} −1.4470 (lit. 1.4470), d_4^{20} −0.8060 (lit. 0.8091), MR_D − 36.41 (lit. 36.38).

Calculated MR_D 36.47.

The structures of the intermediate compounds in the synthesis of vinylcyclohexane were confirmed by their constants and by subsequent transformations.

The polymerization of vinylcyclohexane was carried out by us on two catalysts: an oxide-chromium catalyst and an organometallic catalyst. The catalyst, obtained from aluminosilicate impregnated with chromic anhydride with subsequent activation (^{6}), was charged into an ampoule of 10–12 ml capacity, previously washed by successive evacuation and filling with pure nitrogen. The sealed ampoules were placed in a thermostat, where they were heated for 5–7 hours to 80–85° with stirring. Carefully dried heptane was used as the solvent for the monomer.

To the article by R. B. Golubtsova and L. A. Nuda, p. 318

Fig. 1. Microstructure of the investigated alloys: a —alloy 3, b —alloy 8, v — alloy 21a. 200×

Fig. 4. X-ray diffraction patterns of the Ni_3Nb phase isolated from alloy 8

To the article by A. V. Topchiev, E. A. Mushina, A. I. Perelman, and B. A. Krenzel, p. 344

Fig. 1. X-ray diffraction patterns of crystalline polyvinylcyclohexane obtained on catalysts: chromium oxide (a), chromium oxide with the addition of $(i-C_4H_9)_3Al$ (b) and $(i-C_4H_9)_3Al+TiCl_4$ (v)

or benzene. As is known, in the polymerization of olefins on an oxide-chromium catalyst, the addition of triisobutyl- or triethylaluminum increases the yield and crystallinity of the polymer (^{7}).

As our experiments showed, in the polymerization of vinylcyclohexane with the

Figure: X-ray diffraction patterns of crystalline polyvinylcyclohexane

Figure 3: Figure: X-ray diffraction patterns of crystalline polyvinylcyclohexane

addition of triisobutylaluminum (a 50% solution in heptane), the polymer yield increases twofold; at the same time its properties (m.p., crystallinity, viscosity, etc.) do not change (Fig. 1a,b, see inset, p. 318).

The polymerization of vinylcyclohexane on an organometallic catalyst was carried out in ampoules and in a flask under a stream of purified nitrogen. The catalysts used were triisobutylaluminum and titanium tetrachloride. The process was conducted at 80° with stirring. According to preliminary data, the polymer yield was ∼ 30%. After completion of the reaction, the polymer was washed with methyl alcohol, 10% HCl, and water, and dried at 100°. Polyvinylcyclohexane obtained on (iso-$C_4H_9)_3Al + TiCl_4$ contains 1% ash (because of the difficulty of washing out traces of aluminum); when the polymer is obtained on an oxide-chromium catalyst, no ash content is detected.

Polyvinylcyclohexane is a white, finely dispersed powder with m.p. 325°, soluble in organic solvents.

Table 1

Solubility of polyvinylcyclohexane in various solvents

Catalyst	Cyclohexane, cold	Heptane, cold	Heptane, boiling	Benzene, cold	Benzene, boiling	Toluene, cold	Toluene, boiling	Xylene, cold	Xylene, boiling	Decalin, cold	Decalin, boiling	Tetralin, cold	Tetralin, boiling
(iso-$C_4H_9)_3Al$+ $TiCl_4$	++	−	−	+	++	+	++	+	++	+	++	+	++
CrO_3 on aluminosilicate	++	−	−	+	++	+	++	+	++	+	++	+	++

Note. (−) −insoluble. (+) −partially soluble. (++) −readily soluble.

The intrinsic viscosity of the polymer varied, depending on the nature of the catalyst used. Thus, in polymerization on an oxide-chromium catalyst the intrinsic viscosity was 0.5, whereas on an organometallic catalyst it was 1–1.5. Elemental analysis of the polymer gave the following results:

Found, %: C 87.22; H 12.80
Calculated, %: C 87.27; H 12.72

The X-ray diffraction patterns obtained (Fig. 1) indicate high crystallinity of the polymer. The proposed structure of the polymer is:

$$-CH - CH_2 - CH - CH_2 - CH-$$

|　　　　|　　　　|
cyclohexyl　cyclohexyl　cyclohexyl

It should be noted that in the polymerization of vinylcyclohexane no side reaction products were detected.

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