Letters to the Editor

Dehydrochlorination in the copolymerization of *N*-vinyl-4,5,6,7-tetrahydroindole with vinyl chloride or vinylidene dichloride

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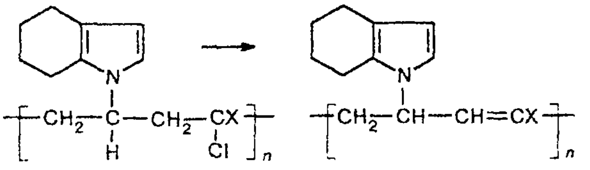
We have established for the first time that the radical copolymerization of *N*-vinyl-4,5,6,7-tetrahydroindole (VTHI) with vinyl chloride (VC) or vinylidene dichloride (VDC) occurs at any initial ratio of the monomers and is accompanied by the dehydrochlorination of the macromolecules formed, although an increase in the content of VTHI in the original mixture results in a decrease in the yield of the copolymer, which agrees with the low rates of radical polymerization of VTHI.[1]

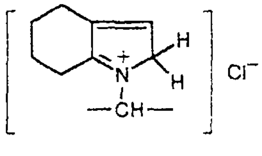


X = H, Cl

The conclusion about the dehydrochlorination of the copolymers is based on the fact that the content of the VC units in the copolymer calculated from the determination of the weight fraction of chlorine is considerably lower than that determined from the concentration of the VTHI units (calculated from the weight fraction of nitrogen). The dehydrochlorination process is also supported by the IR spectroscopic data: ν(C=C) 1640 cm^{-1}.

The dehydrochlorination is more pronounced for the copolymerization of VC with VTHI (up to 90%) as compared to the copolymerization of VDC with VTHI (30%). In both cases, the degree of dehydrochlorination increases in parallel with the content of VTHI in the mixture of the comonomers.

Hydrogen chloride evolving in the elimination reacts partially with the tetrahydroindole fragment of the macromolecule to form the immonium cation. The IR spectrum contains the absorption band at 1680 cm^{-1} (C=N$^+$) corresponding to this cation.[2]

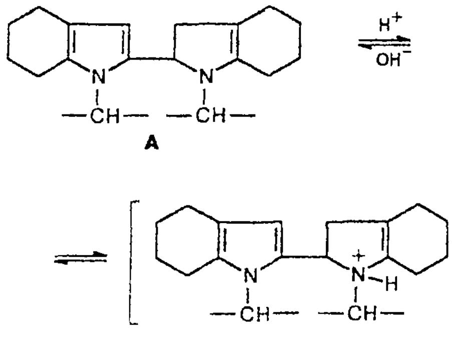


Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2267—2268, December, 1997.

1066-5285/97/4612-2149$18.00 ©1998 Plenum Publishing Corporation

The intensities of the absorption band corresponding to the stretching vibrations of the CH=CH fragment (1640 cm^{-1}) and bands of the δ(CH) (1415 cm^{-1}) and ω(CH) (830 cm^{-1}) vibrations decrease sharply.

The reaction of the immonium cation with the pyrrole fragment of VTHI results in the formation of structure A. The subsequent protonation of the nitrogen atom of the nonaromatic heterocycle affords the ammonium cation **B** with the absorption band at 2400—3600 cm^{-1} (NH$^+$) in the IR spectrum.[2]



In the copolymers of VC with VTHI, the immonium cation predominates, while the copolymers of VDC with VTHI contain predominantly the ammonium cation. The treatment of the copolymer of VDC with VTHI with a solution of potassium hydroxide results in the deprotonation of the ammonium cation (**B** → **A**). In the IR spectra of the copolymer of VDC with VTHI, the "ammonium" band ν(NH$^+$) disappears, while the long-wave band with λ_{max} 360 nm disappears in the UV spectra.

The copolymerization of the monomers was carried out in sealed tubes at 80 °C in the presence of azoisobutyronitrile in an argon atmosphere. The reaction mass was dissolved in benzene, and the copolymer was precipitated with heptane. The copolymers were reprecipitated from a benzene solution with heptane. IR spectra were recorded on a Specord IR-75 spectrometer (pellets with KBr and suspensions in Vaseline oil). UV spectra were recorded on a Specord UV-VIS spectrometer (EtOH, l = 0.5—2.0 cm).

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Received May 12, 1997;
in revised form June 26, 1997

Aluminacyclopropenes, a novel series of organoaluminum compounds

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Cycloalumination of disubstituted derivatives of acetylene with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 leads to 2,3-disubstituted aluminacyclopentenes.[1—4]

To determine the possibility of synthesis of aluminacyclopropenes, we studied the interaction of acetylene derivatives with $EtAlCl_2$ under the action of Ti and Zr complexes, which are widely used as catalysts of hydro-, carbo-, and cyclometallation[2—6] of olefins.

The formation of molecules of zirconacyclopentanes from olefins and zirconacene proceeds[7—12] through the stage of formation of zirconacyclopropenes, while titanacyclopropenes obtained from low-valence Ti complexes and acetylene derivatives are stable. These data allowed us to assume that aluminacyclopropenes can be synthesized by cycloalumination of acetylene derivatives with alkylaluminum dihalides in the presence of Cp_2TiCl_2 and activated magnesium powder as an acceptor of chloride ions according to Scheme 1.

To verify the above assumption, we studied the interaction of 1,2-diphenylacetylene (**1**) and oct-4-yne (**2**) with $EtAlCl_2$, catalyzed by Ti and Zr compounds in the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2269—2270, December, 1997.

1066-5285/97/4612-2150$18.00