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Vinyl-*gem*-dichlorocyclopanes in Radical Polymerization

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Abstract—Vinyl-*gem*-dichlorocyclopropanes in the presence of radical type initiators undergo isomerizational homo- and copolymerization with vinyl monomers to form copolymers with the random distribution of monomer units in the macrochain. As compared to vinyl monomers like methyl methacrylate, acrylonitrile, and styrene they are considerably less active. By means of ^{13}C NMR spectroscopy it was shown that vinyl-*gem*-dichlorocyclopropanes polymerized forming steroblock polymers of mainly *trans*-structure.

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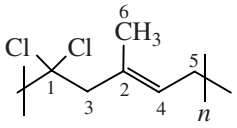
Unsaturated cyclopropanes behave in polymerization like α-olefins or conjugated dienes [1–3]. It was shown that in the presence of the radical initiators vinylcyclopropane was involved in the isomerizational polymerization with the ring opening [4]. No data on the polymerization of vinyl-*gem*-dihalocyclopropanes was reported.

At the same time it is known that cleavage of the *gem*-dichlorocyclopropane ring occurs at temperatures above 150°C [5, 6]. The halogen substitution at 100°C also proceeds with the conservation of the ring [7, 8]. Vinyl-*gem*-dihalocyclopropanes are easily formed by carbenation of available dienes [9] and therefore are interesting as monomers for preparation of high molecular compounds.

This study concerns the investigation of activity of 2-vinyl- and 2-vinyl-2-methyl-1,1-dichlorocyclopropanes **Ia, Ib** in radical polymerization.

Compounds **Ia, Ib** easily undergo batch polymerization to form homopolymers. The yield of polymer in 14 h at 75°C reaches 40–45%. The elemental composition of the isolated polymer purified by threefold reprecipitation fairly corresponds to the composition of starting monomers (for poly-**Ia** found, %: C 44.10, H 4.52, Cl 51.03; calculated, %: C 43.8, H 4.38, Cl 51.82; for poly-**Ib** found.%: C 47.98, H 5.41. Cl 46.40; calculated, %: C 47.68, H 5.30, Cl 47.02). The polymers are yellowish powders soluble in benzene, chloroform, carbon tetrachloride, and DMF, and insoluble in acetone, alcohols, ethyl acetate, etc. The number average molecular mass of the polymer prepared from the compound **Ib** in presence of azoisobutyronitrile is $M_n \approx 2500$.

The ^{13}C NMR spectrum of the homopolymer from the compound **Ib** contains only two sets of signals with the intensity ratio 4:1. Each of six signals of the same multiplicity corresponds to the number of carbon atoms of the *trans*, *cis* isomeric monomer units



VI (*trans*)

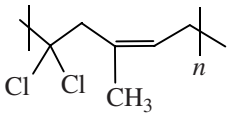
It shows that the polymer possesses high structural homogenity. A set of intense signals including two triplets at δ_C 56.6 and 46.1 ppm from two methylene groups, a singlet at δ_C 134.2 ppm and a doublet at 126.3 ppm belonging to the double bond carbon atoms, a downfield singlet at 93.1 ppm, and a quartet at 19.2 ppm, show that polymerization proceeds with the opening both of the double bond and of the three-membered ring at the C^1–C^2 bond. A set of weak signals with the shifted peaks of two CH_2 groups and the downfield

Table 1. Chemical shifts and multiplicities of signals in ^{13}C NMR spectra (δ_C, ppm, C_6D_6, TMS, +30°C)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Ia	60.7 s	33.9 d	27.6 t	133.9 d	118.9 t					
Ib	66.9 s	32.4 s	33.0 t	139.0 d	116.0 t	19.4 q				
VI	93.1 s	134.2[a] s, 134.1[b] s	56.6[a] t, 49.6[b] t	126.3[a] d, 125.6[b] d	46.1[a] t, 47.2[b] t	19.2[a] q, 26.3[b] q				
VII	91.8 s	129.5[a] d, 127.2[b] d	50.2[a] t, 45.5[b] t	129.5[a] d, 127.2[b] d	50.2[a] t, 45.5[b] t					
VIII	89.9 s	133.5 s	54.0[a] t, 52.3[b] t	126.0 d	46.4 t	19.2[a] q, 26.3[b] q	40.1 d	44.2 t	145.3 s	127.4 d
IX	94.7 s	134.5 s	56.8[a] t, 55.1[b] t	127.0 d	46.5[a] t, 45.4[b] t	19.1[a] q, 26.1[b] q	79.9 d	44.1 t	169.6 s	20.6 q
X	89.5 s	132.4 s	52.2[a] t, 50.5[b] t	126.6 d	47.7[a] t, 46.1[b] t	19.2[a] q, 26.0[b] q	28.3 d	34.7 t	120.2 s	

Note: In the structure **VIII** C_{11} is a doublet at 127.4 ppm, $C1_2$ is a doublet at 125.5 ppm: [a] *trans,* [b] *cis.*

signal of CH_3 group (δ_C 26.3 ppm, δ 2.1 ppm) correspond to the *cis*-stereoisomeric units of the polymer.

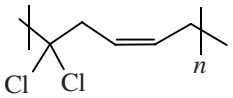


VI (*cis*)

According to ^1H NMR data content of the *trans*- and *cis*-units is 76 and 24 mol% respectively.

The monomer **Ia** polymerizes also with the formation of the *trans*/*cis* stereoisomeric homopolymer. According to ^{13}C NMR data it contains two sets of three signals of carbon atoms belonging to *trans* (129.5, 91.8, and 50.2 ppm) and *cis* (127.2, 91.8, and 45.5 ppm) stereoisomeric units. The ^1H NMR spectrum contains only two groups of signals at 3.0 and 4.0–4.3 ppm from two methylene groups and the protons of the polymer double bond.

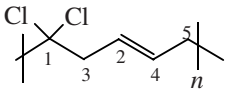
Content of the *trans*/*cis* units is 88 and 12 mol % respectively.



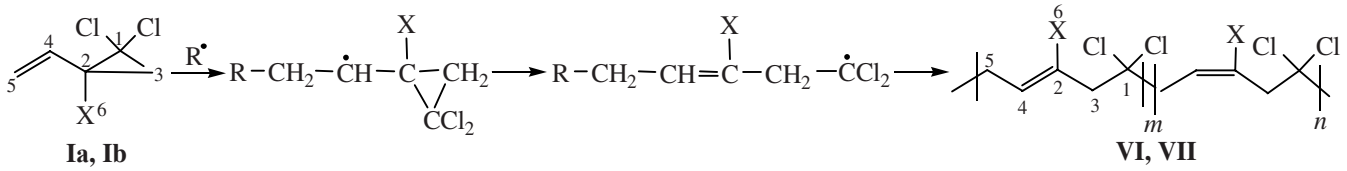
VII (*cis*)

NMR data show that in this case polymerization also proceeds with the cleavage of cyclopropane ring exclusively at the C^1–C^2 bond. It is caused evidently by higher relative stability of the radical center on the C^1 carbon atom bound with two chlorine atoms.

Hence, both monomers form polymers of the *trans*/*cis* stereoblock structure (Table 1). The chain propagation in both polymers occurs as the head-to-tail addition. These results show that the macroradicals formed undergo the skeleton rearrangement with the opening of the cyclopropane ring.



VII (*trans*)



Ia, Ib **VI, VII**

I, X = H (**a**), CH_3 (**b**); **VI**, X = CH_3; **VII**, X = H.

Table 2. Batch homo- and copolymerization of 2-vinyl-2-methyl-1,1-dichlorocyclopropane **Ib** ([**Ib**]:[M] 1:1)

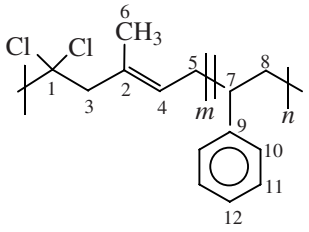
Comonomer (M)	Azoisobutyronitrile, mass %	*T*, °C	Polymerization time, h	Yield, %	Composition of copolymer, %	
					Ib	M
–	3	75	14	41	100	0
II	1	70	2	23	≤3	≥97
III	1	75	25	23	12	88
IV	3	75	27	6	47	52
IV[a]	3	75	27	20	22	77
V	1	80	25	1	26	73
V[b]	1	80	25	21	15	85

[a] **Ib**:M 0.25:0.75, molar fractions. [b] **Ib**:M 0.37:0.63, molar fractions.

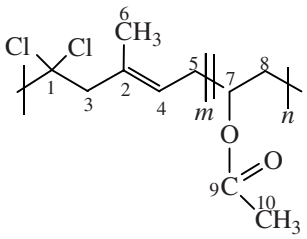
Activity of compound **Ib** in copolymerization (Table 2) depends on the structure of comonomers **II–V**. Copolymerization of cyclopropane **Ib** with ester **II** at the equimolar content of reagents in the starting mixture proceeds at a relatively high rate (10%/h), but the content of the **Ib** units in the polymer does not exceed 3 mol %, and their configuration could not be established reliably by the ^{1}H NMR spectroscopy.

The rates of copolymerization of cyclopropane **Ib** with monomers **III–V** at equimolar ratio in the starting mixture are lower as compared to that with the compound **II**, but introduction of the compound **Ib** units in the polymer chains of macromolecules **IX–XI** is significantly higher (Table 2).

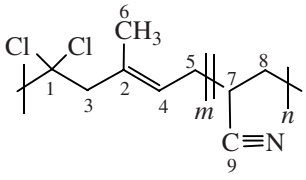
The reaction rates increase significantly with the decrease in the concentration of the monomer **Ib** in the initial mixture.



VIII



IX



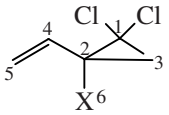
X

Hence, vinyl-*gem*-dichlorocyclopropanes **Ia, Ib** enter the radical isomerizational homo- and copolymerization with the formation of stereoblock polymers mainly of the *trans*-structure. They are less active compared to the common vinyl monomers.

EXPERIMENTAL

^{13}C and ^{1}H NMR spectra were registered on a Bruker AM-300 spectrometer at operating frequencies 75.5 and 300 MHz respectively. ^{13}C NMR spectra were registered with the wide-band proton decoupling and JMOD in benzene-d_0, internal reference TMS.

2-Vinyl-1,1-dichlorocyclopropane **Ia** and 2-vinyl-2-methyl-1,1-dichlorocyclopropane **Ib** were synthesized by carbenylation of butadiene and isoprene respectively according to the procedure [10].



Ia, Ib

X = H (**Ia**), CH_3 (**Ib**).

Methyl methacrylate **II**, styrene **III**, and vinyl acetate **IV** of the chemically pure grade were purified from stabilizer by the three-fold washing with the 7% water solution of sodium hydroxide, washing with distilled water until the neutral pH, drying over the

calcined calcium chloride and two-fold distillation. Acrylonitrile **V** was dried over the calcined calcium chloride and thrice distilled. Characteristics of all the monomers, initiators, and solvents after purification according to the routine procedures were in agreement with the published data.

Batch homo- and copolymerization of vinyl-*gem*-dichlorocyclopropanes **Ia, Ib** was carried out in a vacuum under the action of the free-radical initiators (azoisobutyronitrile, benzoyl peroxide). At the achievement of the desired conversion the reaction was stopped by cooling and subsequent precipitation of polymer. Purification of polymers was carried out by the three-fold reprecipitation from the benzene solution into methanol and drying in a vacuum at 50°C till the constant mass. The composition of copolymers was evaluated on the basis of the elemental analysis data.

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