Synthesis and Cationic Polymerization of Some Substituted of Vinylcyclopropyl Ethers

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Abstract

By cationic polymerization of substituted vinylcyclopropyl ethers a series of polyvinylcyclopropyl ethers has been prepared. By data of spectral analysis the structure of the prepared polymers has been established and it has been shown that the polymerization proceeds only with opening of double bond and conservation of cyclopropane ring. The influence of substituent of three-membered cycle on reactivity of the synthesized monomers has been estimated.

Keywords- synthesis; cyclopropane-containing vinyl ethers; reactivity of monomers; cationic polymerization; model reactions

1 Introduction

It was known that the vinyl ethers (VE) are well polymerized at low temperatures and in the presence of cationic catalysts [1]. Depending on degree of polymerization, length an degree of branching of alkyl substituent R and also on nature of catalyst, the polymers prepared from VE of total formula CH_2=CH–O–R, are basically oligomer, and in a number of cases – high molecular (liquid, rubber-like or hard) products. In particular, it was known that the polymers prepared from vinylalkyl ethers in the presence of complex catalysts are the high-molecular crystalline products [2]. However, up to day an industrial method of polymerization of vinyl ethers on cationic mechanism is absent, i.e. this method has a number of essential lacks connected with difficulties of management and control over reaction course and behavior of side processes.

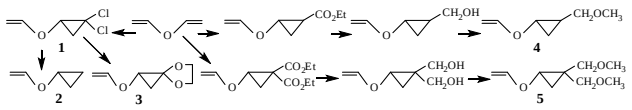
The cationic polymerization of VE can be carried out both in block and in solution of various polar and non-polar, aliphatic, aromatic, alycyclic hydrocarbons and their haloid substituted derivatives. Though, the carrying out of polymerization in solution is more effective from the point of view preparation of stereoregular polymers and polymers with high MM. Polyvinylaryl ethers are solid and transparent polymers and on hardness are sharply differed from polyvinylalkyl ethers [3]. Polyvinyl ethers with MM=10^5÷10^6 are thermostable to 200-250ºC. Under action of light and temperature higher 250ºC they destruct to low-molecular products.

The radical polymerization of VE proceeds considerably difficult than cationic one. The polymer products forming in this case have low MM of order ~10^3 [4]. However, VE are easily copolymerized with vinyl acetate, maleic anhydride, vinyl chloride, acrylonitrile and other comonomers in the presence of radical initiators [5].

2 Results and Discussion

We think that the preparation with side cyclic (in particular – cyclopropane) groups has a definite interest due to possibility of their application as the photosensitive and bioactive materials. This is easily can be realized only in a case of cationic polymerization of vinylcyclopropyl ether (VCPE) and its derivatives [6]. In particular, the polymers containing macromolecules of gem-dichlorocyclopropyl groups in the side chain, prepared on the basis of vinylbutyl or vinyl-gem-dichlorocyclopropyl ether in the presence of trifluoride boron etherate in hexane solution, possess bactericide properties [7]. In addition, it has been also detected the antiblastic action previously unknown for representatives of this class of compounds, which shows a perspectivity of further searches in series of new substances.

With this aim we have synthesized the mono- and gem-substituted vinylcyclopropyl ethers on the scheme stated below :



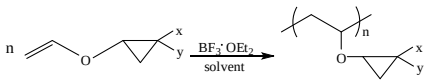
Then the synthesized monomers 1-5 have been involved in the polymerization process in the presence of catalyst

$BF_3{\cdot}O(C_2H_5)_2$. The polymerization of monomers 1-5 was carried out in atmosphere of dry nitrogen. The conversion of monomers was controlled by a method of chromatographic analysis and the yields of polymers were determined by a weight method. As the internal standard it was used a chlorobenzene. The monomers were polymerized under action of $BF_3{\cdot}OEt_2$ in ether at -15ºC, in methylene chloride at -40ºC and in toluene at -75ºC. In all cases the polymerization proceeded without induction period and accompanied almost by quantitative conversion of monomers to polymers. Though, the total polymerization rate under action of trifluoride boron etherate grew with increase of electron-donor ability of substituent being at cyclopropane ring:

$$(CO_2Et)_2 < CO_2Et < Cl_2 < H < CH_2OCH_3 < (CH_2OCH_3)_2$$

MWD of the prepared polymers was determined by means of exclusion chromatography in chloroform. The results showed that the polymers prepared under action of $BF_2{\cdot}OEt_2$, had the high MM and characterized by wide MWD ($\overline{M}_n/\overline{M}_w = 2{,}5-4{,}0$).

It has been revealed by comparison of IR-spectra of the initial monomers and polymers prepared on their basis that in the polymerization process the absorption bands at 1640 cm^{-1} (valence vibrations of C=C-bond) disappear, but the absorption band at 1040 cm^{-1} (skeleton vibrations of trinominal ring) remains without change. In the PMR-spectra of the polymers prepared from monomers 1-5 the signals of protons of double bond at δ= 4.05–6.80 ppm are absent, at the same time the signals at δ=1,6 ppm and 2,5 ppm stipulated by availability of protons of methylene and methane groups in the polymer chain are appeared. These data confirm that the polymerization of monomers 1-5 proceeds due to opening of double bond of vinyl group. In this case the cyclopropane group with substituents remains unaffected. The polymerization reaction proceeds on scheme:



where: x=y=Cl (1); x=y=H (2); x,y=$\begin{matrix}-O\\-O\end{matrix}$ (3); x=H, y=CH_2OCH_3 (4); x=y=CH_2OCH_3 (5)

solvent - ether, CH_2Cl_2, toluene

It should be noted that in the polymerization process the initial monomers 1-5 are converted into polymers, basically with opening of double bond of vinyl group. Although in the polymerization process a small quantity of cyclopropane groups takes part, too. This is confirmed by formation of small quantity of the insoluble products in the polymerization process, which is possible in a case of opening along with double C=C-bond and three-membered cycle.

It has been established that with temperature rise from -75ºC to -15ºC a yield of polymers is slightly increased.

The study of cationic polymerization of monomers of VCPE and its derivatives containing substituents of type of chlorine atom, methoxymethyl and ethoxycarbonyl group in cyclopropane ring showed that a nature of substituent essentially influences on polymerization rate and yield of purposeful products.

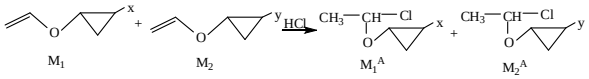
The results of polymerization of monomers 1–5 under action of $BF_3{\cdot}OEt_2$ showed that on reaction course the solution gets dark color, which disappears at planting to precipitant (for ex., to methanol).

It was known that for polymer processing and also for determination of exploitation characteristics its solubility has a great value. The prepared polymers are well dissolved in the polar solvents, such as DMF, THF, chlorinated and aromatic hydrocarbons.

TABLE I. CONDITIONS AND RESULTS OF CATIONIC POLYMERIZATION OF MONOMERS 1-5

Monomer code	T-re, ºC	Time, h	Initiator, mol.%	Solvent	Yield of polymers, %		
					soluble	*insoluble*	*[η], dl/g*
1	-75	2	3	toluene	75.6	5.4	0.12
2	-70	2	5	toluene	76.8	6.8	0.14
3	-40	3	4	CH_2Cl_2	80.2	6.2	0.11
4	-15	4	3	ether	86.9	2.6	0.16
5	-70	2	4	toluene	85.2	5.8	0.14

In accordance with data of PMR-spectra an electron density on vinyl double bond, mainly, depends on nature of substituent of three-membered cycle. For this reason an influence of substituent of cyclopropane ring on polymerization reaction rate is essential. For elucidation of such influence we have carried out the model addition reaction, in which – two different monomers, for ex., 1 and 3 were reacted with one total electrophilic reagent – hydrogen iodide, i.e. in the conditions of competitive reactions. The control for reaction course was carried out by GLC-analysis (loss of monomer) [8].



It has been shown that an addition of HJ (0,08 mol/l) in toluene at -20ºC to equmolar mixture of monomers M_1 and M_2 (on 0.2 mol/l of each) is accompanied by formation of the corresponding adducts M_1^A and M_2^A. As far as the prepared adducts – haloidalkylcyclopropane ethers – due to instability could not be isolated, they were converted *in situ* to more stable – methoxy-derivatives by action on them at low temperatures cooled by CH_3OH and were analyzed by GLC method.

The loss of monomers M_1 and M_2 for 1 min. (~20 and 18% correspondingly) indicated to difference of these monomers in reactivity in relation to electrophilic reagent – HJ. The total quantity of the expended monomers M_1 and M_2 in this case was 0,084 mol/l, which is close to the initial quantity of HJ (0,080 mol/l). This result indicates to quantitative addition of HJ to monomers M_1 and M_2 without formation of polymers.

3 Experimental

3.1 Synthesis of gem-dichlorcyclopropyl vinyl ether (1).

Gem-dichlorcyclopropyl vinyl ether has been synthesized on method described in [9]. Yield – 40 %. B.p. – 32°C/10 mm.merc.c.; $d_4^{20}=1.2179$; $n_D^{20}=1.4625$, ^{1}H-NMR ($CDCl_3$,δ,ppm): 4.21-4.46 (C=CH_2); 6.43 (C=CH); 2.0(O-CH); 1.40 (2H-cycle).

3.2 Reduction of gem-dichlorcyclopropyl vinyl ether (2).

Methodology of reduction of chlorine atoms in the compound (1) has been described in [10]. Yield – 55 %. B.p. – 68°C; $d_4^{20}=0.8452$, $n_D^{20}=1.4079$, ^{1}H-NMR($CDCl_3$,δ,ppm): 4.15-4.63 (C=CH_2); 6.45 (C=CH); 0.43-0.68 (3H-cycle); 2.22 (O-CH).

3.3 Synthesis of 1-vinyloxy-4,7-dioxaspiro-[2,4]-heptane (3)

The synthesis has been carried out similarly methodology described in work [11]. To solution NaH (0.18 g-mol) in DMF (75 ml) at temperature 0°C dropwise was firstly added solution of ethylene glycol (0.075 g-mol) in DMF (20 ml), and then – solution of 1,1-dichlorcyclopropyl vinyl ether (75 ml) in DMF (10 ml). After stirring for 10 h at room temperature 400 ml water was added to reaction mixture. The mixture was extracted by ether (200 ml). The organic layer was twice washed (on 400 ml) by solution $NaHCO_3$, dried over anhydrous solution Na_2SO_4. The ether was distilled off. The residue was distilled in vacuum. It was prepared a colorless oily liquid with yield 47 %. B.p. –25-26°C/4 mm merc.c. $d_4^{20}=0.9512$; $n_D^{20}=1.4288$. ^{1}H-NMR($CDCl_3$,δ,ppm): 4.85-4.95 (C=CH_2); 5.81 (C=CH); 3.37-4.12 (OCH_2CH_2O); 1.68-1.97 (O-CH); 1.03-1.37 (2H-cycle).

3.4 Synthesis of ethyl ether of 2-vinyloxy cyclopropane-1-carboxylic acid has been carried out on methodology described in work [12]. Yield – 61 %. B.p. – 44-46°C/10 mm merc.c. $d_4^{20}=1.0217$; $n_D^{20}=1.4314$, 1H-NMR($CDCl_3$,δ,ppm): 4.35-4.62 (CH_2=C); 6.45 (C=CH); 4.21 (O-CH_2); 1.29 (CH_3); 0.81-1.06 (2H-cycle); 2.22 (O-CH); 1.68 (1H-cycle).

3.5 Synthesis of diethyl ether-2-vnyloxycyclopropane-1,1-dicarboxylic acid

To three-necked flask equipped with mixer, dropping funnel, reflux condenser and thermometer 80 g (2 g-mol) solution of NaOH in 80 ml water was placed and added 4.8 g (5 mol.%) TEBA. Then the solution 0.5 g-mol of 1,2-dibromethyl vinyl ether and 0.45 g-mol of diethyl ether of malonic acid in 220 ml benzene dropwise was added. The addition was completed for 1 h. Then the reaction mass was mixed more 1.5 h and left overnight. The next day the reaction mass was mixed at 50°C for 3 h. After cooling the organic layer was separated, aqueous one – was extracted by benzene. The combined organic layer was washed with water and dried over Na_2SO_4. After removal of solvent the residue was distilled in vacuum. Yield – 92%. %. B.p. 69-71°C/5 mm.merc.c. $d_4^{20}=1.1129$; $n_D^{20}=1.4359$, ^{1}H-NMR($CDCl_3$,δ,ppm): 4.28-4.35 (CH_2=C); 6.45 (C=CH); 4.12 (O-CH_2); 1.33 (CH_3); 1.4 (2H-cycle); 3.30 (O-CH).

3.6 Synthesis of mono- and dihydroxymethyl substituted cyclopropyl vinyl ethers

The synthesis of mono- and dihydroxymethyl substituted cyclopropyl vinyl ethers has been carried out by reduction of the corresponding ethoxycarbonyl substituted vinyloxycyclopropanes on the following methodology. 8.4 g (0.22 g-mol) $LiAlH_4$ in 200 ml of absolute sulphuric acid was placed to three-necked flask by capacity 500 ml, equipped with mechanical mixer, dropping funnel and reflux condenser and during mixing in nitrogen atmosphere from dropping funnel was added 0.2 g-mol of corresponding ethoxycarbonyl substituted vinyloxycyclopropane in 100 ml of dry sulphuric ether for 2.0-2.5 h. In this, the temperature of reaction mixture was maintained for 25-30°C by giving of reducing ether. After addition of all initial ether the

mixing was continued for 30 min. Then to the flask it was added dropwise distilled water and then 5% hydrochloric acid solution. The ether layer was separated, aqueous layer was extracted (twice on 20 ml) by ether. The ether extracts were combined with the ether layer and was dried over calcined Na_2SO_4. After distillation of sulphuric acid the reaction product was distilled in vacuum. Yield – 92 %. B.p. –. 20-23°C/3 mm.merc.c. $d_4^{20} = 0.9939$; $n_D^{20} = 1.4522$, ^{1}H-NMR($CDCl_3$,δ,ppm): 4.06-4.21 (C=CH_2); 6.45 (C=CH); 3.49 (O-CH_2); 3.65 (-OH); 2.26 (O-CH); 0.05-0.30 (3H-cycle).

3.7 Synthesis of mono- and dihmethoxymethyl substituted cyclopropyl vinyl ethers (4,5).

0.52 g-mol corresponding hydroxymethyl substituted cyclopropyl vinyl ether and 60 ml absolute sulphurous ether was placed to round-bottom three-necked flask by capacity 250 ml, equipped with mechanical mixer, reflux condenser chlorocalcium tube and dropping funnel. Then with small pieces 0.52 g metallic sodium atom was added. After that, as all sodium had dissolved, via dropping funnel 0.62 g-mol methyl iodide was added and the mixture was boiled in a water bath at temperature 35-40°C for 2 h. Then the reaction mixture was cooled to room temperature, was added 60-70 ml distilled water. The ether layer was separated; aqueous layer was extracted (twice on 10 ml). The ether extracts were combined with the ether layer and was dried over melted $CaCl_2$. The sulpuric ether was drove in a water bath, and the residual was distilled in vacuum. For monosubstituted compounds: yield – 88 %. B.p. 23-25°C/6 mm.merc.c. $d_4^{20} = 0.9416$; $n_D^{20} = 1.4270$. For disubstituted compounds: yield – 84 %. B.p. 31-34°C/6 mm.merc.c. $d_4^{20} = 0.9490$; $n_D^{20} = 1.4280$, ^{1}H-NMR($CDCl_3$,δ,ppm):4.06-4.20 (C=CH_2); 6.46 (C=CH); 2.25 (O-CH); 3.30 (CH_3); 3.33 (O-CH_2); 0.05-0.30 (2H-cycle); 0.54 (1H-cycle).

3.8 Polymerization of vinylcyclopropyl ethers

The cationic polymerizationof VCPE was carried out as follows: solution $BF_3{\cdot}O(C_2H_5)_2$ (0.341g) in 0.8 ml corresponding solventdropwise at mixing was added to 0.025 mol vinylcyclopropyl ether at the same solvent (8 ml) at various minus temperatures. The mixing was continued for 3 h. The polymerization was interrupted by including a small amount of TEA. Then the solution was poured into methanol, the precipitate was separated, twice reprecipitated from THF into methanol and dried in vacuum at 50°C. The soluble and insoluble products were divided by filtration of solution into THF.

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