



16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”  
dedicated to Professor L.P. Kulyov, CCE 2015

## Research of the formation of regularities siloxane norbornene derivatives by thermal Diels-Alder reaction

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### Abstract

The methods of chromatography-mass spectrometry and <sup>1</sup>H NMR-spectroscopy were used to study the reaction between dicyclopentadiene and vinyltriethoxysilane. The main reaction products are exo- and endo-isomers bicycle [2.2.1] hept-5-en-2-yl(triethoxy)silane. The overall yield of isomers is 55 % of the load components. Co-products are the alkoxysilyl derivatives of dicyclopentadiene. Also the authors of the article paid attention to the problems of the time and temperature reaction, and ratios of starting components on chemical yield.

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Peer-review under responsibility of Tomsk Polytechnic University

*Keywords:* cyclopentadiene, dimerization, dicyclopentadiene, Diels-Alder reaction, vinyltriethoxysilane, silanes, norbornenes;

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### 1. Introduction

Along with the creation of new polymers, is one of the modern trends in the development of structural materials is the processing of thermoplastic polymers, together with additives, allowing further thermosetting material getting by physical or chemical action. This effect is achieved by linking chain of macromolecules by various reagents. To obtain linking chain polyolefines different methods are used, one of which is a silanol linking chain method. The main used agents are di- and tri-functional organosilicone compounds – chlorosilanes and siloxanes. The introduction of the siloxane groups' polymer into the structure of the hydrocarbon chain enables it to form three-dimensional structures with improved physicochemical characteristics: a low water absorption, resistance to high

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temperature and ultraviolet light, corrosion and chemical resistance. Changes in the structure of the silanol agent of linking chain leads to the empowerment of targeted modifications and variations of the molecular and supramolecular polymer structures and compositions. Silanol linking chain method has several advantages over the use of organic peroxides and radiation exposure: high productivity, low capital investment and operational costs, flexibility of the production process, the making of complex configuration of different thicknesses products, the possibility of the use of fillers and modifiers<sup>1,2</sup>. As well as, due to the possibility of hydrolysis of linkages Si–O–C, these polymers are easily linking chain and used as intermediates for the preparation of graft copolymers<sup>3</sup>.

The work is dedicated to the development of the synthesis of the new unsaturated silyl agents on the basis of vinyltriethoxysilane (VTES) and dicyclopentadiene (DCPD). DCPD and structurally similar compounds such as norbornenes and norbornadienes are modern facilities for the production of polymers with unique properties, due to the presence of strained cyclic fragments with unsaturated bonds in the structure of these monomers<sup>4</sup>. Preparation of linking chain agents based on cyclohexane, dicyclopentadiene and silicone compounds may lead to the creation of polymeric composite materials having a number of useful features. Creation of polyfunctional monomers with subsequent polymerization and/or polycondensation is of considerable interest, which is associated with the possibility of polymerization process both in metathesis and for the additive mechanisms. This eventually leads to the polymers with fundamentally different characteristics.

The Diels-Alder reaction nowadays is one of the traditional and currently the most promising methods for the preparation of substituted norbornenes<sup>5</sup>, which flows between the dienophile and a diene. The yield, composition and ratio of products of the reaction depend on the process temperature, structure and reactivity of the diene and dienophile; also sometimes they are determined by pressure and properties of the medium (solvent), catalyst.

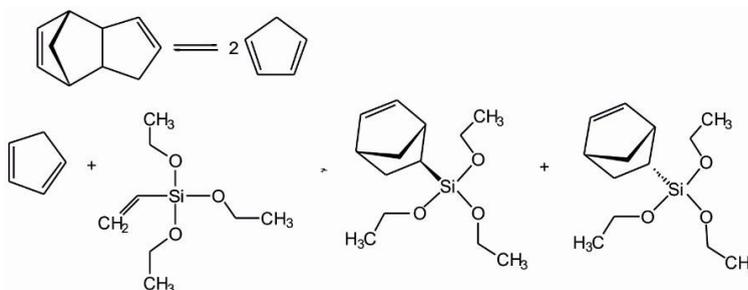
The presence in the structure of monomers of some reactive alkoxy groups makes them indispensable in the preparation of thermoplastic polymers converted into the thermosets by reacting with hydroxyl compounds. This approach is a determining in the preparation of castable, extruded and molded structural materials<sup>6</sup>.

## 2. Experimental

The synthesis of silyl derivatives of norbornene was carried out in glass ampoules at temperatures from 160 to 210 °C and in different reaction time. The ratio of the initial dicyclopentadiene and the vinyl-triethoxysilane is 0.25 : 2, 0.5 : 2, 0.75 : 2, 1.0 : 2, 1.1 : 2 (mole). Analysis of the reaction products was performed using Fourier <sup>1</sup>H NMR-spectroscopy (spectrometer «AVANCE AV 3000») and mass spectrometry (Agilent 7820 spectrometer+7890A, a capillary column HP-INNOWAX (polyethyleneglycol)).

## 3. Results and Discussion

The process looks like a sequence of the steps of dicyclopentadiene monomerization with cyclopentadiene formation and its further cycloaddition with vinyltriethoxysilane due to the Diels-Alder reaction. The desired products of this reaction are unsaturated carbocyclic trialkoxysilane derivatives produced according to the following scheme:



The main product of the reaction is a mixture of exo- and endo-isomers bicyclo [2.2.1] hept-5-en-2-yl (triethoxy) silane. Fig. 1 shows <sup>1</sup>H NMR-spectra of the reaction products.

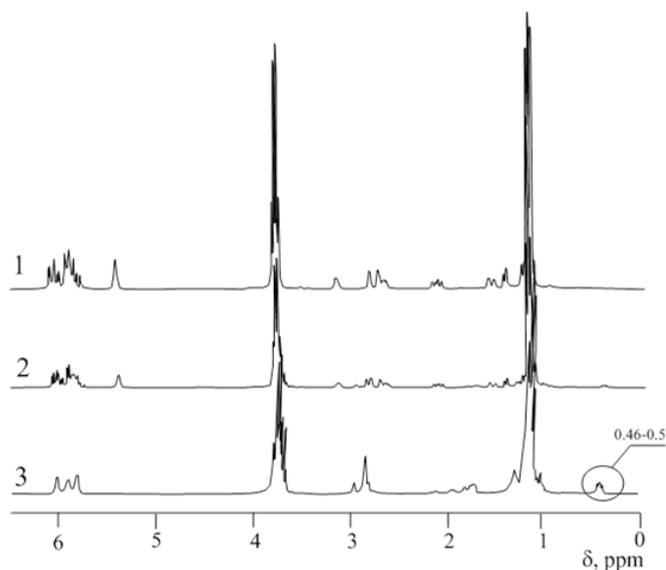


Fig. 1.  $^1\text{H}$  NMR-spectra of the reaction mixtures obtained by reacting DCPD and VTES ratio of 1 : 2 mol, the temperature of 210 °C and reaction time: 1) – 1 h; 2) – 8 h; 3) – 30 h

The signals of protons of double C=C bonds of the monomers in the form of three multiplets are observed in 5.7–6.1 ppm. The multiplet in the area of 6.0–6.1 ppm refers to proton of norbornene double bonds of adduct due to the Diels-Alder reaction. Signals in the 3.2–3.8 and 1.0–1.2 ppm area refer to the methylene and methyl protons of ethoxyl groups of vinyltriethoxysilane and reaction products. The integrated intensity of signal groups in 0.46–0.50 ppm corresponding –Si–C–H– protons of the norbornene hydrocarbon skeleton, with increasing time reaction is rising.

The component composition of the reaction mixtures was determined by means of chromatography-mass spectrometry. The association of the initial content of dicyclopentadiene, vinyltriethoxysilane (ratio 1 : 2 mol., 210 °C) and the amount of end-products of the reaction time were studied. The results are presented in Fig. 2.

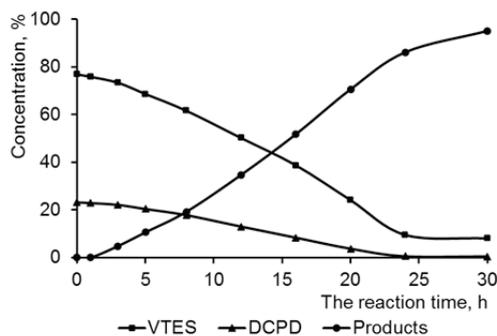


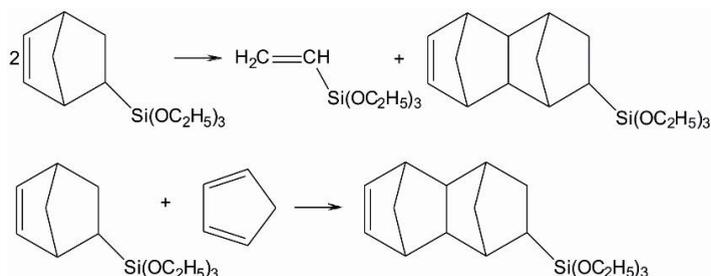
Fig. 2 – The association of concentration of DCPD, VTES and the amount of products from the reaction time at 210 °C and the component ratio 1 : 2 mole.

It is obvious that the concentration of the formed products during the reaction is reduced antipately to the concentrations of initial reagents. The more rapid exhaustion of DCPD indicates the side reactions of

cyclopentadiene interaction with the target products of reaction with the formation of polycyclic compounds. The total concentration of (2R)-bicyclo[2.2.1]hept-5-en-2-yl(triethoxy)silane (exo-product) and (2S)-bicyclo[2.2.1]hept-5-ene-2-yl(triethoxy)silane (endo-product) with a reaction time of 24 hours, up to 75 %, with a further increase of the reaction time the concentration of these products vary slightly.

Simultaneously with the main products the reaction leads to the formation of products which have the higher condensation degree, i.e. the tricyclic derivatives of triethoxysilane – tri(ethoxy[(2S)-1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethylnaphthalene-2-yl]-)silane and tri(ethoxy[(2R)-1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethylnaphthalene-2-yl]-)silane. The appearance of small amounts of the third isomer was also noted. But we did not pay our attention to that isomer due to its low concentration.

Probably, they are formed as the result of retrodiene bicyclo[2.2.1]hept-5-en-2-yl (triethoxy)silane reaction and the adjoining of cyclopentadiene to one of the isomers of «baseline» bicyclo[2.2.1]hept-5-en-2-yl(triethoxy)silane. Otherwise, this reaction can be represented as a disproportionation reaction:



The proposed mechanism is confirmed by the repeated presence of previously exhausted vinyltriethoxysilane ( $^1\text{H}$  NMR and GCMS) in the products reaction. The charts of kinetic dependences are shown in Fig. 3.

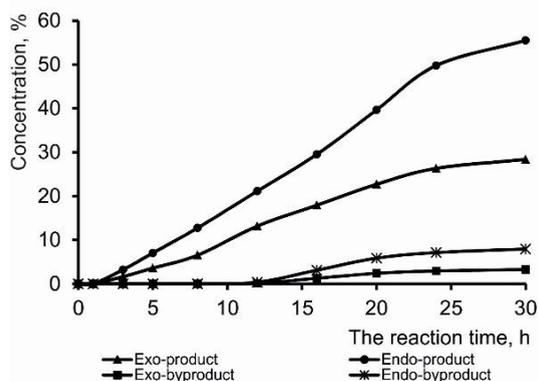


Fig. 3. The association of the concentration the main and byproducts of reaction time.

The ratio of the end- and exo-isomers in the process is in the range of 1.6–2.0 : 1, but the natural growth of endo ratio : exo from 1.61 to 1.96 ranging from 10 hours reaction time should be noted, which coincides with a noticeable appearance of products of a higher degree condensation. This fact can be explained by the predominant reaction of the exo-isomer disproportionation which is more favorable thermodynamically compared with the reaction of the endo-isomer. Separation of the isomers by selective extraction and distillation under reduced pressure, did not lead to satisfactory results. Further intend to divide the of isomers using stereoselective sorbents.

The investigation of the influence of reaction temperature on the yield of products was carried out for the proportions of starting DCPD and VTES – 0.25 : 2, 0.5 : 2, 0.75 : 2 and reaction time 9 hours. The subject reaction time is determined by the unnoticeable occurrence of secondary reactions in this interval (Fig. 4).

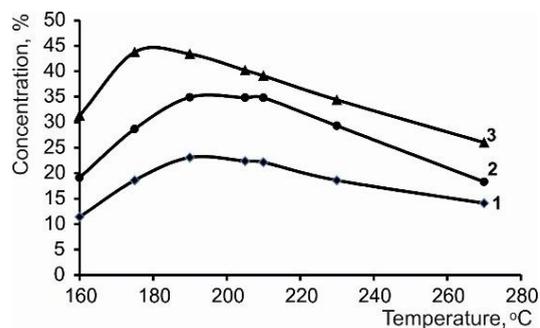


Fig. 4. The association of the concentration of the sum of products on the temperature of components at a ratio DCPD : VTES – 0.25 : 2 (1), 0.5 : 2 (2), 0.75 : 2 (3), and the reaction time 9 hours.

All the graphics are a kind of extreme association with a maximum 175–210 °C, this is probably due to the thermal stability of the target products in this temperature range and the increasing of the disproportionation processes at the higher temperature of synthesis. The influence of the ratio DCPD: VTES ranging from 0.25 : 1 to 1.1 : 1 on the product yield at 175 °C and the reaction time 6, 9 hours was examined afterwards (Fig. 5).

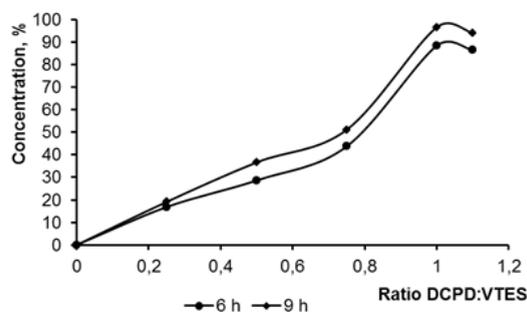


Fig. 5. The association of the sum of the products on the DCPD ratio: VTES at a reaction temperature of 175 °C and a duration of 6, 9 hours

It is obviously that the associations are symbated each other and have the linear character in a ratio of from 0 to 0.75: 1. The increasing of the ratio DCPD: VTES in this range can be recommended to increase chemical yield.

#### 4. Conclusion

Thus, the process of interaction dicyclopentadiene with vinyltriethoxysilane at various process temperatures, the ratio of the initial reactants and reaction time is studied. It is shown that the optimal temperature range is 175–210 °C. Also it has been established that the main resultants are exo- and endo-isomers bicyclo[2.2.1]hept-5-en-2-yl(triethoxy)silane, which total yield of the 24 hours reaction time and 210 °C is 75 %. The authors found that significant increase and temperature duration of the process lead to the obvious degree of tricyclic derivatives triethoxysilyl resulting disproportionation reaction (retro Diels-Alder reaction), preferably by endo-isomer bicyclo[2.2.1]hept-5-en-2-yl(triethoxy)silane.

The new conditions of the processes of synthesis of unsaturated strained carbocyclic siloxane compounds allow obtaining new classes of homo- and copolymers with unique properties in the nearest future.

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