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Esters of Norbornene Series: Synthesis and Application Areas

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Abstract

The results of the studies into the synthesis of ether derivatives of norbornene series, their properties and application areas are analysed. The main directions of the use of ether derivatives of norbornene, as well as the ways and prospects of their further application, are shown. A broad application of norbornene ethers as additives to synthetic oil and fuel compositions, plasticisers, modifying agents and hardeners, as components in the perfumery industry, antimicrobial and antifungal preparations, catalysts and cocatalysts are highlighted. It is demonstrated that adding these esters to diesel fuel leads to a significant improvement in its thermal oxidation stability, a decrease in its pour point and an increase in the flash point. The ethers of norbornene series are considered as new functionally substituted monomers for the synthesis of modified norbornene-containing polymers and co-polymers. It has been established that fluorine-substituted norbornene-containing ethers are applied as a matrix material for photoresists used in microlithography.

Keywords: ethers of the norbornene series, lubricating oils, antimicrobial preparations

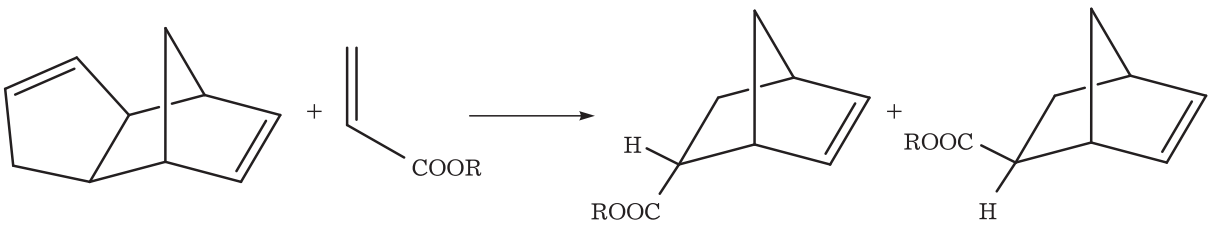
INTRODUCTION

Various functionalised derivatives of norbornene series, in particular ester derivatives, are the object of thorough investigation in the world research centres and have attracted extensive research and practical attention for many years. Results of the studies in the area of synthesis and investigation of the properties of norbornene-containing esters, performed mainly in the XXI century, are described in the present work. The major directions of their application and the outlooks for use in various branches of industry are demonstrated.

ESTERS OF NORBORENE SERIES AS MONOMERS FOR THE SYNTHESIS OF POLYMERS AND COPOLYMERS

One of the main areas of the application of norbornene esters is their use as monomers for the synthesis of polymers and copolymers with various functionalities. For instance, results of the studies aimed at the synthesis of new bicyclic acrylic monomers in two stages are reported in [1]. At the first stage, the reactions of [4+2]-cycloaddition of cyclopentadiene with alkyl acrylates containing alkyl fragments of different lengths (C_1–C_5) using dicyclopentadiene as the initial component were studied. To obtain alkoxycarbonylnorbornenes, a mixture of initial reagents was heated at a temperature of 185 °C for 3 h in the presence of small amounts of the catalyst – nanosized titanium dioxide and hydroquinone. The reaction proceeds according to Scheme 1.

It was established in the experiments that the yield of resulting 5-alkoxycarbonylnorborn-2-enes decreases from 94 to 65.4 mass % (calculated for dicyclopentadiene) with an increase in the length of the indicated alkyl fragment from CH_3 to C_5H_{11}. Thermal isomerisation of the resulting mixture of *endo*- and *exo*-compounds into the *exo*-isomer was carried out; the maximal transformation was



R = CH_3; C_2H_5; C_3H_7; C_4H_9; C_5H_{11}

Scheme 1.

achieved within 2 h at 200 °C. At the second stage, catalytic addition of acrylic acids to the synthesised 5-alkoxycarbonylnorborn-2-enes was carried out in the presence of $BF_3 \cdot O(C_2H_5)_2$ catalyst, and the synthesis of new representatives of acrylic diesters of norbornane hydroxy-acids was performed. The effect of various factors on the addition was studied: reaction temperature, the molar ratio of initial components, amount of catalyst, and reaction. The optimal reaction conditions providing the maximal yield (72.2 %) of bicyclic acrylic diesters were determined (the molar ratio of initial components – 1 : 1.5, the amount of catalyst – 0.15 mass %, reaction temperature is 80 °C, process duration 4 h). The obtained acrylic esters of norbornene series were then subjected to radical polymerisation, by the example of 5-ethoxycarbonylnorborn-2-yl acrylate in the bulk form and in the solution of methyl ethyl ketone using di-*tert*-butylperoxide as the radical initiator. The process was carried out at 140 °C for 3 h, and the maximal yield of the polymer was achieved in the presence of the catalyst in the amount of 0.1 mass %. The obtained polymer product was characterised by the molecular mass 10 000–12 000 g/mol. The coating manufactured by means of pouring the synthesised polymer has a smooth transparent surface without defects and was characterised by rather high hardness, elasticity, adhesion strength, and impact strength. On the basis of the studies and the characteristics of the obtained homopolymer, the possibility of using these polymers as coatings was assumed.

A review [2] described the literature data on the investigations in the area of homo- and copolymerisation of norbornene and its derivatives, in particular the esters of norbornene carboxylic acids. Due to their specific structure, these monomers provide the possibility to synthesise the polymers and copolymers with various functionalities, differing from each other by the structure and physicomechanical properties of the final products. It is demonstrated that the polymers synthesised on the basis of norbornene esters are characterised, depending on polymerisation conditions, by the high optical transparence, hardness, thermal and chemical stability, mechanical strength. The authors state that the availability of the raw material basis of norbornene and its derivatives, in particular esters, and unique performance characteristics of the polymers and copolymers on their basis define attention to the studies in the area of synthesis of new norbornene monomers, as well as the synthesis of polymers and polymers on their basis, having won application in various branches of industry.

Ring-opening metathesis polymerisation is reported to be able to provide a broad range of possibilities for the synthesis of polymers and copolymers. For instance, norbornene and its derivatives, in particular esters, may serve as monomers for the synthesis of high-molecular polymers with the structure variable within a broad range [3]. New polymers based on the dimethyl ester of norbornenedicaboxylic acids were obtained by the authors of the cited work through ring-opening metathesis polymerisation in the presence of a Hoveyda-Grubbs catalyst. The chemical yield of the products exceeded 95 %, and the molecular mass of thus obtained polymers was also relatively high (more than $4.5 \cdot 10^6$ g/mol). The results of investigations showed that the polymers synthesised with bifunctional and trifunctional comonomers exhibit higher thermal stability up to 370 °C. The addition of bi- and trifunctional comonomers promotes substantial improvement of mechanical and physical properties. It is demonstrated that a polymer containing a trifunctional comonomer at a level of 3 mass % is characterised by the largest values of the bending elastic modulus, elongation at break, and tensile strength.

A series of functionalised polynorbornenes containing the side ether or ester bridging chains was synthesised [4]. Norbornene complex with an ether bridge was obtained in the nucleophilic aromatic substitution of iron cyclopentadienyl. This procedure in combination with linking with dicyclohexylcarbodiimide allowed synthesising new oligomeric aryl ethers and the ester substituted complexes of norbornene. The authors state that the structural identification of *exo*- and *endo*-isomers of either metallated or demetallated norbornene derivatives was performed by means of ^{1}H and C^{13} NMR spectroscopy. The ring-opening metathesis polymerisation of these monomers involving $RuCl_3$ (the hydrate form) allows obtaining functionalised polynorbornenes. Thermal analysis of the synthesised polymer materials revealed higher thermal stability with an increase in the number of aryl ether groups.

The synthesised isomerically pure *exo*-norbornene esters are prone to copolymerisation through ring-opening metathesis polymerisation if ruthenium initiator is used [5]. A comparison of pure *exo*-monomers and commonly used mixtures of *endo*-/*exo*-isomers at a ratio of 80 : 20 was carried out. The authors stress that *exo*-isomers exhibit much higher reaction rates under milder conditions in comparison with the *endo*-/*exo*-mixture. Kinetic studies showed that the reaction rate constant is determined by the isomeric purity of initial reagents but is independent of the composition of the end functional groups of the polymer.

In [6], IR Fourier transform spectroscopy (FTIR) was applied to study metathesis-copolymerisation of dicyclopentadiene with a mixture of *exo*-/*exo*- and *endo*-/*endo*-2,3-dicarbomethoxy-5-norbornene over the catalyst of the Hoveyda-Grubbs type. The data obtained in the studies allowed calculating the rations of the reactivities of the monomers of dicyclopentadiene and the isomers of 2,3-dicarbomethoxy-5-norbornene. The authors stress that the relative reactivity of dicyclopentadiene was about eight times lower than the reactivity of the mixtures of isomers.

The reactivity and activation parameters for ring-opening metathesis polymerisation of eight norbornene esters in the presence of N-chelating Hoveyda–Grubbs type catalyst were determined using *in situ* ^{1}H NMR spectroscopy [7]. The authors state that the molecules of norbornene esters differed from each other by the structure of the substituent and the positions of ester groups. Kinetic studies showed that effective polymerisation constants and activation parameters are strongly dependent on monomer structure. Elongation of the aliphatic chain was demonstrated to have almost no effect on the reactivity of the ester but defines activation parameters of the reaction. Branching of the aliphatic substituent has a substantial effect both on the reactivity and on activation parameters. In addition, activation parameters depend on the orientation of ester substituents in the norbornene cycle.

The authors of [8] describe the synthesis of a new helical copolymer based on the ester derivatives of norbornene through binding two homopolymers with the help of molecular coupling. The helical structure is maintained by noncovalent interactions (hydrogen bond, π–π-stacking) and by the effect of hydrophobic and hydrophilic interactions. The characteristics of the copolymer were described in detail, and its superstructure was confirmed by means of dynamic light scattering, scanning and transmission electron microscopy. The observed size of aggregates was reported to be about 200 nm.

Dimethyl ester of 7-oxa-norbornene-2,3-dicarboxylic acid (*exo*-,*exo*-7-oxa-bicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic acid) was polymerised by means of ring-opening metathesis polymerisation using different ruthenium catalysts and solvents based on water [9]. The effect of the solvent on induction time, molecular mass and the yield of the polymer product was considered. It was stressed that norbornene (bicyclo[2.2.1]-hept-2-ene), which has been considered to be completely inert in aqueous solvents, formed copolymers in a high yield with this oxa monomer.

Beta-cyclodextrins (β-CD) based on norbornen-5-yl carboxylic acid and norbornen-5-ylmethylsilyl ester containing up to three units of norbornene-silyl ester were synthesised from β-CD and norbornene-5-chloride of carboxylic acid and norbornen-5-ylmethyldichlorosilane, respectively [10]. Oligomers (n = 2–4) were synthesised from them using ring-opening metathesis polymerisation. Monomer and oligomer substituted β-CD were tested as chiral selectors in non-aqueous capillary zone electrophoresis using 35 mM sodium bicarbonate in N-methylformamide as the base electrolyte. The authors stated that the selectors of the type of monomer and oligomer derivatives of norbornene ester and norbornene-silyl ester exhibited good enantio-resolution of dansyl amino acids with the chiral selector concentration up to 4 mass %. Substantial improvement of the resolution was ob-

served after the introduction of up to five units of norbornene-silyl ester into β-CD molecule, while higher degrees of substitution by norbornen-5-yl carboxylic groups lead to a decrease in enantio-separation of amino acids. In addition, it was discovered that selectors of the type of norbornene-silyl ester are more efficient that the selectors of the type of norbornene ester.

Two new monomers were described in [11]: cyclooctene and the ester derivative of norbornene with trifluoromethylphenyl ester group obtained through chemical modification of 1,5-cyclooctadiene and 5-norbornene-2-carboxylic acid, respectively. Ring-opening metathesis polymerisation of each of these monomers, as well as commercial carboxylic acid, is carried out in the presence of the Grubbs' catalyst of the second generation in CH_2Cl_2 medium. Three functionalised monomers are then copolymerised with *cis*-cyclooctene for the purpose of obtaining modified polycyclooctenes. The solubility was reported to increase due to the inclusion of the functional group. Thermal properties of the synthesised homopolymers and copolymers were studied by means of DSC and TGA. It was shown that the crystal properties of the polymer are strongly dependent on cyclooctene content.

In [12], poly(ethyleneglycol)star polymers with a narrow mass distribution and adjustable nanoscopic dimensions are synthesised as a result of ring-opening metathesis polymerisation of the macromonomer of polyester-containing norbornene. It was demonstrated that the new synthesised polymer compositions might be used as supports for drug delivery, biological visualisation, and catalysis.

The synthesis of new cyclic olefin polymers containing ester groups and possessing high glass transition point, high transparence, good mechanical characteristics and excellent film-forming capacity was described in [13]. The authors performed ring-opening metathesis copolymerisation of *exo*-1,4,4a,9,9a,10-hexahydro-9,10(1′,2′)-benzeno-l,4-methanoanthracene and norbornene-containing ester comonomers (5-norbornen-2-yl-methylacetate, 5-norbornen-2-yl-methyl-2-ethylhexanoate or 5-norbornen-2-yl-methyldodecanoate) in the presence of Grubbs' catalyst of the first generation ($Ru(CHPh)(Cl)_2(PCy_3)_2$, where Cy = cyclohexyl) and subsequent hydrogenation of double bonds in the main chain.

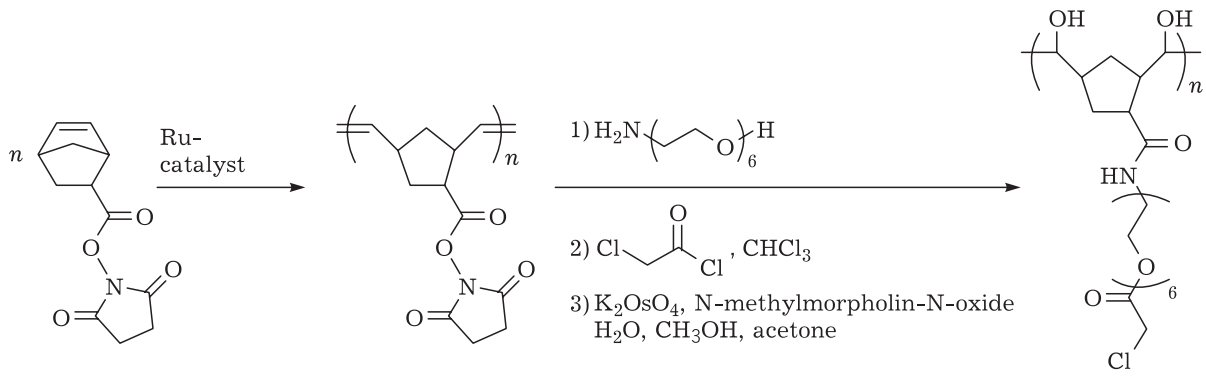
Metathesis polymerisation of the ester derivatives of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride with different types of nonpolar substituting groups using Grubbs' catalyst of the third generation was described in [14]; high-molecular polymers with substantially improved solubility in comparison with the homopolymer of initial anhydride were obtained. It was discovered that the solubility of these polymers increased with an increase in the steric hindrance in the substituting group.

Dimethyl esters of norbornenedicarboxylic acid were synthesised according to Diels-Alder's reaction without solvents by heating a mixture of dicyclopentadiene and a dienophile [15]. Cyclopentadiene, which was formed *in situ*, reacted with a dienophile in thermodynamically controlled reaction. In addition to the absence of solvents, the described procedure allows almost complete consumption of dicyclopentadiene, thus excluding the work with this toxic and dangerous compound.

As described in [16], the anhydride of 5-norbornene-2,3-dicarboxylic acid was used as the initial compound for the synthesis of norbornene derivatives. It was shown that the dimethyl ester of 5-norbornene-2,3-dicarboxylic acid and diphenyl esters of 5-norbornene-2,3-dicarboxylic acid, as well as their polymers, have a broad potential to be applied in many areas. These compounds were synthesised through ring-opening metathesis polymerisation. Polymerisation of norbornene derivatives was investigated in detail, and the results formed the basis to develop the method of controlling molecular masses and decomposition temperatures of copolymer derivatives of norbornene.

Radical copolymerisation of methyl-2-norbornene-2-carboxylate and 2-phenyl-2-norbornene with styrene, alkyl acrylate and methyl methacrylate was studied with different combinations of monomers, leading to the formation of copolymers with their main chains composed of the norbornane framework [17]. The reactivity of monomers for copolymerisation with *n*-butyl acrylate was determined using Fineman-Ross method. Analysis by means of DSC with temperature modulation demonstrated a substantial increase in the glass transition point for the synthesised polymers in comparison with the repeated styrene link, due to the inclusion of norbornane framework into the main polymer chain.

The authors of [18] investigated copolymerisation of methyl acrylate with some norbornene derivatives, in particular 5-*n*-butyl-2-norbornene, 5-methylene-2-norbornene and 5-ethoxy-2-norbornene, for the synthesis of new norbornene-containing polymers.



Scheme 2.

Gas chromatography – mass spectrometry and ^1H NMR were used to study the reaction of dicyclopentadiene vinyl triethoxysilane with vinyl triethoxysilane. The authors of [19] state that the major products of this reaction are *exo*- and *endo*-isomers of bicyclo[2.2.1]hept-5-en-2-yl(triethoxy)silane. The total yield of the isomers is 55 % of the mass of initial components. The effect of reaction duration and temperature, as well as the ratios of the initial components, on the yield of the adduct was studied.

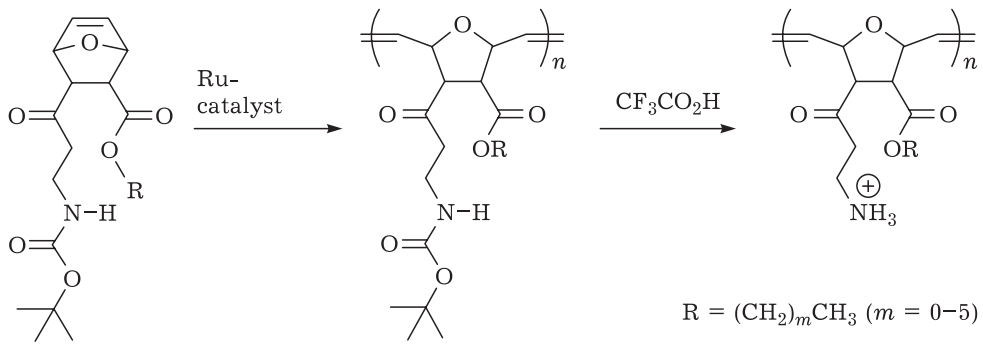
The authors of [20] describe the development of catalysts for ring-opening metathesis polymerisation of functionalised norbornenes, the synthesis of polymers with amino acids and peptides attached, the formation of aggregates and micelles, and the application of these polymers in medical materials. The authors also describe the management of the sequences of monomeric links, that is, living polymerisation for the synthesis of block-copolymers and alternating polymerisation, which is achieved as a result of acid-base interactions (Scheme 2).

Ring-opening metathesis polymerisation of the derivatives of 7-oxabicyclo(2.2.1)hept-5-ene for obtaining new alicyclic polymeric ionophores was described (Scheme 3) [21].

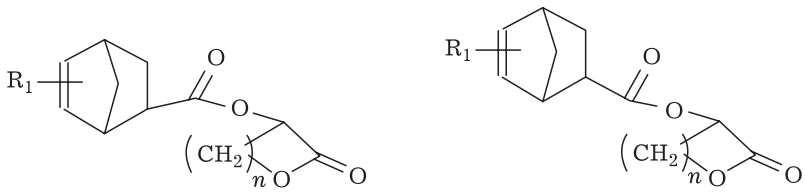
The advances in the ring-opening metathesis polymerisation of norbornene and its functionally substituted derivatives are demonstrated in the review [22]; the mechanism and the nature of catalyst effect on this process were established, the main areas of the application of polymers and copolymers of norbornene series were outlined.

The chiral derivatives of norbornene synthesised with the help of Diels-Alder reaction of cyclopentadiene with unsymmetrical dienophiles in the presence or in the absence of a catalyst were investigated [23]. The catalysts for these reactions are usually chiral diols, diphenols or oxazolines coordinated with the complexes of aluminium, boron, copper, titanium or lanthanides, promoting an increase in synthesis rate, stereo and enantioselectivity of the chiral derivatives of norbornene. The authors distinguish two main areas of the application of norbornene-containing derivatives: photochrome materials, and ion exchange membranes (including anionic, cationic and composite).

Various methods of opening the ring of norbornane derivatives leading to the stereoselective



Scheme 3.



R_1 = H; alkyl radical C_1–C_{18} of linear, branched or cyclic structure

Scheme 4.

synthesis of substituted cyclopentanes, cyclohexanes, condensed and bridging rings were considered in brief in review [24].

The polymerisation of the esters of 5-norbornene-2-carboxylic acid with vinyl monomers in the presence of various palladium catalysts with the formation of the polymers with high molecular mass is reported [25]. Computer simulation showed that these polymers demonstrate rigid statistical chain conformation, and thus they are one more example of the polymers with a strong restriction of rotation. The polymers are soluble in various solvents, in spite of their rigidity, they are amorphous, their glass transition point is much higher than 250 °C, and they exhibit high packing density. The dipoles located in the side groups participate in secondary relaxation processes, similarly to the case of flexible or rigid rod-like polymers containing ester groups.

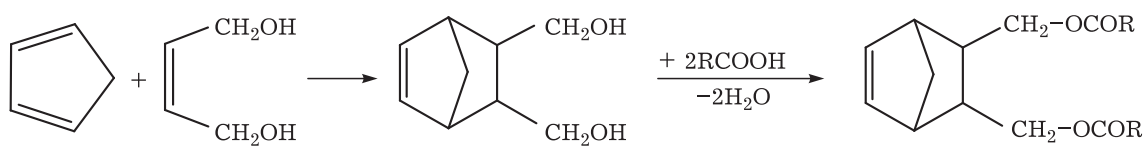
Ring-opening metathesis polymerisation in the presence of Grubbs' catalyst was used to synthesise diblock copolymers of norbornene and norbornenedicarboxylic acid possessing narrow polydispersity [26].

In [27], a method to synthesise the high-purity ester of norbornene lactone with improved physical characteristics, in a high yield, by adjusting the ratio of *endo*- and *exo*-isomers of norbornene-containing lactones was proposed. This method includes the stages: 1) Diels–Alder reaction of cyclopentadiene with acrylic acid to obtain norbornenecarboxylic acid; 2) esterification of the latter compounds by halogen-containing lactone (or hydroxylactone compounds) in the presence of a base, for example, tertiary amine, sodium carbonate and sodium hydrocarbonate, to obtain the ester of norbornene lactone; 3) recrystallisation of the synthesised lactone from a polar solvent (ethylacetate, methyl-*tert*-butyl ether) or nonpolar solvent (hexane, heptane, pentane) to decrease the ratio of *endo*-/*exo*-isomers. The authors stress that the obtained adduct may be used as a monomer in metathesis polymerisation (Scheme 4).

NORBORNENE-CONTAINING ESTERS AS ADDITIVES TO FUEL AND OIL

One of the essential directions in the application of norbornene-containing esters is their use as additives to oils and fuel. For instance, the authors of [28, 29] describe the synthesis of diesters of norbornene series on the basis of bicyclic diols (Scheme 5) and their physicochemical, viscosity-temperature and thermooxidative properties.

It is demonstrated that the addition of these esters to diesel fuel allows substantial improvement of thermooxidative stability, decrease in chilling temperature and increase in flash point. The esters were synthesised through esterification of bicyclic alcohols and an acid (caprilic, pelargonic) at the molar ratio of 1 : 2.2 in the presence of *para*-toluenesulphonic acid in the amount of 1 mass % of the reacting mixture. The yield of adducts is 83.9–88.2 mass % of the theoretical value. The authors stress that the synthesised esters possess high viscosity index (122–151.3 units), high flash temperature (205–246 °C) and low chilling



R = *n*-C_6H_{13}, *n*-C_8H_{15}

Scheme 5.

R_1-2,2-$(CH_2OCOR_3)_2$; R_1-2,3-$(CH_2OCOR_3)_2$; R_2-2,3-$(CH_2OCOR_4)_2$;
R_1-2,2-$(CH_2OCOR_4)_2$; R_1-2,3-$(CH_2OCOR_4)_2$; R_2-2,2-$(CH_2OCOR_4)_2$,

where R_1 =  , R_2 =  , $R_3 = n\text{-}C_6H_{13}$, $R_4 = n\text{-}C_8H_{17}$

Scheme 6.

temperature (−56...−64 °C), good viscosity characteristics in the negative temperature range. in addition, the thermooxidative stability of the synthesised esters is characterised by not very high acid numbers after oxidation (3.96−6.46 mg KOH/g), viscosity at 100 °C (after oxidation 4.42−6.72 mm^2/s; before oxidation 2.83−4.20 mm^2/s), a small amount of the precipitate insoluble in iso-octane (0.020−0.045 mass %), insignificant corrosion of AK-4 electrodes (0.04−0.08 mg/cm^2) and ShKh-15 electrodes (0.01−0.20 mg/cm^2), and low vapourisability (0.6−0.8 mass %). It was shown that the synthesised norbornene-containing esters exceed the known antioxidative additives, such as screened phenols and their compositions, and thus may be recommended as efficient antioxidative additives.

The compositions of alkyl-substituted bicycloalkyl ethers suitable for obtaining synthetic lubricating oils through the interaction of 2-alkylnorbornene with a monoalcohol in the presence of acid catalyst were proposed in the patent [30]. The new synthesised norbornene-containing ethers possess valuable properties (high boiling point, good stability and required viscosity), so they may find application in commercially significant areas such as the manufacture of lubricating compositions.

The synthesis of new ether lubricating oils, development of the compositions of their basis, and investigation of their properties were described in the monograph [31]. It was revealed that the performance characteristics of chemical compounds are determined first of all by their chemical structure and the positions of functional centres within the molecules. Among the compounds described by the authors, there are esters of norbornenecarboxylic and 2-methyl-norbornenecarboxylic acids, as well as oligoesters synthesised on the basis of these compounds.

The effect of the chemical structure of the esters of 2,2-dimethylolbicyclo[2.2.1]-heptene-5 with aliphatic monocarboxylic esters (C_6, C_8) and their phosphorus- and silicon-containing derivatives on thermooxidative stability was studied [32]. The revealed regularities allow carrying out directed and selective synthesis of the esters with required properties. The authors stress that thermooxidative stability of ester-type oils depends first of all on the number and positions of ester groups, the length and structure of acid and alcohol fragments, the types of functional groups or heteroatoms in esters, on the kinds and conformation states of the cyclic fragments, and other factors (Scheme 6).

It was shown that diesters with ester groups occupying gem-position lag behind the esters with the groups in the vicinal position. The authors explain this fact as follows: both ester groups are at the same carbon atom, so their interaction with each other causes weakening of their interaction with the quaternary carbon atom in the cycle. As a result, these ester groups are more readily oxidised, which affects the quality of oils: acid index, viscosity increment, deposit formation, and metal corrosion increase.

ESTERS OF NORBORNENE SERIES AS MODIFIERS OF CHEMICAL COMPOUNDS

Esters of norbornene series also find application as modifiers of chemical compounds. For instance, the authors of [33] carried out the synthesis of 2-(hydroxy)ethylbicyclo[2,2,1]hept-5-ene-2-carboxylates and studies their reaction with epichlorohydrin. On the basis of these reactions, a method was developed for the synthesis of di-, tri- and polyesters with useful characteristics. It was established that modification of epoxy-diane resin ED-20 with the synthesised polyfunctional esters allows obtaining polymer compositions with good physicomechanical properties and electrical strength, and halogen-containing esters serve as efficient antiseize additives to lubricating oils and possess high biological activity.

It was demonstrated in [34−36] that synthetic resins based on the esters of carboxylic acids find broad application in various areas of technology and economy due to their valuable performance characteristics. However, the low thermal stability of these resins causes a restriction of their

practical use to a definite extent. The authors state that one of the tasks of modern organic chemistry is the search for efficient methods to obtain functionalised organosilicon monomers, in particular, the esters of silicon-containing acids, which may be successfully used either for manufacturing heat-resistant polymer with required properties or for modification of the existing resins. In these works, the composition and structure of the products formed in the interactions of organosilanes with methyl and allyl esters of norbornenecarboxylic acid in the presence of platinum catalysts were investigated. It is demonstrated that hydrosilylation of the allyl ester of the indicated acid with the equimolar reagents ratio proceeds readily with the formation of the corresponding adducts; only the double carbon-carbon bond of the allyl radical participates in the process, while the −CH=CH− bond of the norbornene ring is conserved in this reaction. Quite contrary, hydrosilylation of the methyl ester of norbornenecarboxylic acid at the double bond of the cycle proceeds at a relatively high temperature in the presence of an excessive amount of the catalyst. The synthesised organosilicon esters of norbornene series were used for chemical modification of the properties of epox-diane resin and as a stabilising agent in suspension polyvinyl chloride compositions.

The synthesis of norbornene-containing polyesters from cyclopentadiene (dicyclopentadiene) and butyl methacrylate (BMA) was carried out, and the possibility to use the synthesised polymers as modifiers of polymeric petroleum resins was demonstrated [37−39]. The authors studied the kinetics of copolymerisation of the fractions of liquid pyrolysis products (C_9, dicyclopentadiene and cyclopentadiene fractions) and individual monomers incorporated into the fractions (styrene, indene, cyclopentadiene (CPD), dicyclopentadiene (DCPD) with BMA under the action of titanium tetrachloride (TTC) and revealed that the first stage of the process is the formation of TTC−BMA complex with the 1 : 2 composition. It was demonstrated that the complex can initiate copolymerisation; the activity of monomers in this process decreases as a sequence: indene > CPD > DCPD > styrene. The basic regularities of copolymerisation were established, and a method to obtain modified resins was developed, allowing the synthesis of modified petroleum polymer resins under mild conditions (60−80 °C, atmospheric pressure) under the action of TTC and Ziegler-Natta catalytic system (TTC concentration 2 %, the ratio of TTC/diethylaluminium chloride = 1 : 1) with a high rate (reaction time 0.5−1.5 h) and het high transformation degree of the fractions of unsaturated compounds (46.6−77.9 %), with the yield of 37−54 % and a complex of new properties. It was demonstrated that the characteristics of modified petroleum polymer resins (adhesion 1−2 points, bending strength 1−4 mm, compatibility with oxidised vegetable oils and pigments) substantially exceed those of nonmodified resins obtained under the action of TTC and Ziegler-Natta catalyst, and may find application as film-forming substances in the paint-and-varnish industry. Pigmented paint-and-varnish materials with a set of properties better than those of the compositions with nonmodified resins were developed on the basis of the compositions of modified petroleum polymer resins and oxidised vegetable oil.

The authors of [40] described the effect of *exo*,*exo*-N,N′-hexylene-di(5-norbornene-2,3-dicarboximide) on the degree of linking and the glass transition point of the polymers obtained from a mixture of the dimethyl esters of *exo*,*exo*- and *endo*,*endo*-5-norbornene-2,3-dicarboxylic acid. It was discovered that *exo*,*exo*-N,N′-hexylene-di(5-norbornene-2,3-dicarboximide) might be used as a linking agent in ring-opening metathesis polymerisation. It was demonstrated that the glass transition temperature of the polymers increases with an increase in the concentration of the linking agent.

Patent [41] describes a composition composed of a thiol, polymer resin based on the esters of norbornene series, and methacrylate. The proposed composition may be used as thermoreactive resin for construction-related purposes. This solidifying resin is used to improve the mechanical strength, adhesion of concrete and steel.

ESTERS OF NORBORNENE SERIES AS PLASTICISERS

Diesters of norbornenedicarboxylic acid were synthesised and tested as plasticisers for PVC-compositions as described in [42].

A method for obtaining new plasticisers based on the ester derivatives of norbornene was described in patents [43−45]. It is claimed that a good plasticiser should possess low volatility at high and low temperatures, stability, flexibility at low temperatures. In addition, a softening agent is used to improve several functions, including electric insulation characteristics, viscosity, cold

resistance, *etc*. The proposed plasticiser not only meets all the listed requirements but is ecologically safe and may substitute dialkyl phthalate substituents that are used in industry and possess high genotoxicity.

PHOTORESISTS BASED ON THE ESTERS OF NORBORNENE SERIES

The ester derivatives of norbornene series also find application as photoresists. For instance, patent [46] described a radiation-sensitive photoresist composition containing a photoinitiator, solvent, inhibitor of dissolution, and a polymer containing repeated polycyclic units with acid-labile groups, with molecular mass from 500 to 1 000 000 – the product of polymerisation of polycyclic monomers. The ester polymers of norbornenecarboxylic acids (Scheme 7) were used as the polymer.

The authors state that irradiation with a source forming the image makes the acid photoinitiator form an acid splitting the side labile acid groups, which leads to a change in the polarity of the polymer. The polymer attains solubility in the aqueous solution of a base in the sites irradiated with the image-forming radiation source. So, the proposed photoresist composition provides compatibility with the general scheme of chemical amplification and is transparent with respect to the short-wavelength radiation forming the image.

During recent years, much attention is paid to the polymers and especially copolymers of norbornene with fluorine-containing substituents [47]. This attention is due to the possibility of using them as a matrix material for photoresist in microlithography. It is demonstrated that these materials possess rather high transparency in the region of vacuum ultraviolet radiation. This allows using the lasers operating at a wavelength of 157 nm, which provides higher resolution in microlithography. The material of photoresistor should contain carboxylic group, so the majority of works dealt with copolymerisation of fluorine-containing norbornene with a comonomer containing an ester substituent with readily removable *tert*-butyl group, for example, *tert*-butyl ester of norbornenecarboxylic acid (Scheme 8).

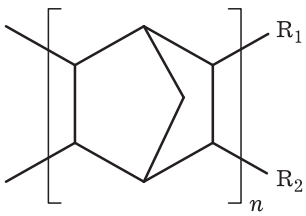
A new composition was proposed for obtaining a positive photoresist: a multicomponent copolymer on the basis of the esters of norbornene series, with the average molecular mass within the range 3000–50 000 and molecular mass distribution from 1.0 to 3.0, a low-molecular additive, acid generator, and a solvent [48].

The authors of [49] described a simple, efficient and stereoselective synthesis of 5-norbornene-2-carboxylic acid and its derivatives and studied their properties as photoresists. At first, with the help of the Diels–Alder reaction, methyl-5-norbornene-2-carboxylate was synthesised. Then isomerisation and *exo*-selective hydrolysis of the synthesised compound was performed in the alkaline medium for the synthesis of the *exo*-isomer of 5-norbornene-2-carboxylic acid. The *exo*-isomer of *tert*-butyl-5-norbornene-2-carboxylate was synthesised by means of nonselective esterification and isolated after purification. Random copolymers composed of *exo*- and *endo*-isomers of *tert*-butyl-5-norbornene-2-carboxylate and maleic anhydride were synthesised as resist materials by means of free radical polymerisation. The resulting copolymers were characterised by means of GLC and ^{1}H NMR spectroscopy. The authors suppose that the ratio of *endo*-/*exo*-derivatives of norbornene affects the reactivity, reaction rate, polymer and monomer properties, and the lithographic characteristics of photoresist.

It is stressed that the copolymers of norbornene and its various derivatives with acrylates may be used in optical-electrical engineering [50].

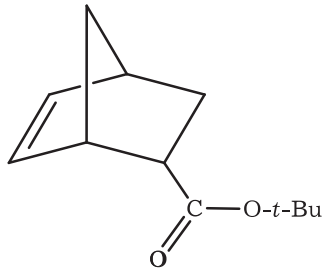
ESTERS OF NORBORNENE SERIES IN OPTICAL ENGINEERING

Copolymerisation of ethylene with norbornene derivatives, as well as their terpolymerisation



R_1 = H; alkyl radical C_1–C_{10},
R_2 = $-(CH_2)_nCOOR$; $-(CH_2)_nOR$; $-(CH_2)_nOCOR$

Scheme 7.

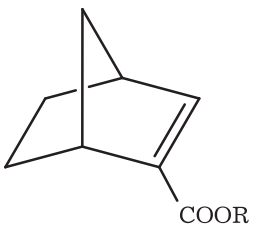


Scheme 8.

with 1-alkenes in the presence of a number of flat square nickel complexes containing anion chelates has been described in [51]. It is demonstrated that copolymerisation results in obtaining up to 50 mol. % norbornene units, in fact, an alternating copolymer. It is stressed that the glass transition temperature for the synthesised polymers of ethylene and the derivatives of norbornene increases smoothly with an increase in norbornene content. The films of these polymers poured from solutions possess good optical transparency and may be used in optical technologies.

ESTERS OF NORBORNENE SERIES AS CO-CATALYSTS IN CHEMICAL REACTIONS

The development of asymmetrical annelation of aryl iodides with racemic epoxides in the presence of palladium catalyst with the chiral norbornene co-catalyst for the synthesis of 2,3-dihydrobenzofurans was described in [52]. Following a reliable synthesis route, a number of enantiopure ester-, amido- and imido-substituted norbornenes were synthesised. Substantial enantioselectivity (42–45 %) was observed in the case when the isopropyl ester of norbornenecarboxylic acid and amido-substituted norbornene were used. The reaction under study was carried out in dimethylformamide at a temperature of 120 °C in the presence of 5 mol. % ruthenium catalyst and 20 mol. % co-catalyst based on the ester derivatives of norbornene (Scheme 9).



R = *iso*-Pr; *iso*-Bu; sec-Bu

Scheme 9.

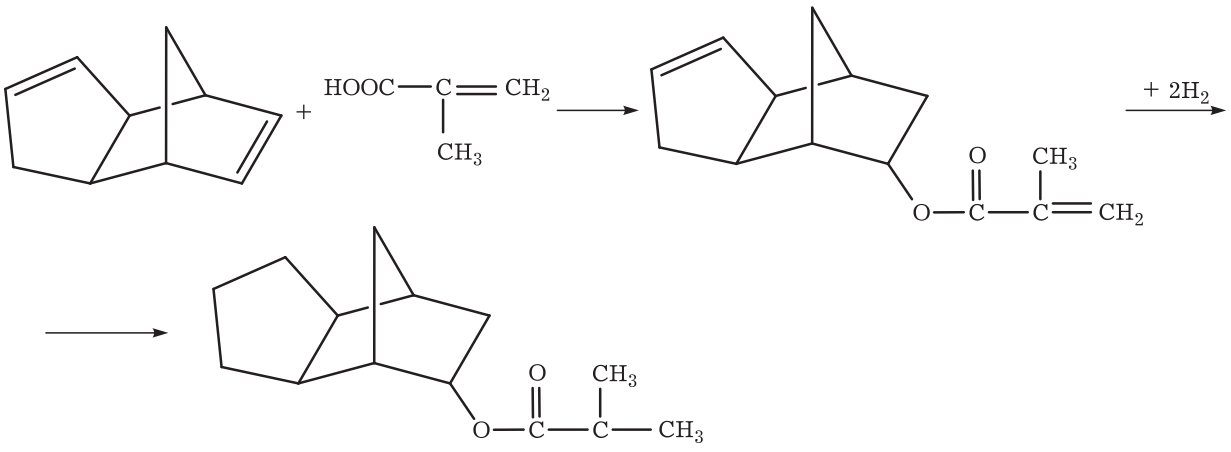
The yield of the adduct in the case of isopropyl ester of norbornenecarboxylic acid was 68 % (enantioselectivity was 42 %), in the case of isobutyl ester the yield did not exceed 10 % (enantioselectivity was 31 %), in the case of sec-butyl ester – 67 % (enantioselectivity was 38 %) and in the case of amide – 12 % (enantioselectivity 45 %).

APPLICATION OF NORBORNENE SERIES ESTERS IN PERFUMERY AND COSMETICS

Patents [53, 54] describe the synthesis of some ester derivatives of norbornene with a pleasant odour. The authors state that due to the odour the indicated compounds are of great interest for perfumery, for the production of cosmetic and skin care means.

The authors of [55] studied the addition of methacrylic acid to tricyclo-[5.2.1.0.2,6]deca-3.8-diene in the presence of KU-2-8 catalyst. As a result, norbornene-containing methacrylate was synthesised, which is a reactive monomer for obtaining high-molecular compounds. Saturated and unsaturated tricyclic esters and alcohols that may be used as the components of synthetic fragrances were synthesised from them (Scheme 10).

The authors determined the effect of various reaction parameters on the yield of the target product. The optimal reaction conditions for the addition of methacrylic acid to dicyclopentadiene in the presence of the catalyst were determined:



Scheme 10.

temperature, 100 °C; the ratio of diene/acid = 1 : 2.75; KU-2-8 catalyst (H-form) content: 5 mass % per acid, reaction time, 5 h. Under these conditions, the yield of the adduct was 81.8 %.

ESTERS OF NORBORNENE SERIES AS ANTIMICROBIAL SUBSTANCES

A series of norbornane-bis-ester diguanidines were synthesised and studied as antibacterial agents with respect to some microorganisms. The high antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* was revealed [56].

In the studies carried out at the Institute of Petrochemical Processes, NAS of Azerbaijan (Baku, Azerbaijan) [57], were synthesised the esters of norbornene series, outlined the major areas of their application, and demonstrated the potential for their use as antimicrobial preparations, etc.

CONCLUSION

The results of research in the area of the synthesis of ester derivatives of norbornene series, their properties and the directions of their application were analysed. A broad application of the esters of norbornene series as additives to synthetic oils and fuel compositions, as plasticisers, modifying and solidifying agents, as components in perfumery, as antimicrobial and antifungal preparations, catalysts and co-catalysts was stressed. It is demonstrated that the addition of these esters to diesel fuel causes a substantial improvement of thermooxidative stability, a decrease in chilling temperature, and an increase in flare temperature. The esters of norbornene series are considered as new functionally substituted monomers for the synthesis of modified norbornene-containing polymers and copolymers. It is established that fluorinated norbornene-containing esters are used as the matrix material for photoresist used in microlithography.

Results of the studies provide unambiguous evidence of the permanent attention to the ester derivatives of norbornene. The number of works dealing with the studies in this area is permanently increasing, and their relevance remains significant up to date.

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