Chemistry for Sustainable Development **27** (2019) 473–480

UDC 541.64:547.538.141

DOI: 10.15372/CSD2019168

Homo- and Copolymerization of Norbornene and its Derivatives

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(Received April 23, 2019; revised May 12, 2019)

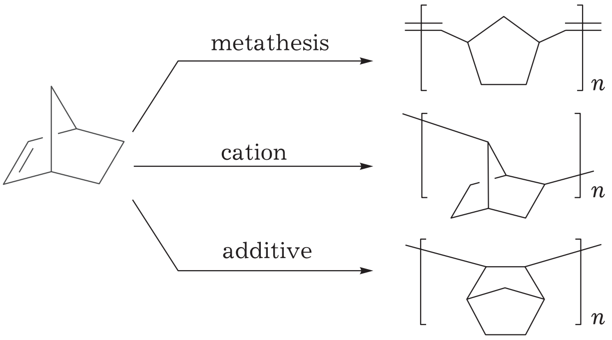
Abstract

The literature data on the research in the field of homo- and copolymerization of norbornene and its derivatives are discussed in the review. Due to specific structure, norbornene and its derivatives provide the basis to synthesize the polymers and copolymers with various functionalities, differing from each other in the structure and physical-mechanical characteristics of final products. Depending on polymerization conditions, the polymers synthesized on the basis of norbornene are characterized by high optical purity, high thermal and chemical stability, mechanical strength. Copolymers of norbornene with olefins and acrylic monomers combine the properties typical for norbornenes with such characteristics of polyolefins or polyacrylates as high adhesion, elasticity, flexibility of macromolecules, which promotes broadening of their application range. Thus, the availability of the raw material basis of norbornene and its derivatives, together with the unique performance characteristics of the polymers and copolymers based on them, attracts the attention of researches to the studies into the synthesis of new norbornene monomers and the synthesis of polymers and copolymers on their basis for use in various branches of industry. The data presented in the review provide evidence of the promising character of studies in the area of the synthesis of high-molecular compounds with valuable performance characteristics on the basis of norbornene hydrocarbons.

Keywords: norbornene, homopolymerization, (meth)acrylic esters, (co)polymerization, catalyst

ROUTES OF NONBORNENE'S POLYMERIZATION

Norbornene and its derivatives are among unique monomers for the synthesis of various polymer materials with valuable physicochemical properties. High strain energy renders increased reactivity to these compounds in comparison with open-chain or less strained homologues. These compounds come from the available raw material of petrochemical synthesis and allow synthesizing a broad range of compounds differing in the number, nature and relative positions of substituents. It is known that homopolymerization of norbornene itself may proceed *via* three routes depending on the type and nature of initiator involved: metathesis, additive, and cation (isomerisation) polymerization, with the formation polymers differing by the structure of units and by the properties of resulting products [1–3]:



Metathesis polymerization of norbornene is the best studied kind. Polymers obtained in this process are called polyalkeneamers. Metathesis polymerization with cycle opening proceeds relatively easily in comparison with additive polymerization. As a result, unsaturated polymers with alternating cyclopentenylene and vinylene groups are formed. Vulcanised polynorbornenes obtained on this basis are used as vibration- and sound-absorbing elastomeric materials. Porous metathesis polymers are good adsorbents to collect oil spillage. They are able to sorb oil up to 400 % of the sorbent mass.

At the initial stage of development, metathesis was carried out using homogeneous systems based on the salts of transition metals; organoaluminium compounds were mainly used as co-catalysts. Examination of research and patent publications revealed that mainly heterogeneous catalysts based on transition metals in the form of halides, oxides or oxochlorides of metals in combination with alkylating (R_4Sn, Et_2AlCl) and promoting (O_2, EtOH, PhOH) agents, where R is C_1–C_2 alkyl, Et is ethyl, Ph is phenyl, are used in the recent years for metathesis polymerization of norbornene and its derivatives [4]. As a rule, these are complexes based on tungsten [5–7], molybdenum [8–13] and ruthenium [14–18]. However, metathesis polymerization with cycle opening is possible also in the presence of catalytic systems based on zirconium and hafnium [19], titanium [20], niobium [21], vanadium [22, 23], osmium [24], tantalum [25–27] and rhenium [28].

The least studied kind is cation or radical (isomerisation) polymerization of norbornene because cation and radical initiators used in these processes (for example, azoisobutyronitrile, tert-butylperacetate etc.) lead only to the formation of oligomer products. Polymerization of norbornene with the transfer of the reaction centre leads to saturated polymers with bicyclic units of 2,7-structure. This route was described for the first time in 1967 [29–31], and $EtAlCl_2$ was the first catalyst with which the cation polymerization of norbornene was carried out [29].

Norbornene polymerization only with opening of the double bond in the cycle, with the formation of saturated polymers with bicyclic units in the main chain, is called additive. Catalysts for the additive polymerization of norbornene may be divided into three groups: metallocenes of zirconium and titanium [32–39], which also provide excellent results for copolymerization of norbornene with ethylene; rarely used complexes of chromium [40, 41], cobalt [42], iron [43] and copper [44]; highly active catalysts based on metals – nickel and palladium [45, 46]. It should be stressed that zirconium complexes served earlier as the catalysts for the additive polymerization of norbornene, but impossibility to isolate them from the resulting polymer required the improvement of the catalysts based on palladium and nickel [47–52].

Saturated (additive) polymers of norbornene possess good mechanical strength, chemical and thermal stability, hardness, high optical transparency, good solubility in organic solvents, low moisture absorption and other characteristics. They are used as ultraviolet photoresists and interlayer dielectrics in microelectronics [53].

However, additive polynorbornene has a very rigid chain, so its vitrification temperature is high and close to the decomposition temperature (~410 °C). This excludes the possibility to process this material using usual methods and to obtain high-quality films on its basis. A decrease in the rigidity of chains in additive polynorbornene may be achieved by introducing flexible units (for example, ethylene, propylene and other vinyl).

There are the data on obtaining copolymers of norbornene with ethylene, with the participation of original inexpensive chelate complexes of nickel, palladium, titanium [54–65]. One of the disadvantages of this method is the necessity of thorough, labour-intensive purification of the synthesized copolymer from the catalyst to obtain highly transparent materials. Another disadvantage is the necessity of copolymerization at a pressure of 7–20 atm, which requires special equipment. This problem was solved by obtaining norbornene copolymers in which the role of the flexible unit is played also by other vinyl monomers, in particular acrylic.

COPOLYMERIZATION OF NORBORNENE AND ITS DERIVATIVES

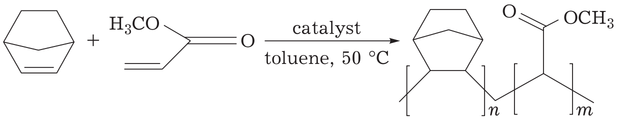
Copolymerization of norbornene and its derivatives with acrylates is of substantial interest for investigation. Polyacrylates possess good adhesion and are widely used as photoresist materials. On the other hand, polynorbornenes are distinguished by excellent stability against aggressive media, thermal and chemical stability. Therefore, due to norbornene copolymerization with acrylates, it is possible to synthesise polymer materials with optimal properties. Copolymers of norbornene and acrylates are important photolithographic materials.

At present, only limited data on copolymerization of acrylates with norbornene are available in the literature. This is connected with the difference in the mechanisms of their polymerization: acrylate polymerization proceeds according to the radical mechanism or is initiated by anion catalysts, while that of norbornene follows the cation or coordination mechanism. This is why their joint polymerization is somewhat hindered.

In 1970, R. E. Morris had patented the synthesis of acrylate/norbornene copolymers initiated by radicals, but the maximal norbornene content of the polymer was only 5 % [72–74].

E. L. Goodall with co-authors studied additive copolymerization of norbornene with acrylates in the presence of catalysts based on the transition metals of the VIII group [65]. Copolymerization was carried out at 50 °C under the effect of $(\eta^3\text{-}C_4H_7)Ni(\eta^4\text{-}C_8H_{12})PF_6$ or $(\eta^3\text{-}C_3H_5)Pd(PCy_3)Cl$, where Cy is cyclohexyl. Copolymers obtained in a low yield contained 15 to 85 mol. % norbornene units. Water suspension copolymerization in the presence of $(\eta^3\text{-}C_3H_5PdCl)_2\text{–}P(C_6H_4SO_3Na)_3\text{–}Li[(B_6F_5)_3]_4$ leading to copolymers with the molar content of norbornene units equal to 54 % proceeded with higher efficiency.

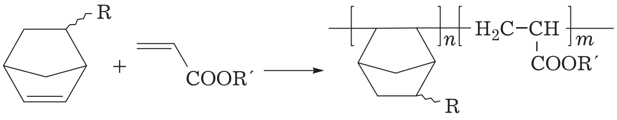
Bimetal allyl complexes of palladium were used for norbornene polymerization with methylacrylate [68]:



where n and m are degrees determining the composition of the polymer.

Through a serial reaction of $\{(All)Pd(\mu\text{-}Cl)\}_2$ (where All is allyl) with $AgPF_6$ and PCy_3 in CH_2Cl_2, a mixture of $[\{(All)Pd(PCy_3)\}2(\mu\text{-}Cl)][PF_6]$, $[(All)Pd(PCy_3)_2][PF_6]$ and $(All)PdCl(PCy_3)$ was obtained, and only after polymerization for 20 h at 23 °C pure $[\{(All)Pd(PCy_3)\}2(\mu\text{-}Cl)][PF_6]$ was obtained. Results showed that in the presence of this catalyst the ratio of norbornene to methylacrylate in the polymer varied from 91 : 9 to 72 : 28, and the molecular mass varied from 64 800 to 84 500 after polymerization for 1-5 h [69].

V. I. Bykov with co-authors [66] described the synthesis of copolymers on the basis of norbornene and its derivatives, in particular *tert*-butyl ester of norbornenecarboxylic acid with methylacrylate, *tert*-butylacrylate and acrylic acid. The reaction was carried out in the presence of benzoyl peroxide as an initiator at 30 °C:



R = H, COOBu-*t*; R′ = H, Me, *t*-Bu

where Me is methyl, *t*-Bu is *tert*-butyl, n and m are degrees determining the composition of the copolymer.

In the case of norbornene copolymerization with methylacrylate, the yield of the copolymer was 43–45 %, the temperature of decomposition of these copolymers is higher than 310 °C. A decrease in the ratio of norbornene/acrylate from 10 : 1 to 1 : 1 leads to a decrease in the content of norbornene units in the resulting copolymer and, as a consequence, to a decrease in vitrification temperature; the molecular mass increases. Copolymers of norbornene with methylacrylate and *tert*-butylacrylate possess high transparency (93–94 %) in the region 380–780 nm, which allows considering them as promising materials for optoelectronics. They appear to be a comfortable basis – a polymer matrix possessing good mechanical properties, adhesion to metals and glass. Nanoparticles can be uniformly distributed in them, because copolymers and nanoparticles are well soluble in the same solvents (for example, in toluene). All of this is necessary for the development of new nanocomposite materials for various photoelectron devices: photodiodes, flexible screens, light-generating devices with low energy consumption, solar energy converters, *etc.* Copolymers are efficient stabilisers of semiconductor nanoparticles, in particular, nanoparticles of cadmium selenide in the volume of a polymer matrix, that is, they do not distort photoluminescence signal of a nanocomposite material in comparison with the signal from nanoparticles in solution.

Chinese scientists [68] synthesized grafted copolymers based on polynorbornene according to the mechanism of radical polymerization with atom transfer. At the first stage, copolymerization of norbornene with 1,4-di-vinylbenzene was carried out using a chelate complex β-ketoamine–nickel–methylalumoxane. An irregular copolymer containing several side styrene fragments was obtained. At the second stage, the side styrene groups were quantitatively polymerised with methylacrylate under initiation with copper dichloride and 2,2'-azobisisobutyronitrile.

A. Sen with co-authors described polymerization of methylacrylate with norbornene in the presence of a solvent using a neutral palladium complex (L_2)Pd(Me)(Cl) or (L)Pd(R)(X), where L means monodentate phosphines or one bidentate phosphorus- or nitrogen-containing ligand, R is alkyl or aryl group, X is anion group [72, 73].

Results of the radical copolymerization of methylacrylate with norbornene and its various derivatives with atom transfer in the presence of copper catalysts and radical initiators are reported in [76]. With methyl-2-bromopropyonate, ethyl-2-bromopropyonate and ethyl-2-bromoisobutyrate as initiators, similar results were obtained in the three cases. Copolymerization of methylacrylate and norbornene was also studied with adding two different ligands *N*,*N*,*N*',*N*',*N*''-pentamethyldiethylenetriamine and 1,1,4,7,10,10-hexamethyltrie thylenetetramine. Changes in ligand/copper ratio (1 : 1, 5 : 1 or 10 : 1) had no effect on the reaction.

To synthesize copolymers of norbornene and acrylates without involving metal atoms in the composition, the authors of [77] carried out copolymerization in the medium of nitroxide initiators: 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide.

E. Ihara with co-authors studied radical copolymerization of alkyl-2-norbornene-2-carboxylates (alkyl = Me, *n*-Bu) with alkylacrylates (alkyl = Me, Et, *n*-Bu). In the presence of 1,10-azobis(cyclohexane-1-carbonitrile) at 85 °C, the reaction proceeds with the formation of irregular copolymers, while homopolymerization of methyl-2-norbornene-2-carboxylate alone under these conditions is insignificant. Polymerization with ethylacrylate at a ratio of 1 : 3 results in copolymers with the molecular mass 33 300, containing 19.4 mol. % units of methyl-2-norbornene-2-carboxylate in the composition. Ternary radical copolymerization of alkyl-2-norbornene-2-carboxylate/alkylacrylate/N-phenylmaleimide resulted in obtaining copolymers with three repeated units in the main chain [74].

Continuing the works in this area, the authors studied the behaviour of methyl-2-norbornene-2-carboxylate and phenyl-2-norbornene during copolymerization with styrene, alkylacrylates and methylmethacrylate [75]. Various combinations of monomers were used, but copolymers with mainly norbornene structure in the main chain were obtained. The relation between the reactivity of monomers for copolymerization of methyl-2-norbornene-2-carboxylate and phenyl-2-norbornene with *n*-butylacrylate determined using Feynman-Ross method at 85 °C is (2.5 : 1)–(1 : 3) and (1 : 3)–(1 : 1), respectively. Because of the presence of norbornene fragments, the vitrification temperature of the obtained copolymers is higher in comparison with styrene-containing monomers.

Copolymerization of norbornene with methylacrylate was carried out using neutral palladium complexes containing β-ketoimide ligand $Pd[CH_3C(O)CHC(NAr)CH_3](PPh_3)(Me)$ (where Ar is naphthyl or fluorenyl) activated with methylalumoxane. Analysis of the products with the help of NMR ^{1}H and ^{13}C spectroscopy showed that copolymers have irregular structures. The obtained products were extracted consecutively with acetone and chloroform. Soluble products contained copolymers which were strongly enriched with acrylate units (53–90 mol. %); their molecular mass decreased substantially with an increase in the number of norbornene units [80].

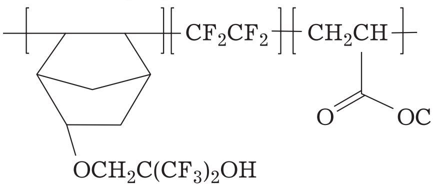
For additive homopolymerization of norbornene and its copolymerization with methylacrylate, four Pd-diimine catalysts with different ligands $\{[RC_6H_3N{=}C(R')-C(R'){=}NC_6H_3R]Pd(CH_3)(N{=}CMe)\}SbF_6$ (R = 2,6-(iPr)$_2$, CH_3; R' = H; CH_3), where *i*Pr is isopropyl, were studied. Additive polynorbornenes were successfully obtained with all the four catalysts. Systematic investigations of the effect of ligands, temperature and time on the activity of norbornene in polymerization were carried out, and the stability of the catalyst and molecular mass of the polymers were studied. It was revealed that radicals formed in the decomposition of palladium ligands, similarly to the case of norbornene homopolymerization, easily initiate homopolymerization of methylacrylate. When these catalysts are used for copolymerization of norbornene and methylacrylate in the absence of light, low-molecular copolymers with the end methylacrylate units are obtained [81].

The polymerization and the structure of the synthesized copolymers of norbornene with methylacrylate in the presence of the catalyst $Nd(Naph)_3-Al(iBu)_3$, where *i*Bu is isobutyl, Naph is naphthyl was studied [82]. Reactions were carried out in the atmosphere of nitrogen. Analysis of the resulting copolymers showed that the content of norbornene and methylacrylate in the copolymer is 22.2 and 77.8 mol. %, respectively. Molecular masses of copolymers changed depending on the ratio of monomers in the polymer composition, and it decreased with an increase in the ratio of norbornene to methylacrylate. The authors demonstrated the possibility to carry out copolymerization also in the solvent, for which aromatic hydrocarbons were used. It was shown that copolymerization proceeds even at room temperature, but the yield of copolymers increases with an increase in reaction temperature. The yield of copolymers also depends on the Al/Nd ratio in the catalyst and reaches the maximum (78.5 %) for the molar ratio Al/Nd = 30.

Homo- and copolymerization of tert-butylmethacrylate and norbornene in the presence of $Ni(AcAc)_2$ (where AcAc is acetylacetate) in combination with methylalumoxane was studied. This catalytic system demonstrated high activity in homopolymerization of norbornene and *tert*-butylmethacrylate. However, catalyst activity decreased in copolymerization, so copolymers were obtained with very low yield (<4 %), and they contained a small amount of norbornene units. In the opinion of authors, the determined constants of copolymerization of *tert*-butylmethacrylate ($r_{TBMA} = 4.14$) and norbornene ($r_{NB} = 0.097$) point to the coordination nature of the process. Vitrification temperature of the obtained copolymers was 100–250 °C [83].

High activity in homo- and copolymerization of norbornene and butylmethacrylate was revealed by a nickel-containing catalyst (NiL_2Br_2) (where L is a complicated α-diimine ligand) after activation with $B(C_6F_5)_3$ [84]. The content of butylmethacrylate monomers in copolymers was controlled within the range 6.0–78.7 % by changing the ratio in supplying this monomer from 10 to 90 %. The obtained copolymers had high thermal stability (decomposition temperature $T_d > 390$ °C), high molecular mass and narrow molecular mass distribution (dispersity coefficient ≤1.4). Materials based on these polymers may be processed into films with good transparency and mechanical properties.

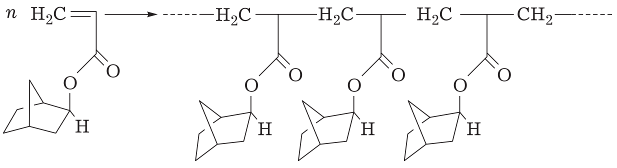
Copolymerization of fluorine-containing derivative of norbornene with tetrafluoroethylene and *tert*-butylacrylate, a potential source of carboxylic groups, resulted in the formation of copolymers which are interesting as photoresist materials [85]:



Copolymerization proceeded *via* the free radical mechanism in the medium of fluorinated solvent in the presence of peroxide carbonate as initiator. The resulting copolymer was characterised by vitrification temperature 140–150 °C, its molecular mass was about 10 000. The exchange of norbornene co-monomer for the derivative of tricyclononene caused an improvement of the transparency of the copolymer.

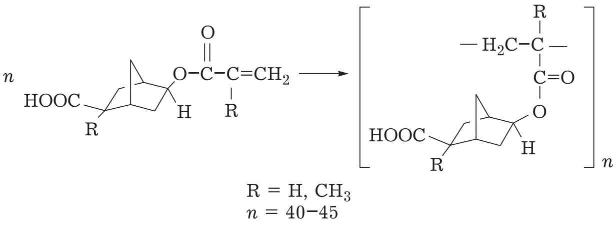
In the Institute of Petrochemical Processes, NAS of Azerbaijan, under the supervision of M. K. Mamedov, a number of reactive monomers readily polymerising in the presence of radical initiators were synthesised from norbornene and its derivatives [86–88]. Along with norbornylacrylate [89–91], various functionally substituted Cl- [92], CN- [93, 94], acetoxy-, acetoxymethyl- [95, 96], butoxy- [97] and octyloxycarbonyl- [98] containing bicyclic (meth) acrylates were obtained.

The radical polymerization of exo-norbornylacrylate in the presence of *tert*-butylperoxide, ammonium and potassium persulphates was investigated [99]:



The resulting polymers are transparent vitreous substances, well soluble in CCl_4 and $C_2H_4Cl_2$. The softening temperature of the polymers is 108–116 °C, their molecular mass is 50 000–60 000. In the diffraction patterns, only one intense diffraction maximum was detected at the background line: it appears at ~(11–23)°, and its interplanar spacing is α = 5.033 Å, which proves that the polymer is amorphous at room temperature. The synthesized polymers may be used as a film-forming material in the paint and varnish industry, and as an efficient glue for various products.

Taking into account the potential of the application of bicyclic (meth)acrylates, an efficient method was developed for the synthesis of 5-carboxyl-5-methylbicyclo[2.2.1]-hept-2-yl-methacrylate through thermal addition of acrylic acids to cyclopentadiene [100]. The formed (meth) acrylates have exclusively *exo*-orientation of the cycle with respect to the norbornane fragment. This is especially important for the involvement of these monomers into polymerization, because *exo*-substituted norbornenes are much more active in polymerization than *endo*-isomers. The maximal yield of the polymers with molecular mass 10 000 is achieved through the radical polymerization of 5-carboxyl-bicyclo[2.2.1]hept-2-yl(meth)acrylates in the presence of di-*tert*-butylperoxide [101]:



The synthesised polymers may be used as coatings.

Investigations in the area of copolymerization of norbornene hydrocarbons with acryl esters are continuing their intense development. This opens the outlooks for obtaining new polymer materials with improved properties, combining the properties of polynorbornenes and polyacrylates.

CONCLUSION

Thus, the presented material points to the promising character of the studies in the area of the synthesis of high-molecular compounds with valuable performance characteristics, based on norbornene hydrocarbons. This opens broad possibilities for obtaining new polymer materials possessing a set of properties inherent to norbornene and comonomers, in particular polymethacrylates.

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