UDC 547.291/293+547.599

DOI: 10.15372/CSD2022378

EDN: CWDEDB

Synthesis of Polycyclic Acrylic Monomers

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(Received 29.07.21; revised 17.11.21)

Abstract

Analysis of literature data in the field of synthesis and study of the physical and chemical properties of mono-, bi-, tri-, tetracyclic and adamantyl-containing esters of (meth)acrylic acids is systematized and presented in the review. The reactions under consideration involve the synthesis of these compounds by means of esterification of acids with cyclic alcohols, transesterification, as well as the addition of (meth)acrylic acids to unsaturated alicyclic hydrocarbons, *etc*. The main directions of the practical application of polycycloalkyl-containing (meth)acrylates are indicated. It is stressed that the functionalization of the double bond in norbornene-containing compounds makes it possible to obtain a wide class of functional derivatives with potential chemical activity. The results of studies carried out by the authors of this review on the addition of acrylic acids to the derivatives of cyclo- and polycycloolefins are presented. Studies on the synthesis of the derivatives of acrylic esters of cyclohexene, norbornene, dicyclopentadiene and tetracyclododecene containing hydroxyl, alkoxy, carboxyl, as well as siloxane, isocyanate and other nitrogen-containing groups are considered. It has been shown that these compounds are reactive monomers for obtaining practically valuable polymers used in many industrial areas.

Keywords: reactive monomer, dicyclopentadiene, alkoxycarbonylnorborn-2-yl acrylate

INTRODUCTION

The range of research in the area of the synthesis of alicylic, in particular norbornene esters of acrylic and methacrylic acids, is broadening in the recent years. Attention to norbornyl-containing acrylic compounds is explained by the fact that they are active monomers able to undergo polymerization according to various mechanisms, which broadens the range of commercially available acrylic polymers. The production of (meth)-acrylic polymers is currently reaching a broad scale because these polymers possess excellent optical properties, high transparence within the visible spectral range, increased thermal and atmospheric resistance, hardness, shock strength, stability against petrol and oil, good mechanical, film-forming and adhesion properties, as well as high vitrifying temperature. The synthesis of alicylic acrylic monomers is a very relevant task and broadens the range of substrates allowing the synthesis of new acrylic polymers on the basis of these compounds [1–3]. Numerous methods of the synthesis of these compounds are known. The goal of the present work is to analyze the published information on the synthesis, properties and applications of polycyclic acrylic monomers.

SYNTHESIS OF ACRYLATES THROUGH ESTERIFICATION

Direct esterification is the interaction of (meth)acrylic acids ((M)AA) with alcohols

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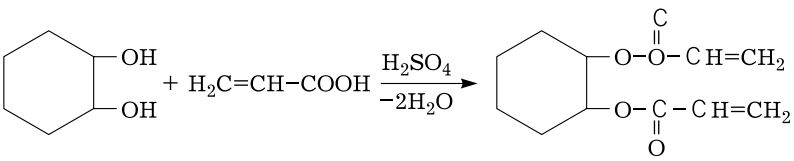
(mono- and bicyclic), and transesterification of esters is one of the basic and convenient methods to obtain either mono- or bi- and tricyclic (meth)acrylates. Reacting with most of the compounds possessing odour, they form copolymers with no odour or with weak odour. Esterification usually proceeds rather slowly, so the process is carried out in the presence of catalysts in most cases. The catalysts can be Brønsted acids (H_3PO_4, H_2SO_4) or Lewis acids ($BF_3 \cdot OEt_2$, $AlCl_3$, $ZrCl_4$, *etc.*), salts, oxides, ion exchange resins, *etc.* As a rule, the known Lewis acids allow obtaining esters that are stable against rearrangements and polymerization only in reactions with primary alcohols [4–7]. At increased temperature and pressure, the reaction can be performed in the liquid or gaseous phase. Esterification of cyclopentanol and its methyl-substituted derivative with (M)AA in the presence of catalysts (KU-2-8 cation exchange resin and naphthalenedisulphonic acid) was successfully used to synthesize cyclopentyl(meth)acrylates and their methyl-substituted derivatives in the yields of 90.2–95 % [8–10]. Cyclohexylacrylate, its methyl- and ethyl-substituted derivatives were synthesized by esterification of cyclohexanol, methyl-, ethylcyclohexanol with (meth)acrylic acids in the presence of sulphuric acid [11] and naphthalene-1,5-disulphonic acid. Cyclohexylacrylate was proved to exhibit higher activity in esterification [12]. The yield of esters is 88.9–90.1 %. Transesterification of cyclohexylacrylate with *n*-butanol and 2-ethylcyclohexanol was studied in the presence of such catalysts as tetrabutyl titanate, ion exchange resins and zeolites [13]. In order to search for the optimal conditions of transesterification, the effect of various factors on the conversion of cyclohexylacrylate and on the selectivity of cyclohexanol formation was investigated. Experimental results of transesterification of cyclohexylacrylate with *n*-butanol in the presence of Engelhard F-24 catalyst were processed with the help of a kinetic model based on Langmuir–Hinshelwood mechanism and Hougen–Watson method, and the kinetic parameters of this reaction were calculated.

The synthesis of cyclohexyl(meth)acrylate [14] and 3,3,5-trimethylcyclohexylacrylate [15], in addition to sulphuric acid, involves other acid catalysts (*p*-toluenesulphonic acid, phosphoric acid, zeolites HZSM-5, H-mordenite, *etc.*). The synthesis is very simple, is carried out under mild conditions and provides high yields of the product.

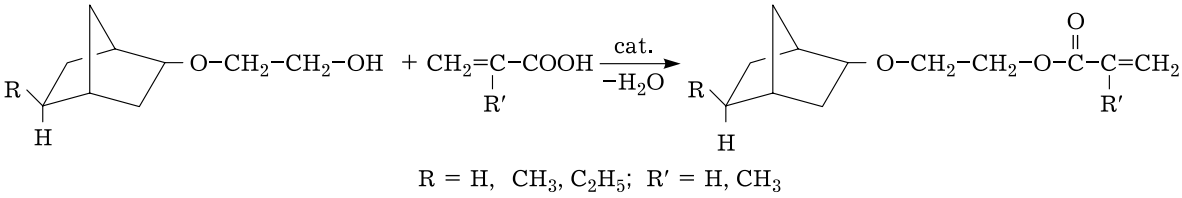
For the synthesis of methylcyclohexyl(meth) acrylate through transesterification of C_1–C_4-alkyl(meth)acrylate with methylcyclohexyl alcohol, in which methyl group may occupy positions 2, 3 and 4 with respect to the hydroxyl group, the alcoholates of metals (Ti, Sn, Zr, Ca, Mg, K, Li) were used as catalysts [16]. Optimal technological conditions were determined for the synthesis of diacrylate of 1,2-cyclohexanediol (1,2-CHD) through esterification of the latter compound with acrylic acid in the presence of a homogeneous catalyst (concentrated sulphuric acid) at a molar ratio of 1 : 2.2 for 5 h with water separation (Scheme 1) [17]. The reaction was carried out in cyclohexane. The compound used as polymerization inhibitor was $MeOC_6H_4OH$. The chosen catalyst is homogeneous, which brings complications into its recovery from the catalyzate. The yield of diacrylate was 87.3 %.

The synthesis of norbornyl(meth)acrylates for use as monomers to obtain optical fibres, distinguished by high thermal stability and transparency, was described in a patent [18]. As a result of (M)AA esterification with bicyclic monoethers of ethylene glycol with the application of naphthalene-1,5-disulphonic acid, bicyclo[2.2.1]-hept-2-yloxyethylacrylates were synthesized (Scheme 2) [19].

A method of obtaining tricyclic (meth)acrylic monomers was described in [20]. It involves esterification of tricyclo[5.2.1.$0^{2,6}$]decan-8-ol with (M)AA at a temperature of 115 °C for 2 h. Purity degree and the yield of tricyclic (meth)acrylic esters were 99 and 70–80 %, respectively. The polymers of thus synthesized tricyclic (meth)acrylates were



Scheme 1.



Scheme 2.

characterized by high transparency, thermal stability and high resistance against humidity.

SYNTHESIS OF ACRYLATES *VIA* ADDITION REACTION

The reaction of (M)AA addition to cyclic olefins is preferable in comparison with acid esterification with cyclic alcohols. Since the efficiency of the catalysts of addition reaction is higher than for esterification, in this case: 1) the stage of obtaining alcohols from cycloalkenes is excluded; 2) it is not necessary to remove water; 3) in the large excess of cycloalkane, the synthesized ester is characterized by the higher purity degree. Comparative characterization of the catalysts shows that, in view of the simplicity of reaction mass separation from the catalysts and selectivity of ionites, the ion exchange resins have advantages over homogeneous catalysts. Their application provides the possibility to obtain esters in high yields and high quality; also washing of the product is not necessary, and the risk of corrosion of the equipment is excluded (or reduced).

Chinese scientists synthesized cyclohexyl(meth)acrylates *via* (M)AA addition to cyclohexene. Cation exchange resin – macroporous polystyrene sulphonate – was used as a catalyst. The effect of reaction temperature, catalyst amount, the molar ratio of (M)AA to cycloalkane and reaction time on conversion degree was investigated, and reaction selectivity was studied. The results have shown that the cation exchange resin is an efficient catalyst for the synthesis of cyclohexyl(meth)acrylates. The optimal reaction conditions are: temperature 85–90 °C, catalyst amount – 3 % (calculated for the total mass of initial compounds), the molar ratio (M)AA/cycloalkene = 2 : 1, reaction time 5 h. Under these conditions, cyclohexene conversion reaches 87.2–89.0 %, and reaction selectivity is 90.1–95.3 %. It is demonstrated that catalyst activity and structure remain almost unchanged after repeated use of the catalyst up to 10 times [21, 22]. Saha B. and Sharma M. also carried out the interaction of (M)AA with cyclohexene in the presence of various catalysts [23]. The yields of cyclohexyl(meth)acrylates synthesized under the optimal conditions (temperature 100 °C, molar ratio (M)AA/cyclohexene = 4 : 1, catalyst amount 5 wt. %, reaction time 5 h) are shown in Table 1.

The interaction of (M)AA with cyclohexene and its alkyl-substituted derivatives was performed in the presence of $BF_3 \cdot O(Et)_2$ according to Scheme 3 [24]. The yields of cyclohexyl(meth)acrylates synthesized under optimal conditions (temperature 80 °C, molar ratio (M)AA/cyclohexene = 1.5 : 1, catalyst amount 0.1 % of the mass of cyclohexene, reaction time 2 h) are within the range 79–82 %.

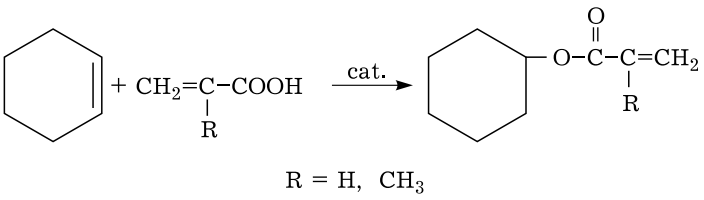
The addition of acryl esters to 2-norbornene in the presence of ruthenium-containing catalysts proceeds in somewhat different manner [25]. In the case of the use of the catalyst system $RuCl_3/Zn$ or $[RuCl_2(C_6H_6)]_2/Zn$ (in alcohols) at

TABLE 1

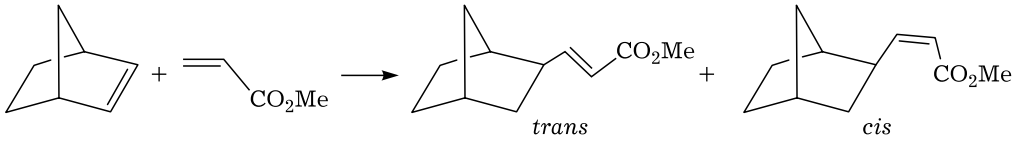
Yields of cyclohexyl(meth)acrylates in the presence of catalysts

Catalyst	Yield, %	
	Cyclohexylacrylate	Cyclohexylmethacrylate
Indion 130	95.8	90.6
Amberlyst	92.9	85.6
Amberlite IR 120	52.7	–*
Engelhard F-24	–*	51.2
p-TSA	39.5	33.8

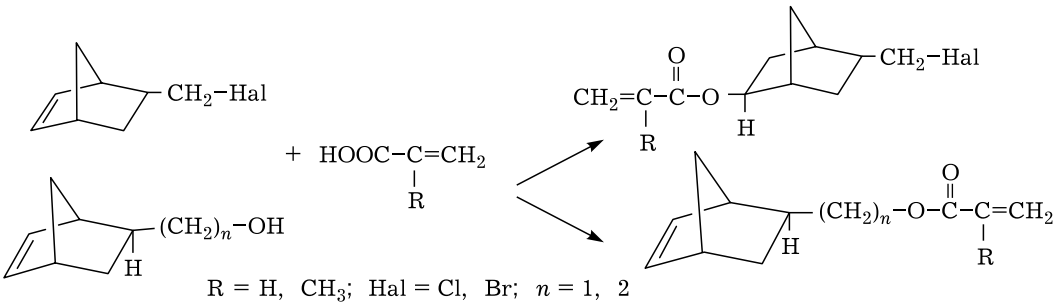
* No data.



Scheme 3.



Scheme 4.



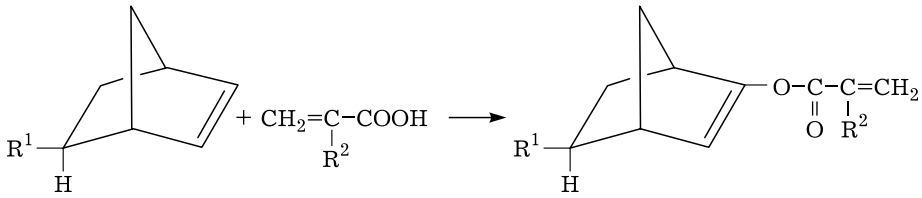
Scheme 5.

80 °C, the addition of hydrogen atom of the vinyl group of acryl ester to the double bond of norbornene proceeds within 1 h, with the formation of *exo-trans*-2-norbornylacrylates as the major products, in the yield of 87 % and with the *trans-/cis*-isomer ratio equal to 40 : 1 (Scheme 4).

The authors of the present article, under the direction of Mamedov M. K., developed an efficient method to synthesize bicyclo[2.2.1]-hept-2-ylacrylate in the yield of 80 % and its C_1–C_5-alkyl-substituted derivatives in 65–77 % yield in the presence of $BF_3 \cdot O(Et)_2$ as a catalyst, which is readily removed from the reaction mixture by washing with distilled water [26]. Optimal reaction conditions were determined: temperature 80 °C, molar ratio acrylic acid/bicycloolefins = 1.2 : 1, catalyst amount 0.5 wt. %, reaction time 3 h. For the purpose of simplifying the process technology and preventing polymerization of initial (M)AA and cycloolefin hydrocarbons, (M)AA addition to the latter compounds was carried out thermally in the inert gas under the pressure of nitrogen [27, 28].

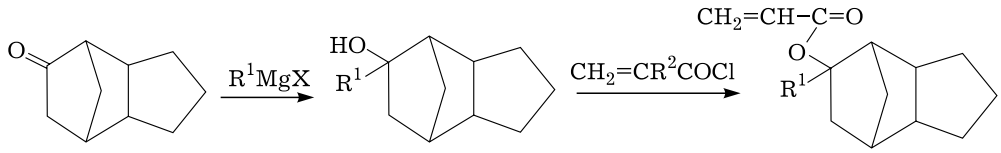
(Meth)acrylic acids undergo stereo- and regioselective addition to halogen-substituted bicycloheptene compounds without any catalysts. The reaction proceeds at 120 °C in the presence of anthraquinone as inhibitor, and leads to the formation of halogen-substituted alkylbicycloheptyl acrylates (yield 75–89 %), which are of interest as initial compounds for obtaining insecticides. It has been proven that acrylic acids themselves play the part of the catalyst in the system, which results in the formation of the corresponding bicyclic (meth)acrylates. The addition of (M)AA to norborn-5-en-2-ylmethanol and to bicyclic monoester of ethylene glycol has been studied in detail (Scheme 5). The substances used as heterogeneous catalysts were KU-2-8 cation exchange resin (ester yield 70.8–71.5 %) and naphthalenedisulphonic acid (ester yield 90.6–92.4 %) [29–31].

Monograph [32] presents the information on the methods of obtaining various preparative and commercial monomers as a basis for high-molecular compounds to be obtained by means of polymerization and polycondensation. Physical and chemical properties of olefins, dienes, chlorinated, aromatic, heterocyclic, vinyl and acryl monomers are presented. During the interaction of cyclo-



R^1 = CH_3COO-, CH_3COOCH_2-, C_4H_9O-, CH_3OCO-
R^2 = H, CH_3

Scheme 6.



R^1 = CH_3, C_2H_5; R^2 = H, CH_3; X = Cl, Br

Scheme 7.

pentadiene with (M)AA in a closed system at increased temperature and in the excess of acids, in addition to cyclopentadiene condensation with acids, the addition of initial acids to bicylic unsaturated acids proceeds [33].

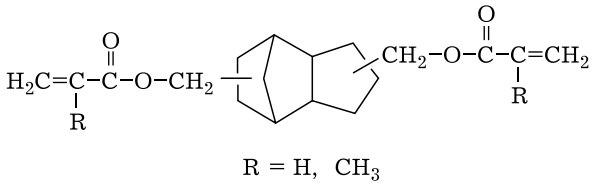
It is known that norbornenes substituted at position 2 by alkoxycarbonyl (ester) or phenyl group are sufficiently active in usual radical polymerization reactions. So, these monomers may be efficiently copolymerized with alkyl acrylates. In particular, as a result of the inclusion of norbornene structure into the main chain by means of radical copolymerization, the glass-transition temperature of the obtained copolymer is sometimes much higher (190–196 °C) than that of the homopolymer of polyalkylacrylates (8–10 °C) [34–37]. Considering this, we synthesized a number of compounds with norbornene skeleton and ester group. Diesters of norbornane-2,5-diol and oxy-acids of bicycloheptane were obtained in high yields through (M)AA addition to *exo*-5-methoxycarbonyl- [38], 5-acetoxy-, 5-acetoxymethyl- [39] and butoxybicyclo[2.2.1]hept-2-enes [40] in the presence of $BF_3 \cdot O(Et)_2$ catalysts (Scheme 6).

As a result of thermal and catalytic addition of (M)AA to 5-methyl-5-octyloxycarbonylnorborn-2-ene (MOCN), which was obtained as a result of the reaction of [4+2]-cycloaddition of cyclopentadiene to octylmethacrylate, at the reagents ratio (M)AA/MOCN = 2 : 1, temperature 140 °C and reaction time 3 h, 5-methyl-5-octyloxycarbonylnorborn-2-yl(meth)acrylates were synthesized in 75–82 % yield [41]. Investigation of the synthesis of bicyclic acrylates with conjugated cycles was carried out by German scientists Moszner N., Zeuner F., *et al.* They synthesized methyl-2-(bicyclo[3.1.0]hex-1-yl)acrylate from methyl-2-(cyclopenten-1-yl)-2-hydroxyacetate by means of cyclopropanation, followed by oxidation, and studied polymerization of this compound [42]. They synthesized a series of bicyclic acrylates and demonstrated their application as monomers for obtaining dental composites [43–45].

The authors of [46] described the method to synthesize tricyclodecanyl(meth)acrylate in two stages. At the first stage, 8-alkyl-8-tricyclodecanol is synthesized through the reaction of tricyclodecan-8-one with Grignard reagent. At the second stage, the alcohol formed at the first stage reacts with (meth)acryloylchloride (Scheme 7).

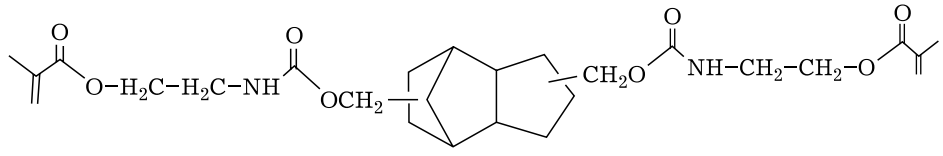
Patent [47] describes the synthesis of a new photosensitive monomer 8-methyltricyclo [5.2.1.$0^{2,6}$]-dec-8-ylmethacrylate. At the first stage, 8-methyltricyclo[5.2.1.$0^{2,6}$]decan-8-ol is obtained from tricyclic ketone in tetrahydrofuran in the presence of CH_3MgCl. At the second stage, the product of this reaction interacts with methacrylchloride.

In [48], Japanese scientists proposed the application of copolymers obtained on the basis of tricyclo[5.2.1.$0^{2,6}$]dec-3-en-8(9)-ylacrylate and other representatives of this class as film-forming agents in ink, adhesives, insulators, optically transparent sheets, as well as in semiconductor processes, in lithography, in manufacturing protective and dielectric coatings of the electronic parts of integrated circuits.



R = H, CH_3

Scheme 8.



Scheme 9.

New tricyclodecane-containing siloxan (meth)acrylates were obtained by the interaction of (M)AA with hydroxymethyltricyclo[5.2.1.$0^{2,6}$]-decanyl siloxanes. These compounds were proposed as monomers to manufacture materials for dentistry [49].

Patent [50] describes the studies in the area of synthesis of bi- and tricyclic (meth)acrylates. The addition of (M)AA to dicyclopentadiene was carried out in the presence of K-10 montmorillonite as catalyst at 90 °C for 6 h, and monomethyl ether of hydroquinone was used as inhibitor of polymerization. After reaction, the catalyst was removed by filtering, and catalyzate separation was performed by means of vacuum filtration. As a result, 11 wt. % of unreacted (M)AA, 22 % dicyclopentadiene, 6 % dicyclopentadiene oligomer, 0.6 % bis-adduct and 60 % tricyclo[5.2.1.$0^{2,6}$] dec-3-en-8(9)-ylacrylate were isolated.

The synthesis of tricyclic isocyanate (meth)acrylates in 70–90 % yields is described in patents [51–56]. It is demonstrated that these monomers possess high mechanical strength and can be used as solidifying agents (filling material) in dentistry.

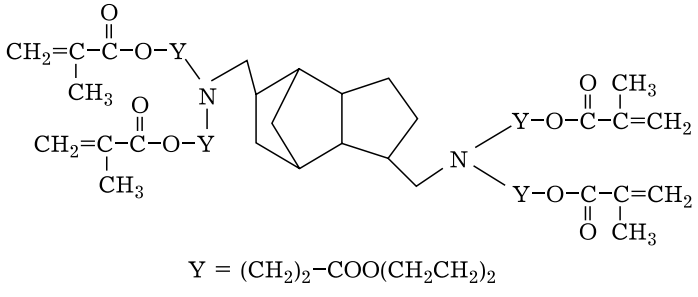
The author of [57] describes the synthesis of (meth)acrylic monomers with alicyclic structure (Scheme 8). The author proves that these compounds are reactive monomers, and demonstrates the application of polymers synthesized from these monomers as coatings.

In patent [58] tricyclic methacrylic esters with formylpiperazine group are proposed as an auxiliary component for collagen materials.

Winkel J. *et al.* obtained tricyclic nitrogen-containing methacrylates (Scheme 9) [59]. To carry out polymerization, methacrylate monomer was placed in a cylindrical glass bottle 3 cm in diameter, 2 % benzoylperoxide was added, and the mixture was kept for 80 °C for 1 h, and then at 130 °C for 15 min. Polymerization was also carried out with other initiators.

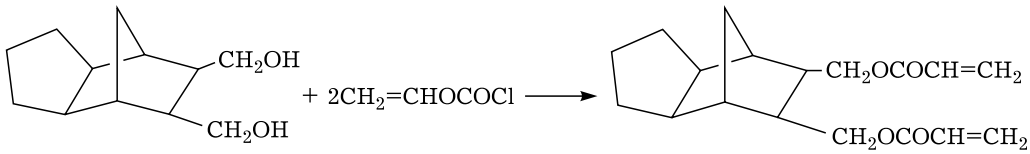
Moszner N. *et al.* synthesized nitrogen-containing derivative of tricyclo[5.2.1.$0^{2,6}$]decanylacrylate monomer (Scheme 10), which was proposed as a component for dental compositions [46, 60, 61].

Reactions of the synthesis of tricyclic (meth) acrylates through the interaction of acrylic and methacrylic acids with 5,6-dihydrotricyclodecadiene and polymerization of these compounds are described in European patent [62]. Polymers obtained on the basis of the indicated acrylates are used to prepare moisture-resistant dyes.



Y = $(CH_2)_2$–COO$(CH_2CH_2)_2$

Scheme 10.

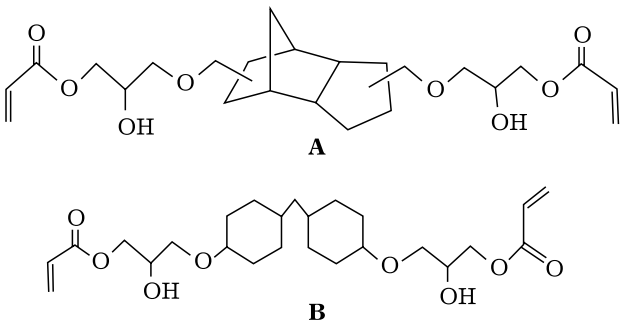


Scheme 11.

Suzuki H. *et al*. studied the interaction of (M)AA, acryl chloride and 2-chlorovinyl ether with 8,9-bis-hydroxymethyltricyclo[5.2.1.$0^{2,6}$]-decane in the presence of a catalyst leading to the formation of corresponding (meth)acrylates (Scheme 11) and demonstrated that these monomers may be used to make light-sensitive resins [63].

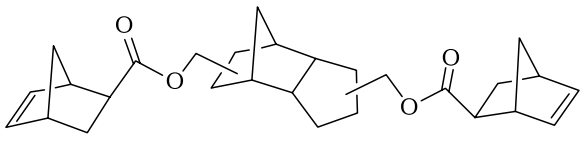
In [64], preparation of radical-solidified adhesive compositions, which included mono-, bi- or tricyclic (meth)acrylate component, as well as epoxidized alkyl and cycloalkyl bi- and tricyclic (meth)acrylate was described. Reaction products exhibit excellent stability against thermal decomposition.

German scientists synthesized diacrylates of diglycidyl ether of tricyclodecanedimethanol [65]. Epoxyacrylates of **A** and **B** types (Scheme 12) and mixtures of epoxyacrylates containing at least one of the compounds **A** or **B** are new and find application as coatings or adhesives with high stability against UV radiation.



Scheme 12.

An interesting research work was carried out to synthesize tricyclic ester (Scheme 13). For this purpose, 90 g of crystallized cyclopentadiene was slowly added into a dried round-bottomed flask with 175 g of tricyclodecane dimethanolacrylate. This solution was mixed at 55 °C for 20 h, and then excessive cyclopentadiene was removed by vacuum distillation. Thus obtained ester was used without additional purification [66].



Scheme 13.

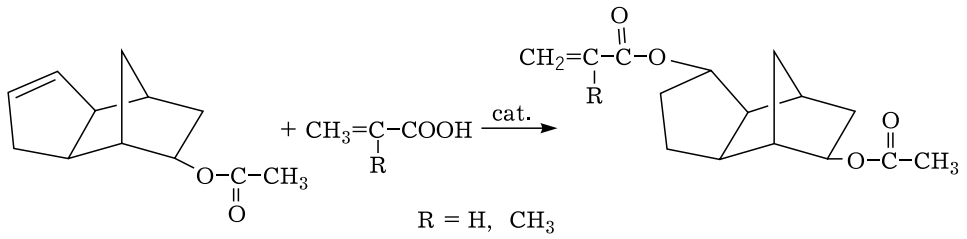
The synthesized tricyclic ester is applied to obtain polymers that are able to recover their shape after deformation or any other modifications, so-called polymers with shape memory. Polymer materials differing from each other in structure, with the shape memory effect, are widely used in medicine, dentistry and other areas. Tricyclo[5.2.1.$0^{2,6}$]-dec-3-en-8(9)yl(meth)acrylates were synthesized by us in high yields in the presence of catalysts: $BF_3 \cdot O(Et)_2$ and KU-2-8 [67, 68]. The reaction of thermal addition of (M)AA to tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene has been studied for the first time, optimal conditions were determined, and scientific foundations for technologically simple and waste-free synthesis of these monomers (in 81.8–96.0 % yield) were elaborated [69].

In the presence of the above-indicated catalysts, the synthesis of new monomers of tricyclic acrylates with acetoxy group (Scheme 14) was carried out [70].

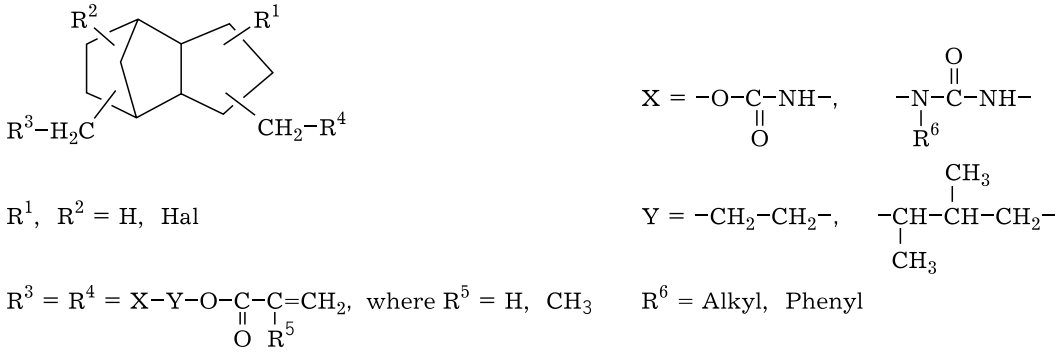
Highly branched methacrylate was synthesized by the interaction of technical-grade (4),8(9)-bis-(aminomethyl)tricyclo[5.2.1.$0^{2,6}$]decane with (acryloxy)ethylmethacrylate. The product is a monomer in composites for dentistry [71]. Polymeric compression is always observed in dental compositions obtained on the basis of methacryl esters of tricyclodecanes. Winkel J. *et al*. [59] synthesized new methacrylic derivatives (Scheme 15). Dental compositions in which these derivatives of (M)AA are initial materials exhibit substantially lower shrinkage during polymerization, so they are especially convenient for practical application.

The synthesis of (meth)acrylic esters of tricyclodecanediols is resented in patent [72], and the possibility of their application for making dental recovering materials and glue substances is indicated. The interaction of dicyclopentadiene with the esters of bicycloheptenecarboxylic acid with the formation of the ester of tetracyclododecenecarboxylic acid is described in [73]. Then the addition of acrylic acid to tetracyclic esters in the presence of concentrated sulphuric acid was carried out.

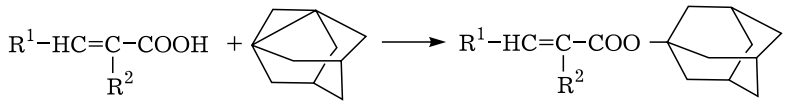
The authors of [74] studied the reaction of 1,3-dehydroadamantane with unsaturated acids



Scheme 14.



Scheme 15.



$R^1 = H$, $R^2 = H$ (1); $R^1 = H$, $R^2 = CH_3$ (2); $R^1 = C_6H_5$, $R^2 = H$ (3)

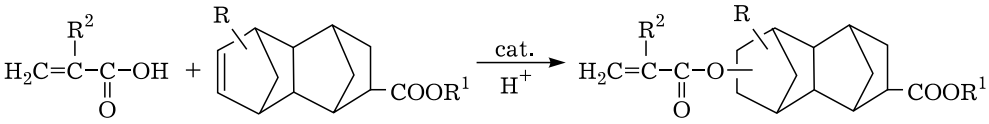
Scheme 16.

at a molar ratio of 1 : (1.5–2), and the corresponding monomers of adamantine acrylate were obtained (Scheme 16).

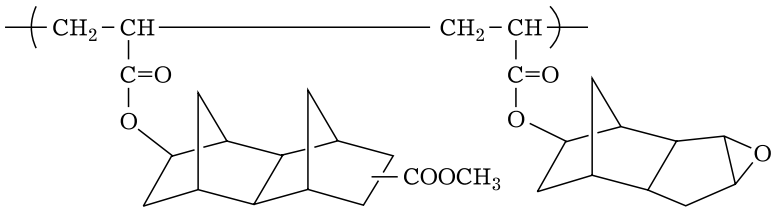
Inventions [75, 76] relate to the method of synthesis of 2-alkyl-2-adamantyl-(meth)acrylates from 2-alkyl-2-adamantanols, which were synthesized at 70–75 % yields and proposed as the material for obtaining resists intended for semiconductor lithography.

Various methods of obtaining adamantylacrylates are presented in [75–85]. These compounds may be used as the raw material for manufacturing the materials that are able to absorb electron beams and X-rays, and also for manufacturing optical lenses that do not transmit ultraviolet rays, and resists for lithography. Adamantan-containing methacrylates were synthesized by the interaction of 2-alkyl-2-adamantanols with the anhydride of methacrylic acid in tetrahydrofuran, and their application in laser photolithography was demonstrated [86].

Japanese scientists developed a two-stage method of obtaining the compounds of adamantyl-acrylate through the interaction of 2-adamantanone with alkyl halogenide in the presence of metal lithium particles, followed by the addition of acrylic ester in the presence of an inhibitor of polymerization containing nitroso group [78, 87]. The synthesized compounds of adamantly acrylate may also be used as the raw material for manufacturing resists for laser devices, X-ray radiation, *etc.* The method of synthesizing 2-alkyl-2-adamantyl esters [75] includes the interaction 2-adamantone and alkyl halogenide with lithium in a solvent to form lithium 2-alkyl-2-adamantyl alcoholate and the reaction of the latter with chloroanhydrides of (M)AA. The synthesized 2-C_1–C_6-alkyl-2-adamantyl (meth)acrylates are used as monomers to obtain polymers for photoresist compositions used in the production of semiconductor materials. Catalytic and thermal addition of acrylic acids to tetracyclo[4.4.$1^{2,5}$.$1^{7,10}$.$0^{1,6}$]-dodec-3-ene, its 8-methyl- and



Scheme 17.



Scheme 18.

acetoxy-substituted derivatives was used to synthesize the corresponding esters; the optimal reaction conditions were determined [88, 89].

The method of synthesizing tetracyclic (meth)acrylates that can be used as photosensitive resists is described in one of the American patents [73]. These compounds are synthesized in the presence of an acid catalyst through the addition of (M)AA to alkyl-substituted tetracyclododecenecarboxylic acids; initial compounds to synthesize these acids are alkylcyclopentadienes and esters of norbornenecarboxylic acids (Scheme 17).

Recent studies have shown that the new alicyclic acrylate polymers are widely used in various areas, in particular for making materials that do not transmit ultraviolet and radioactive rays [90–94]. Copolymers of tri- and tetracyclic acrylate monomers (Scheme 18) are used to manufacture liquid crystal displays [95].

Transparent resins for use in the production of liquid crystal displays for modern television sets and computer monitors are obtained on the basis of acetoxytetracyclo[4.4.0.1.^{2,5}1^{7,10}]-dodecylacrylate-3,4-epoxytricyclo[5.2.1.0^{2,6}]-decylacrylate [96]. The works of Japanese scientists [97–102] deal with the synthesis and applications of (co)polymers based on 3-oxycyclohexyl-, carboxytricyclo[5.2.1.0^{2,6}]-decylmethyl-, tricyclo[5.2.1.0^{2,6}]decanyl-, oxytricyclo[5.3.1.0^{6,10}]undecanyl-, tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodecylmethyl(meth)acrylates, adamantylmethacrylate and its 2-alkyl-2-derivative as chemically strengthened resists. These polymers are distinguished by high transparency, good adhesion to silicon substrates and the properties necessary for lithography [103–108].

APPLICATION OF POLYMERS BASED ON ACRYLIC MONOMERS

Cyclohexylacrylate is a component of the polymer mixture with high heat resistance for making shock-resistant [109] and frostproof [110] molded products for use in mechanical engineering. Acrylates with an alicyclic (norbornyl) part and a hydrophilic group, such as hydroxyl, ether, acetate, or γ-lactone, have been developed. Chemically reinforced resist compositions composed of a thermopolymer synthesized on the basis of these monomers exhibit high thermal stability and hydrophilic properties. The use of polynorbornylacrylate and oligocyclopentadiene as a highly efficient adsorbent for oil and oil products to collect them from water surface is demonstrated in [111]. Tricyclo[5.2.1.0^{2,6}]dec-3-en-8-ylacrylate, C_2–C_{36}-alkylacrylates and C_3–C_{12}-alkylmethacrylates in the form of various copolymers are included in elastomer-grafted polymers that are suitable for improving the quality of macromolecular materials [112]. Japanese scientists propose to use the polymers of tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-ylacrylate, 3,4-epoxytricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-ylacrylate and other representatives of this class as materials for coatings, ink, glues, insulators and optically transparent sheets. In addition, it is demonstrated that copolymers with 3,4-epoxytricyclo[5.2.1.0^{2,6}]decane structure are suitable for use in lithography, in semiconductor devices, as resins sensitive to radiation, as well as for devices with liquid crystal display, integrated circuits and solid displays [48]. Tricyclodecenylacrylate and tricyclodecenyloxyethylmethacrylate are the components of glue compositions [113], and functional bicyclic (meth)acrylates

with norbornyl or norbornadienyl group, as well as methacrylic esters of tricyclodecanediol are suitable as components for dental glues [72, 114].

The optical resinous material, which includes a polymer containing norbornylacrylate or methacrylate (or its derivatives) as the major component is characterized by excellent waterproof characteristics and can be used to form optical elements, such as lenses, optical discs, *etc.* [115, 116]. It is also demonstrated that polymers based on norbornene compounds with acryl groups exhibit excellent solubility and optical properties, and high transparency. They are suitable for the production of hybrid materials with high thermal stability and chemical resistance [117]. The new (meth)acrylates of siloxanes containing tricyclodecane groups were obtained through the reaction of poly(hydroxymethyltricyclo[5.2.1.$0^{2,6}$]-decanyl)siloxanes with M)AA. These compounds may also serve as monomers for making materials for dentistry [49].

Armah K. synthesized 3-(methacryloxymethyl)bicyclo[2.2.2]oct-2-ylmethacrylate and 3-(acryloxymethyl)-2-bicyclo[2.2.2]oct-2-ylacrylates, and investigated their properties. Polymers obtained on the basis of these compounds were proposed as a new generation of acryl monomers for 193-nm lithography due to their high thermal stability and resistance to plasma poisoning [118].

The authors of [119] obtained substituted 2-bicyclo[3.1.0]hex-1-ylacrylates from 1,6-enines with propargyl carbonates in the presence of palladium catalyst. It is shown that these compounds are new monomers for the synthesis of polymers.

CONCLUSION

Thus, it is clear from the presented review that acrylic and methacrylic monomers find broad applications in obtaining polymer products. In view of the significant practical importance of (meth) acrylates, a permanent trend to improve the methods of their synthesis is implemented, and intense search for the development of efficient and improved synthesis methods is carried out. Comparative analysis of the works in this direction shows that reactions involving addition of acrylic acids to cycloolefine hydrocarbons are ecologically and economically more favourable than esterification reactions.

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