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*Review*

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**Abstract:** In recent years, polymer chemistry has experienced an intensive development of a new field regarding the synthesis of aliphatic and aromatic biobased monomers from renewable plant sources. A one-step process for the synthesis of new vinyl monomers by the reaction of direct transesterification of plant oil triglycerides with N-(hydroxyethyl)acrylamide has been recently invented to yield plant oil-based monomers (POBMs). The features of the POBM chemical structure, containing both a polar (hydrophilic) fragment capable of electrostatic interactions, and hydrophobic acyl fatty acid moieties (C15-C17) capable of van der Waals interactions, ensures the participation of the POBMs fragments of polymers in intermolecular interactions before and during polymerization. The use of the POBMs with different unsaturations in copolymerization reactions with conventional vinyl monomers allows for obtaining copolymers with enhanced hydrophobicity, provides a mechanism of internal plasticization and control of crosslinking degree. Synthesized latexes and latex polymers are promising candidates for the formation of hydrophobic polymer coatings with controlled physical and mechanical properties through the targeted control of the content of different POBM units with different unsaturations in the latex polymers.

**Keywords:** Biobased polymers; plant oil-based monomers; mixed micelles; methyl-β-cyclodextrin inclusion complex; emulsion polymerization.

## 1. Introduction

The problem of depletion of fossil raw materials has become of global importance and is complicated not only by economic but also environmental and political factors [1]. However, synthetic polymers are still one of the most widely used materials in everyday use. Environmental analysis shows that huge amounts of plastic waste are found in the environment, and their contribution to the ever-increasing amount of solid waste is a significant environmental threat [2]. Plant oils are low-cost raw materials for the manufacture of monomers and polymers [3-5], which have several advantages over conventional polymeric materials, namely biodegradability, non-toxicity, biocompatibility, and hydrophobicity. Therefore, an important task for synthetic chemists is to consider renewable raw materials as an alternative to raw counterparts of fossil origin. Due to the wide range of plant oils, the variety of their chemical compositions, and, in many cases, abandon of resources, they became an interesting object to be used in polymers synthesis as a renewable raw material.

The total production of plant oils in the world in 2019 amounted to more than 200 million tons, of which about 15% are used as raw materials for the synthesis of new chemical compounds and materials [6]. The presence of plant oils or their derivatives (fatty acids) in various compositions of polymeric materials improves their optical (gloss), physical (flexibility, adhesion) [7,8], and chemical (resistance to water and chemicals) properties [9]. The synthesis of biobased monomers from renewable resources is a promising platform for the synthesis and implementation of new environmentally friendly industrial polymer materials [10]. It should be noted that methods for the synthesis of vinyl monomers based on soybean, olive, and linseed oils through plant oil direct transesterification with N-(hydroxyethyl)acrylamide [10-12] has been recently developed along with methods of their copolymerization [13]. The ability of these plant oil-based monomers (POBMs) to undergo free radical (co)polymerization reactions has been confirmed and demonstrated [11,13,14]. The conversion, polymerization rate, and molecular weight of the polymers have been shown to depend on unsaturation of the plant oil chosen for POBMs synthesis [11,13].

## 2. Features of Synthesis of Vinyl Monomers from Plant Oils

Harrison and Wheeler have shown for the first time [15] that the polymerization rate decreases with increasing unsaturation degree of acrylates containing acyl moieties of unsaturated fatty acids. They explained that the retarding of the polymerization rate and the low conversion are due to the interaction of radicals with the mobile hydrogen atoms in the acyl moieties. This leads to the formation of new allylic radicals of low activity which retards propagation of polymer chains (chain transfer reaction, retardation of the process) [15].

Through the esterification reaction of fatty alcohols with acryloyl chloride, Chen and Bufkin synthesized a range of acrylates, including linoleyl acrylate, oleyl acrylate, and lauryl acrylate, and studied their copolymerizability. They showed that the presence of fatty fragments in acrylate molecules determines their polarity, which leads to alternating copolymerization with methyl methacrylate [16].

In their next study [17], Chen and Bufkin confirmed the results of Harrison's research [15] and showed that the presence of fatty acid moieties in the structure of the new acrylates leads to a decrease in both the polymerization rate and polymer molecular weights because of chain transfer reactions. Increasing the content of unsaturated acyl groups in the copolymer also reduces its glass transition temperature. The authors suggested the mechanisms for crosslinking acrylate copolymers and studied their physical and mechanical properties [17].

Through amidation of triglycerides with amino alcohols, natural derivatives of surfactants and lubricants were obtained [18].

Tang et al. [19] reported on the synthesis of N-hydroxyalkylamides and methacrylate hydrophobic monomers through the interaction of plant oil triglycerides with amino alcohols (Figure 1). They developed a new interesting approach that involves the use of a two-step process. In the first stage, the interaction of triglycerides with amino alcohols with the formation of N-hydroxyalkylamides by the amidation reaction:

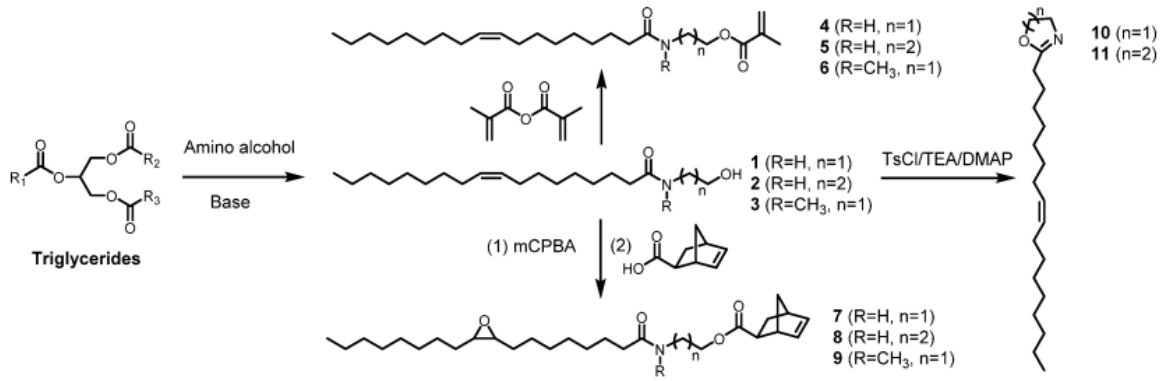


**Figure 1.** Transformation of triglycerides in N-hydroxyalkylamides and methacrylate monomers. Reprinted with permission from [19]. Copyright (2015) American Chemical Society.

Aminoalcohols, namely ethanolamine (R = H, n = 1), 3-amino-1-propanol (R = H, n = 2), and N-methylethanolamine (R = $CH_3$, n = 1), were used as chemicals which enables the synthesis of a wide range of new monomers. In the second stage, the corresponding monomers were synthesized by the interaction between N-hydroxyethylamides R'–C(O)–N(R)–$(CH_2)_n$–$CH_2OH$ and methacrylic anhydride. In such a way, methacrylate monomer based on high oleic soybean oil was synthesized:

$$CH_2=C(CH_3)–C(O)–O–CH_2–(CH_2)_n–N(R)–C(O)–(CH_2)_7–CH=CH–(CH_2)_7–CH_3.$$

A study of free radical polymerization of these monomers revealed that the double bonds in the fatty acid chains remain unaffected during the reaction. The synthesized methacrylate monomers based on high oleic soybean oil, depending on the nature of the branches in the side chain, have a wide range of glass transition temperatures [19]. In further studies, Tang and co-authors used more than twenty amino alcohols to establish the mechanism of amidation of plant oils, in particular high-oleic soybean oil [8]. Depending on the nature of the acyl fatty acid and amide structures, the polymers have a wide range of glass transition temperatures – from viscoelastic to thermoplastic materials. The possibility of controlled hydrogenation of unsaturated double bonds was also shown, which provides control over thermal and mechanical properties of polymers [8].

It was demonstrated that the high reactivity of the vinyl group of the acrylate monomers based on plant oils determines the course of their polymerization and copolymerization by a free radical mechanism [20]. Caillol et al. [21,22] proposed methods for the synthesis of a new monomer from cardanol (Figure 2), which is isolated from cashew nuts. Reactivity of the cardanol-based monomer in the copolymerization reactions with the POBMs was studied [23].

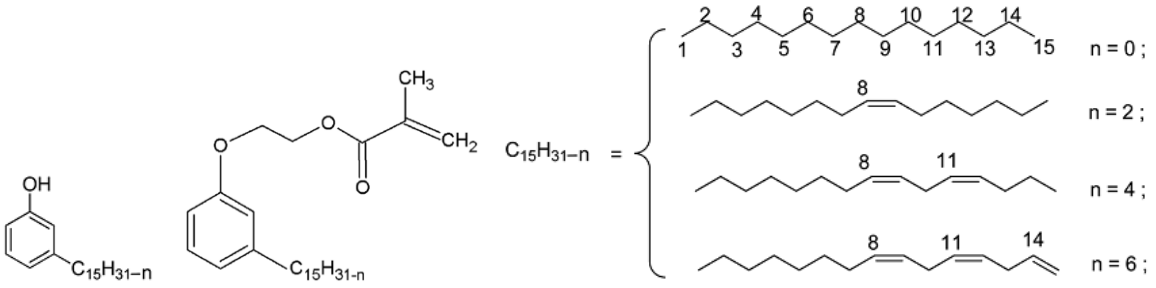


**Figure 2.** Structure of cardanol and a cardanol-based monomer. Adapted from Ref. 21 with permission from The Royal Society of Chemistry.

Cardanol-based polymers have a controlled flexibility due to "internal plasticization", which occurs due to the presence of a long side chain. The presence of these fragments also provides polymeric materials based on cardanol with hydrophobic properties. It should be noted that cardanol exhibits antimicrobial and anti-thermite properties and, under certain conditions, can provide them to copolymers based on it. It is compatible with a wide range of polymers, such as alkyds, melamines, polyesters, *etc.* [21].

In the study [22], synthetic pathways to molecular blocks from cardanol by one- or two-stage methods were reported. In particular: 1) dimerization/oligomerization of cardanol, to increase its functionality; 2) synthesis of reactive amines by thiol-ene coupling; 3) epoxidation and (meth)acrylation of cardanol for the synthesis of polymers and materials with oxirane or (meth)acrylate groups.

A feature of cardanol-based monomers and polymers is the presence of aromatic fragments and fatty moieties in their structure at the same time. The authors showed that cardanol-based polymeric materials have prospective properties for manufacturing coatings, in particular, with enhanced mechanical and thermal properties [22].

Recently, methacrylated ricinoleic acid monomer (Figure 3) was synthesized by the esterification reaction of ricinoleic acid with 2-hydroxyethyl methacrylate [24]:

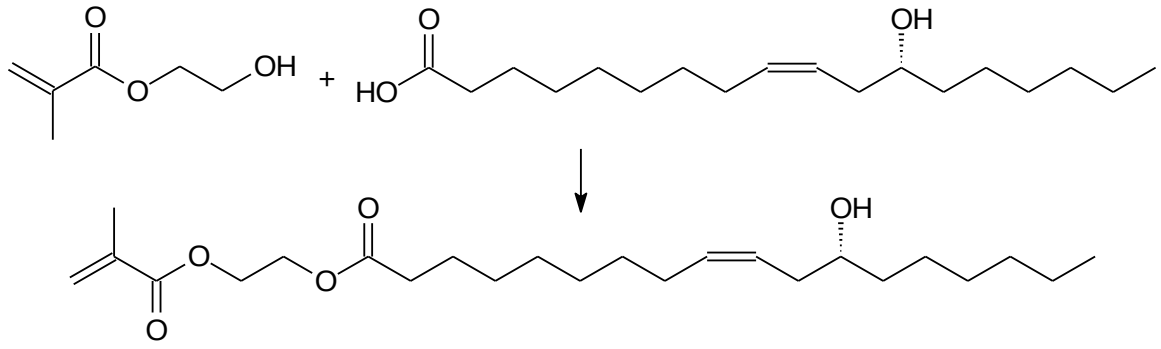

**Figure 3.** Schematic of synthesis of methacrylated ricinoleic acid monomer [24].

It should be noted that all known methods for the synthesis of monomers from plant oil triglycerides are multi-stage and involve several steps, which makes their implementation in industry more challenging.

Recently, we developed a one-step process for the synthesis of new vinyl monomers by the direct transesterification reaction of plant oil triglycerides with N-(hydroxyethyl)acrylamide (Figure 4) [12,25].

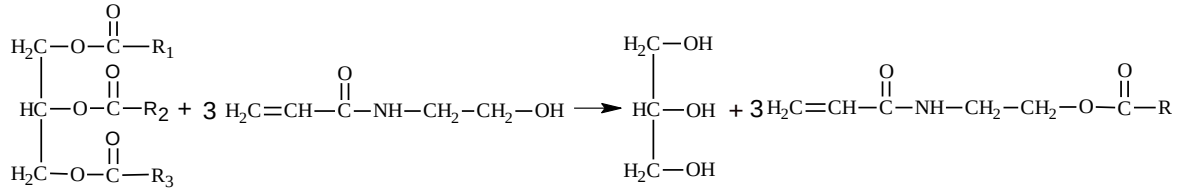

**Figure 4.** Schematic of synthesis of acrylic monomers based on plant oil triglycerides where $R_1$, $R_2$, $R_3$ are saturated and unsaturated fatty acid chains with one or several double bonds. Reprinted with permission from [10]. Copyright (2015) American Chemical Society.

Using this process, a range of plant oil-based monomers – POBMs was synthesized by the direct transesterification reaction between N-(hydroxyethyl)acrylamide and plant oil triglycerides (Figure 4) [10,11]. In the reaction, N-(hydroxyethyl)acrylamide can be considered as an alcohol ROH – where the unsaturated fragment $CH_2$=CH–C(O)–NH–$CH_2$–$CH_2$– is a residue –R. Upon the alcoholysis (transesterification), a residue exchange between the triglyceride and N-(hydroxyethyl)-acrylamide occurs leading to formation of the corresponding monomers.

The POBMs synthesis was conducted in THF with an excess of N-(hydroxyethyl)acrylamide (molar ratio of N-hydroxyethylacrylamide to triglyceride as 5.9: 1) in order to achieve complete transesterification of the triglycerides. The yield of the desired monomers was about 94-96%. The reaction by-product (glycerol) and the excessive (N-hydroxyethyl)acrylamide are easily removed by washing with brine after diluting the reaction mixtures with $CH_2Cl_2$. The POBMs sparingly soluble in water remain in the organic phase. To avoid free radical polymerization, 2,6-di-*tert*-butyl-p-cresol (0.05 to 0.1% by weight) was added as an inhibitor to the reaction mixtures prior the synthesis.

Upon the alcoholysis of olive oil with N-(hydroxyethyl)acrylamide, 2-N-acryloylaminoethyl oleate is predominantly formed:

$$CH_2=CH–C(O)–NH–CH_2CH_2–O–C(O)–(CH_2)_7–CH=CH–(CH_2)_7–CH_3$$

This monomer contains one double bond in the acryloylamide moiety and one double bond in the fatty acid chain. Such a structure, in comparison with the soybean oil-based monomer – 2-N-acryloylaminoethyl linoleate:

$$CH_2=CH–C(O)–NH–CH_2CH_2–O–C(O)–(CH_2)_7–CH=CH–CH_2–CH=CH–CH_2–(CH_2)_3–CH_3$$

reduces the extent of the chain transfer reaction. Accordingly, fewer less active radicals are formed and the polymerization reaction proceeds to higher conversion with a less pronounced retardation effect. This leads to the formation of polymers (copolymers) with a higher molecular weight and a lower polydispersity index.

The composition of plant oils is known to depend on the type of crop raw material. Therefore, an important step was to determine the content of different fatty acid chains in the mixture of monomers obtained upon the transesterification of olive oil with N-(hydroxyethyl)acrylamide. The content of fatty acid chains in the oil was determined from the integral intensities of the characteristic proton signals of each fatty acid chain and glycerol fragments using $^1$H NMR spectroscopy of the plant oil [26] (Figure 5).

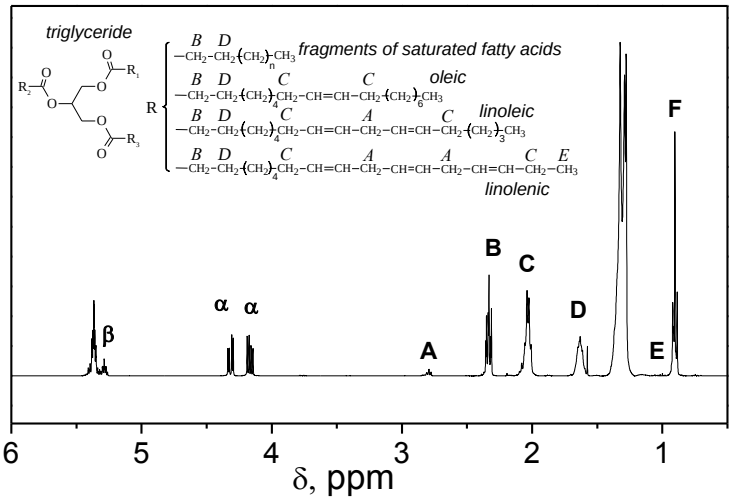


**Figure 5.** $^1$H NMR spectrum of olive oil. Adapted with permission from [11]. Copyright (2016) American Chemical Society.

The content of the linolenic acid units (linolenate) in olive oil was calculated by measuring the integral value of the signal at 1 ppm, which corresponds to the protons of the methyl group in a linolenic acid chain (signal E in Figure 5). Taking into account only one of the signals of α-protons of glycerol, *i.e.* the signal at 4.27 ppm (Figure 5), the ratio of the integral values is two α-glycerol protons to three protons of the linolenic acid methyl group. It should be kept in mind that three linolenic acid chains can undergo transesterification in the same glycerol molecule. A field correction factor is the ratio of two protons of glycerol to nine protons of the linolenic acid methyl groups. By converting the ratio of these areas to percentages, a ratio of 22.2% glycerol to 100% linolenic acid was obtained [26]. Calibration of the integral value of one of the glycerol α-proton signals to the value in the $^1$H NMR spectrum in the signal region at 0.98 ppm directly gives the percentage of linolenic acid in the sample – 0.73%.

The percentage of linoleic acid chains (linoleates) in olive oil was determined from the ratio of the integral value of the signal at ~ 2.74 ppm, which corresponds to the methylene protons between two double bonds (signal A in Figure 5), to the integral value of one of glycerol α-protons. The field correction factor (33.3) is the ratio of two glycerol protons to six possible methylene protons in linoleate. The amount of linoleic acid is calculated by subtracting the twiced content of linolenic acid, determined from the peak at 2.74 ppm [26].

The percentage of oleic acid chains (oleates) was determined from the ratio of the integral value of the signal at ~ 2.02 ppm, which corresponds to the protons in the α-position to the double bond of all unsaturated fatty acids (signal C in Figure 5), to the integral value of one of glycerol α-protons. Accordingly, the ratio of two glycerol protons to twelve possible protons in the α-position to the double bond of all unsaturated fatty acids is the field correction factor equal to 16.7. The percentage of oleic acid was calculated by subtracting the content of unsaturated linolenic and linoleic acid chains from the determined value [26].

The content of saturated fatty acid chains was determined from the fact that the total content of fatty acids is 100%, and the amount of unsaturated fatty acid chains was subtracted from 100%. The determined content of fatty acid chains is given in Table 1. These data are in a good agreement with the literature data obtained by gas chromatography of olive oil [27].

Thus, according to $^1$H NMR spectroscopy, the olive oil triglycerides include: saturated fatty acid chains (C18:0) – 12.44%; oleic acid chains (C18:1) – 80.23%; linoleic acid chains (C18:2) – 6.60%; and linolenic acid chains (C18:3) – 0.73%.

**Table 1.** Content of fatty acid chains in olive oil.

| Fatty acid chains | Signal (protons) | Field correction factor | | Content of fatty acids in the oil, % | |
|---|---|---|---|---|---|
| | | | % | Calculated | Literature data |
| linolenate (E) | 0.95-1.05 ppm (-C**H**$_3$) | 2H/9H | 22.2 | **0.73** | < 1 % |
| linoleate (A) | 2.75-2.85 ppm (-CH=CH-C**H**$_2$-CH=CH-) | 2H/6H | 33.3 | 8.06 - 2·0.73 = **6.6** | 3.5-21 |
| oleate (C) | 1.97-2.11 ppm (-C**H**$_2$-CH=CH-C**H**$_2$-) | 2H/12H | 16.7 | 87.56–(0.73+6.6)==**80.23** | 55-83 % |
| Content of saturated fatty acid chains: | | | | 100–(0.73+6.6+80.23)=**12.44** | 1-20 % |

These results are consistent with the literature data obtained by gas chromatography of olive oil, where the saturated chains make up 1-20%, oleic acid chains 55-83%, linoleic acid chains 3.5-21%, and linolenic acid chains less than 1% [28]. Using this approach, monomers based on various plant oils were successfully synthesized and characterized (Table 2).

**Table 2.** Physico-chemical characteristics of POBMs.

| Monomer from Oil | Content of unsaturated fatty acids, % | | | Iodine value (same for oil), g/g | Molar mass, g/mol |
|---|---|---|---|---|---|
| | $C_{18:1}$ | $C_{18:2}$ | $C_{18:3}$ | | |
| High Oleic Sunflower Oil (HOSFM) | 86-89 | 3-6 | 0.5-1 | 105 (82) | 379.0[1] |
| Olive Oil (OVM) | 65-85 | 3.5-20 | 0-1.5 | 110 (90) | 379.3[2] |
| High Oleic Soybean Oil (HOSBM) | 70-73 | 13-16 | 0-1 | 124(105) | 379.3[2] |
| Canola Oil (CLM) | 60-63 | 18-20 | 8-10 | 137 (96) | 379.0[2] |
| Corn Oil (COBM) | 23-31 | 49-62 | 0-2 | 139 (120) | 377.0[1] |
| Sunflower Oil (SFM) | 14-35 | 44-75 | 0-1 | 146 (128) | 377.5[2] |
| Soybean Oil (SBM) | 22-34 | 43-56 | 7-10 | 149 (139) | 377.3[2] |
| Linseed Oil (LSM) | 12-34 | 17-24 | 35-60 | 194 (177) | 375.6[1] |

[1]Calculated.[2]Experimental.

The monomer structure was confirmed by FTIR and $^1$H NMR spectroscopy [11]. A $^1$H NMR spectrum of the olive oil-based monomer is shown in Figure 6 where the characteristic peaks at 6.6 ppm indicate the presence of an acryloylamide moiety (protons of the acrylic double bond) whereas the peaks at 3.6 and 4.2 ppm correspond to the protons of two methylene groups between the amide and ester groups. Similar spectra are recorded for other POBMs, which confirms the presence of the similar acryloylamide moiety (protons of the vinyl double bond) in their molecules. This allows for predicting similar reactivity of the vinyl group in the monomers acryloylamide moiety in the radical polymerization [11].

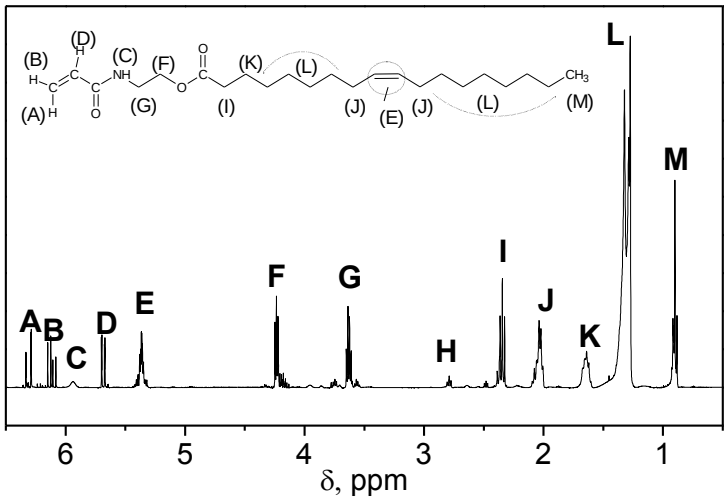


**Figure 6.** $^{1}$H NMR spectrum of the olive oil-based monomer. Adapted with permission from [11]. Copyright (2016) American Chemical Society.

The peaks in the range from 0.8 to 2.8 ppm correspond to the fatty acid chain protons. The peaks at 5.3 – 5.44 ppm imply the presence of protons at the carbon-carbon double bonds in the fatty acid chain. The peaks at 1.98 – 2.14 ppm indicate the presence of protons in the α-position to the double bond (allylic hydrogen), capable of the chain transfer reaction and the formation of less active free radicals [11].

According to the FTIR spectroscopy data, the appearance of the strong absorption bands at 3400 – 3200 cm$^{-1}$ (NH bonds), at 1670 cm$^{-1}$ (the carbonyl group, amide I), and at 1540 cm$^{-1}$ (NH, amide II) in the spectra of the POBMs (*e.g.*, the olive monomer – Figure 7) indicates the addition of fatty acid acyl moieties to the acrylamide fragment. The absorption bands at 1740, 1245, and 1180 cm$^{-1}$ confirm the presence of an ester group in the monomer molecule. The absorption bands at 1665–1635 cm$^{-1}$ indicate the presence of a carbon-carbon bond double in the fatty acid chains [11]. FTIR spectra of monomers based on other plant oils are pretty similar. Hence, the synthesized POBMs can be attributed to the conventional vinyl monomers because the acryloylamide moiety provides the participation of these monomers in the free radical polymerization.

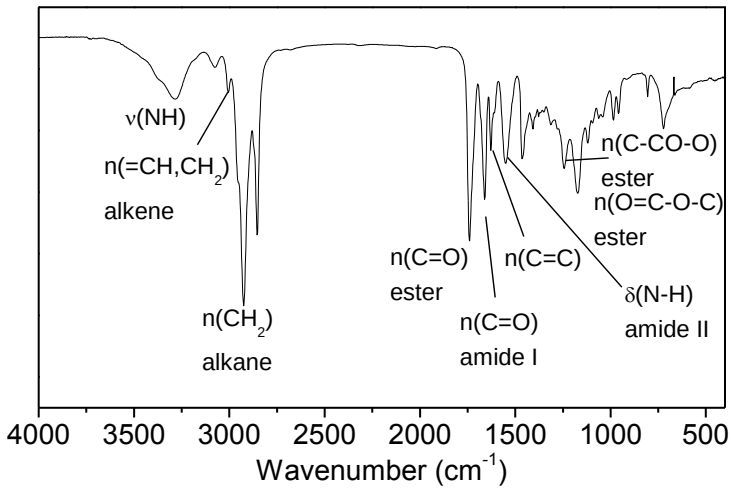


**Figure 7.** FTIR spectrum of the olive oil-based monomer. Adapted with permission from [11]. Copyright (2016) American Chemical Society.

The content of fatty acid chains in the monomer mixture produced by the transesterification of plant oils with N-(hydroxyethyl)acrylamide was determined on the example of the olive monomer by calculating the ratio of the integral values in the $^{1}$H NMR spectra of the commercial oil and the resulting monomer mixture (Figure 8).

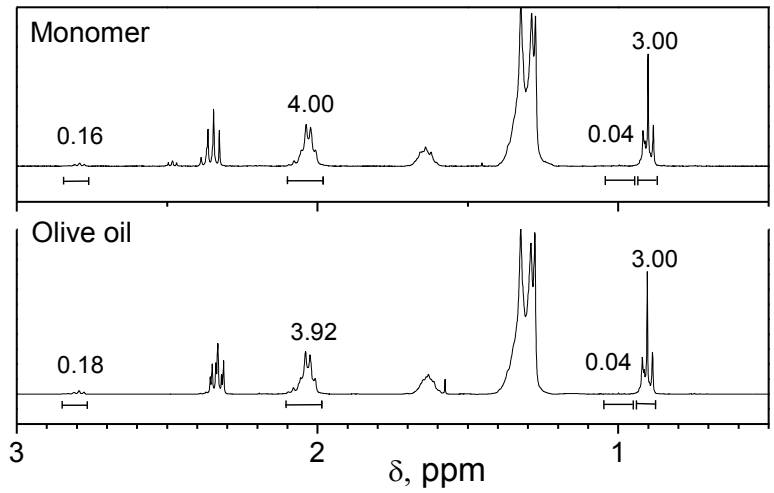


**Figure 8.** $^{1}$H NMR spectra of the olive oil and the olive oil-based monomer.

According to the $^{1}$H NMR spectroscopy data, the monomer mixture consists of: saturated fatty acid chains (C18:0) – 11.47% (stearic and palmitic); oleic acid chains (C18:1) – 81.9%; linoleic acid chains (C18:2) – 5.9%; and linolenic acid chains (C18:3) – 0.73% after the olive oil transesterification.

Thus, the major component of the olive monomer is a monomer with oleic acid chains (81.9%) – 2-N-acryloylaminoethyl oleate. The soybean monomer is mainly a monomer with linoleic acid chains (57.5%) – 2-N-acryloylaminoethyl linoleate whereas the linseed monomer predominantly consists of a monomer with linolenic acid chains (58%) – 2-N-acryloylaminoethyl linolenate.

One of the most important characteristics of monomers is the unsaturation degree, which for POBMs is determined by the number of the double bonds in the fatty acid chains. To compare the monomers in terms of the unsaturation degree, their iodine values were determined and compared with those for the corresponding plant oils used for the synthesis of the POBMs (Table 2). The obtained results show that the iodine value for the monomers is higher than those for the oils, due to the presence of an unsaturated acryloylamide moiety. Depending on the type of oil, the iodine values for various monomers differ. For instance, the iodine value for 2-N-acryloylaminoethyl oleate (110 g / 100 g) is significantly lower than that for 2-N-acryloylaminoethyl linoleate (149 g / 100 g) due to the different unsaturation degree of the molecules. Besides the acryloylamide moiety, there are two double bonds in the fatty acid chain of the soybean monomer molecule [10]. The low solubility of these monomers in water implies their **highly hydrophobic** nature [11].

Analysis of the data obtained from the synthesis and characterization of plant oil-based acrylic monomers allows for drawing the POBM general formula (Figure 9) as:

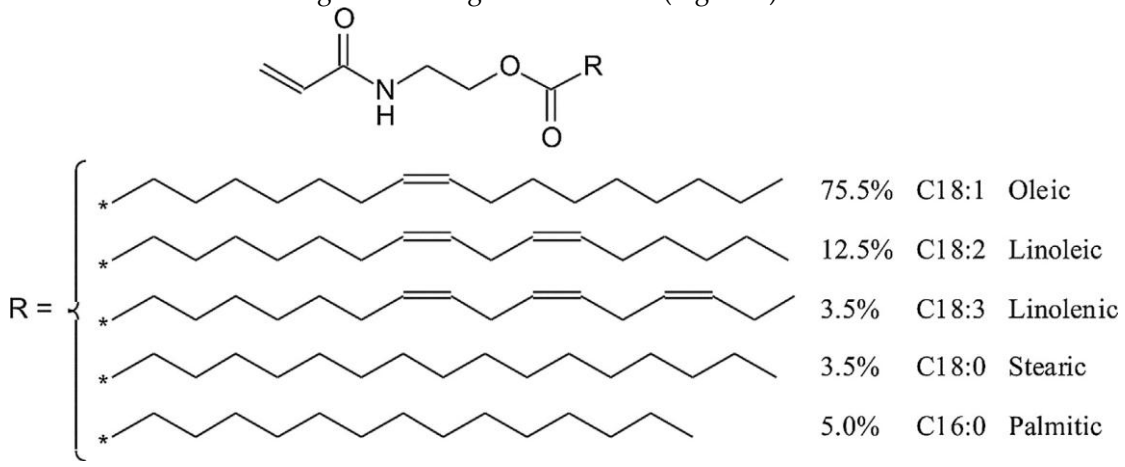


**Figure 9.** General formula of the plant oil-based monomers. Reprinted from Ref. 35, Copyright (2018), with permission from Elsevier.

## 3. Features of Homo- and Copolymerization of Plant Oil-Based Acrylic Monomers

The reactivity of the plant oil-based monomers in the free radical polymerization reactions (chain growth reaction) is determined by the presence of an acryloylamide moiety containing a vinyl group which is common for all monomers. However, the POBMs contain a certain amount of unsaturated fatty acid chains of various structure (the different numbers of both double bonds and hydrogen atoms in the α-position to the double bonds). This causes the monomers to participate in chain transfer reactions due to the abstraction of the allylic hydrogen atoms and the formation of less active radicals. Hence, the monomer chain transfer constants $C_M$ clearly depend on monomer structure as follows: 0.033 (most unsaturated LSM) > 0.026 (SBM) > 0.023 (SFM) > 0.015 (least unsaturated OVM) with respect to decreasing number of C−H groups in the α-position of the fatty acid double bonds) [11]. This impacts the polymerization conversion and molecular weights of the resulting polymers (copolymers) from the POBMs.

The features of **homopolymerization** kinetics for 2-N-acryloylaminoethyl oleate revealed that the orders of reaction with respect to monomer and initiator are 1.06 and 1.2, respectively. The unsaturation degree of fatty acid chains in the POBM molecules was used as a criterion for comparing the kinetic data of homopolymerization of 2-N-acryloylaminoethyl oleate and 2-N-acryloylaminoethyl linoleate. The observed deviations of the orders of reaction are due to the specific mechanism of the homopolymerization reaction of 2-N-acryloylaminoethyl oleate which includes two simultaneous reactions (chain propagation and transfer) [11]. Although the propagating radicals might be very reactive, once the chain is transferred to the allylic C−H, the newly formed radical becomes more stable due to resonance stabilization and does not readily initiate new chains. In comparison with the soybean monomer, the olive monomer is less involved into the chain transfer reactions (the chain transfer constant $C_M$ = 0.015 for OVM while for SBM $C_M$ = 0.026). As a result, the homopolymerization of the olive monomer occurs at a higher rate of 12.2 - 45.3 $\cdot$ $10^{-5}$ mol/(L $\cdot$ s) when compared with the more unsaturated soybean monomer - 4.3 - 11.3 $\cdot$ $10^{-5}$ mol/(L $\cdot$ s). The molecular weights of the homopolymers were determined by gel permeation chromatography. The resulting homopolymers from OVM have higher number average molecular weights and lower polydispersity indexes (16 800–23 200 g/mol for 2-N-acryloylamino-ethyl oleate compared to 13 600–14 300 g/mol for 2-N-acryloylaminoethyl linoleate).

The reactivity of the plant oil-based monomers in chain **copolymerization** was studied in POBMs reactions with styrene and vinyl acetate. A characteristic feature of the POBMs is the presence of the acryloylamide fragment ($CH_2$=CH–C(O)–NH–$CH_2$–$CH_2$–) in their structure, which determines the monomer reactivity in copolymerization. The composition of the copolymers was determined from $^1$H NMR spectroscopy data. Radical copolymerization of the plant oil-based monomers is described with the classical Mayo–Lewis equation. The Alfrey−Price Q (0.41−0.51) and e (0.09−0.28) parameters are close for all POBMs and do not essentially depend on the monomer structure [13]. This is due to the presence of the same acryloylamide moiety in the POBM molecules which determines the monomer reactivity in polymerization reactions.

The features of copolymerization are determined by the structure of monomers based on plant oil triglycerides along with the degradative chain transfer by formation of less active radicals. Nevertheless, the growth of macrochains can be described with the conventional features of chain copolymerization, yielding copolymers with a potential to be used in a broad variety of applications.

Vinyl monomers from plant oils that have different degrees of unsaturation, soybean and olive oils, were copolymerized in emulsion with styrene to investigate the kinetics features and feasibility of latex formation. The kinetics of emulsion copolymerization of styrene with the olive and soybean monomers agree with the Smith-Ewart theory since the number of nucleated latex particles is proportional to the surfactant and initiator concentration to the powers 0.58–0.64 and 0.39–0.46, respectively [29]. Copolymerization of styrene with plant oil-based monomers follows the typical phenomenology for emulsion polymerization of hydrophobic monomers with a micellar nucleation mechanism. When the POBMs were copolymerized in emulsion with significantly more water soluble comonomers, methyl methacrylate and vinyl acetate, latex particle nucleation mainly occurred through homogeneous mode. For the emulsion copolymerization of methyl methacrylate

with OVM and SBM, the reaction orders with respect to emulsifier and initiator are 0.33–0.67 and 0.56–0.69, respectively. It was shown that upon adding the highly hydrophobic POBMs into the monomer mixture, the latex polymer particles originating from micellar nucleation essentially increases [14].

Using emulsion and miniemulsion copolymerization of the olive and soybean monomers with styrene or methyl methacrylate, stable aqueous dispersions of polymers with latex particle sizes of 40–210 nm were produced. The content of the POBM units in the macromolecules of the latex polymers is 5–60 wt.%. The average molecular weight of the synthesized polymers varies in the range of 30 000–391 500. It was found that the molecular weight of the latex copolymers decreases with increasing unsaturation degree of the POBMs and their content in the reaction mixture, which is explained by degradative chain transfer to unsaturated fatty acid chains [14,29].

An analysis of the literature shows a rapid development of a new branch in polymer science related to the chemistry of aliphatic and aromatic biobased monomers from renewable plant sources. The synthesis of such monomers allows for producing fully biobased polymers with biocompatible and biodegradable properties which do not pollute the environment. Copolymerization of monomers synthesized from various plant oils, which have different unsaturation, enables formation of copolymers with side branches of the macrochain with different unsaturation degrees. A large variety of the POBMs allows to synthesize polymers having moieties with different unsaturation, and to make coatings with adjustable cross-linking degree thereof, including latex copolymers from fully biobased monomer mixtures [23]. Remarkably, copolymerization of the POBMs with commercial vinyl monomers enables synthesis of polymers with enhanced hydrophobicity along with the mechanism of internal plasticization.

Synthesized latex polymers and copolymers are prospective candidates for the formation of moisture-/water-resistant polymer coatings with controlled physical and mechanical properties using controlled content of incorporated POBM units with different unsaturation in the latex structure.

## 4. Preparation of Polymeric Coatings from Plant Oil-Based Monomers

As shown by Solomon [30], both crude and modified plant oils are common film-forming materials for the production of paints and varnishes. Despite the emergence of various synthetic polymers based on vinyl and acrylic monomers, crude plant oils are still the basis of some paints for painting the roofs of houses and other outdoor objects. One of the disadvantages of such materials is the slow drying and relatively low moisture resistance. The synthesis of plant oil-based acrylic monomers opens new avenues for producing homo- and copolymers thereof with adjustable physical and mechanical properties (*e.g.*, flexibility, strength, *etc.*) due to formation of three-dimensional networks with controlled cross-linking density. The development of such coatings was shown to be carried out through oxidative cross-linking of the polymer network [31].

It should be noted that upon POBM application for the synthesis of latex polymers as highly hydrophobic film-forming protective coatings, they form three-dimensional networks with adjustable cross-linking density through the oxidative cross-linking mechanism.

Triglycerides of linseed oil contain about 52% of linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acid chains which have three isolated carbon-carbon double bonds in their structure (Figure 10). Other fatty acids in linseed oil are oleic (*cis*-9-octadecenoic, 22%) and linoleic (*cis*,*cis*-9,12-octadecadienoic, 16%) acids. Hence, linolenate is a major constituent of LSM.

**Oxidative cross-linking** of the LSM-based copolymers is a free radical chain process consisting of chain initiation, propagation, and termination steps. Initiation, *i.e.* the formation of a fatty acid chain radical, can occur by thermal homolytic cleavage of a C–H bond or by a hydrogen atom abstraction from C–H by an initiator free radical. The bond dissociation energy of a bisallylic hydrogen is approximately 42 kJ/mol lower than that of an allylic hydrogen. As a result, linoleates and linolenates are more readily autooxidized and cross-linked in comparison with oleates.

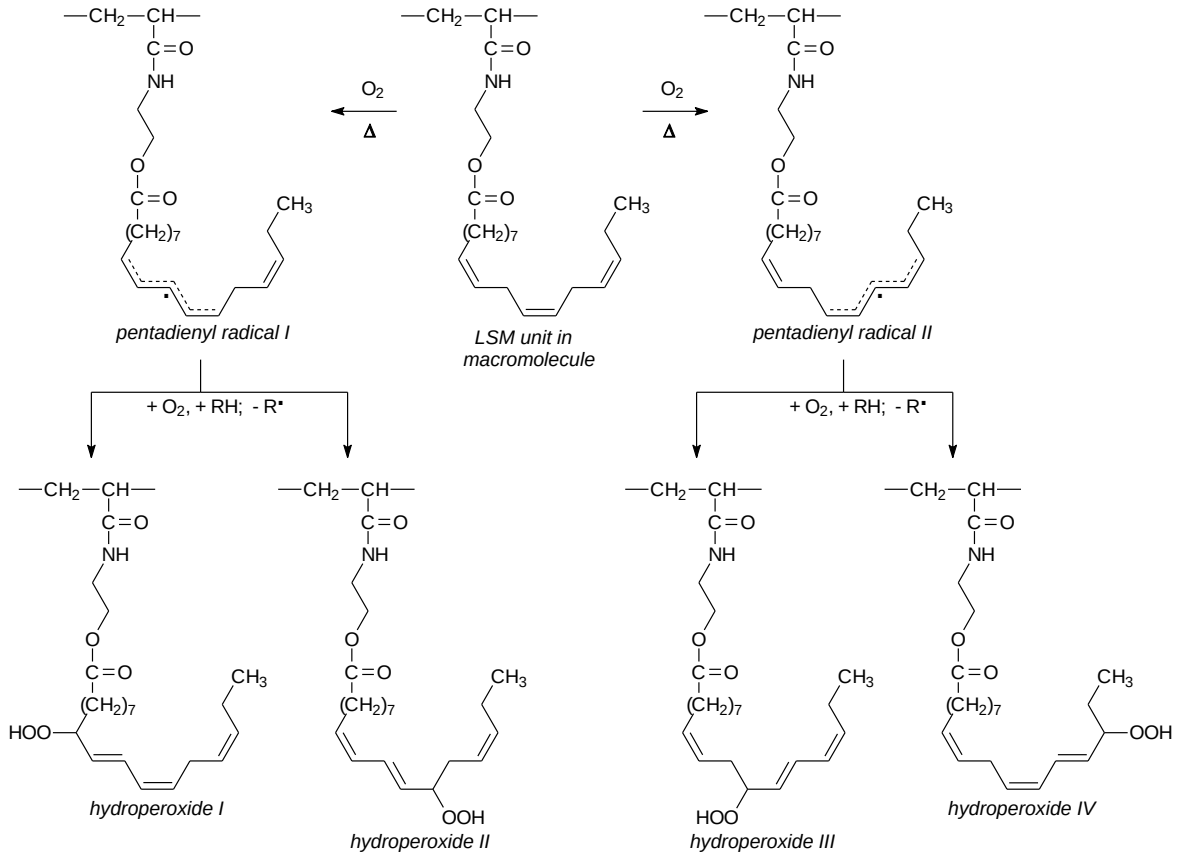


**Figure 10.** Formation of radicals and hydroperoxides during oxidative cross-linking of polymers from linseed oil-based monomer (LSM).

Hydrogen atom abstraction from C-11 or C-13 of the linolenate moiety leads to pentadienyl radicals I and II (Figure 10). Subsequent oxygen addition to radicals I and II generates peroxyl radicals which are able of abstracting a hydrogen atom from a donor such as another linolenate moiety to form conjugated *trans,cis*-hydroperoxides I-IV (Figure 10). The hydroperoxides undergo decomposition reaction (Figure 11). The last three reactions lead to cross-linking of the macromolecules and formation of a polymer network.

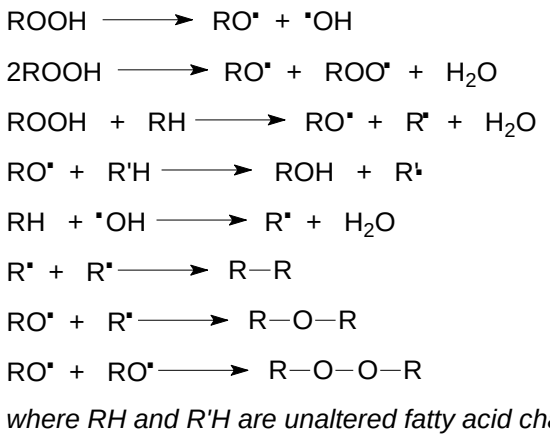


**Figure 11.** Oxidative cross-linking of polymers from linseed oil-based monomer (LSM).

The main mechanical characteristics of films from latex polymers based on styrene or methyl methacrylate and the POBMs were determined. The composition of the copolymers was calculated from the $^1$H NMR spectroscopy data. The content of the olive and soybean monomers in the reaction mixture varied from 10 to 40 wt. % for copolymers with methyl methacrylate and from 25 to 60 wt. %

for copolymers with styrene. A plasticizing effect and enhanced hydrophobicity were observed for the copolymers synthesized from 2-N-acryloylaminoethyl oleate and 2-N-acryloylaminoethyl linoleate as comonomers. The unsaturation degree of the olive and soybean monomers was used as an experimental parameter to control the latex properties. The effect of monomer unsaturation on the cross-linking density of the latex films and, thus, on the physical and mechanical properties of the coatings was demonstrated [31].

The decrease in the glass transition temperature of the latex copolymers (from 105 to 57°C for the copolymers of the olive and soybean monomers with methyl methacrylate and from 100 to 5°C for the copolymers with styrene) indicates that the presence of the OVM and SBM units in the macromolecules affects thermomechanical properties of the resulting latex copolymers. The olive and soybean monomer units impart flexibility to the macromolecules, improve the conditions of film formation, increase the strength in comparison with conventional polystyrene and poly(methyl methacrylate). Moreover, the OVM and SBM units in the macromolecules increase the hydrophobicity of polymeric latex films thus reducing the negative impact of water on the properties of the coatings.

Therefore, the incorporation of the hydrophobic fatty acid chains into the macromolecules of latex polymers allows for formation of polymer networks with a controlled cross-linking density along with enhancing the water resistance of the coatings. The copolymers based on the olive and soybean monomers enable the formation of coatings with low surface energy and water-repellent properties.

## 5. Formation of Micelles from the Complexes of Highly Hydrophobic Plant Oil-Based Monomers with Sodium Dodecyl Sulfate

The synthesized POBMs contain $CH_2$=CH–C(O)–NH–$CH_2CH_2$–O–C(O)– as a hydrophilic fragment in their chemical structure and R– as a hydrophobic constituent in the fatty acid chain. Such a monomer structure imparts unique properties to the POBMs associated with the ability to participate in intermolecular (electrostatic and/or van der Waals) interactions to produce complexes (aggregates). The formed complexes can open up new opportunities for micellization and, thus, new approaches to conducting heterophase polymerization (*e.g.*, conventional emulsion and mini-emulsion polymerization).

The effect of highly hydrophobic olive oil-based and high oleic soybean oil-based (HO-SBM) acrylic monomers on micellization of sodium dodecyl sulfate (SDS) was examined at different surfactant and monomer concentrations by determining micellar parameters, size and structure, as well as surface tension measurements. The obtained results indicate SDS ability to solubilize sparingly soluble in water plant oil-based monomer molecules and facilitate formation of mixed (SDS/POBM) micelles (Figure 12). Surface activity of a surfactant/monomer mixture varies by adding the POBM and is generally higher than for SDS [32]. Comprehensive trends were observed for micellar aggregation number and number of micelle-bound monomer molecules demonstrating that POBM molecules replace SDS counterparts in the mixed micelles. Based on the dynamic light scattering measurements, it was hypothesized that incorporation of POBM into the mixed micelles promotes micellar association and formation of 25–30 nm size structures, also detected using transmission electron microscopy. Practical importance of these findings is the fact that solubilization of POBM by surfactant molecules can have an impact on reaction kinetics and mechanism of emulsion polymerization, as well as affect latex particles formation and, respectively, resulting particle morphology.

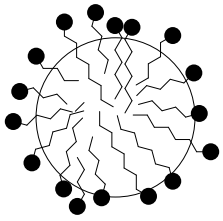

**Figure 12.** Possible location of the polar "heads" in a direct micelle from the SDS molecules and the POBM/SDS aggregate.

Surfactants form direct micelles due to the interactions between hydrocarbon parts of their molecules. Usually the micelle has a layered structure depending on the packaging of surfactant molecules. A micelle contains a hydrocarbon nucleus, a water-hydrocarbon layer, which includes 2–3 methylene groups, and a layer of hydrated polar groups. It should be noted that surfactant molecules are freely localized in the micelle. They can leave the micelle or move to a different position; they can even be engulfed into the nucleus, which is determined by the hydrophobicity of the surfactant fragment [33,34].

The feature of micellization of sodium dodecyl sulfate (SDS) in the presence of the plant oil-based monomers is SDS ability to solubilize sparingly soluble in water POBM molecules and facilitate formation of mixed (SDS/POBM) micelles. As shown by Kingsley et al. [32], the packing of surface-active SDS/POBM complexes (aggregates) and the SDS molecules occurs upon micellization. In this event, the SDS molecules can be squeezed out of the micelle and localized at the interphase reducing the interfacial tension. Sodium dodecyl sulfate is known to have a micelle aggregation number of 60-70 [34]. It was found that the aggregation number decreases to 10-48 (Table 3) upon micellization of the SDS/POBM complexes. The micellar size depends on the packaging of the surfactants. Their length and packing density in the micelle determine the radius of the hydrocarbon nucleus. The formed colloidal solution simultaneously contains the SDS micelles and the mixed SDS/POBM micelles. It should be noted that their size is 18-38 nm (Table 3, Figure 13) whereas the SDS micellar size is 1.7-3.1 nm.

**Table 3.** Micellar parameters for SDS and POBM at different concentrations.

| **SDS + POBM (x,mol : y,mol)** | $N_{agg}$ | $N_{POBM}$ | $I_1/I_3$ | **d,nm** | **PDI** | **σ, mN/m** |
|---|---|---|---|---|---|---|
| SDS at 0.02 M | 41 | 0 | 1.04 | 3.1 | 0.006 | 36.2 |
| + HO-SBM 0.01 M | 25 | 20 | 0.94 | 18.2 | 0.02 | 34.1 |
| 0.02 M | 15 | 25 | 0.94 | 23.3 | 0.05 | 31.2 |
| 0.04 M | 12 | 39 | 0.92 | 25.4 | 0.04 | 30.4 |
| SDS at 0.05 M | 57 | 0 | 1.03 | 1.7 | 0.003 | 34.9 |
| + HO-SBM 0.02 M | 46 | 22 | 0.96 | 27.3 | 0.03 | 31.5 |
| 0.04 M | 38 | 34 | 0.95 | 28.5 | 0.05 | 29.8 |
| SDS at 0.02 M | 41 | 0 | 1.03 | 3.1 | 0.006 | 36.2 |
| + OVM 0.01 M | 27 | 22 | 0.95 | 22.6 | 0.06 | 32.4 |
| 0.02 M | 19 | 31 | 0.93 | 28.7 | 0.04 | 31.1 |
| 0.04 M | 10 | 33 | 0.93 | 37.8 | 0.04 | 30.1 |
| SDS at 0.05 M | 57 | 0 | 1.03 | 1.7 | 0.003 | 34.9 |
| +OVM 0.02 M | 48 | 23 | 0.95 | 28.2 | 0.02 | 32.6 |
| 0.04 M | 31 | 28 | 0.94 | 33.9 | 0.04 | 30.2 |

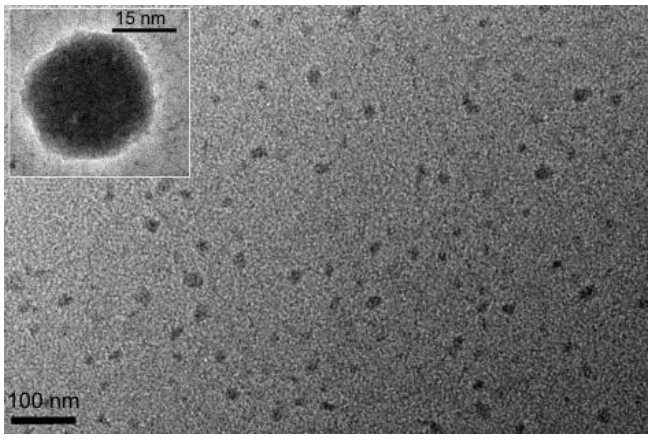

**Figure 13.** TEM micrograph of micelles prepared by mixing SDS (0.02M) and HO-SBM (0.01M) (inset shows morphology of selected individual micelle). Reprinted from Ref. 32, Copyright (2019), with permission from Elsevier.

If the fatty acid chain cannot leave the hydrocarbon nucleus, the polar group can be even drawn into the hydrophobic nucleus [34], which also affects the aggregation number. The authors explain the features of micellization (micellar parameters, size, structure, and surface tension) and the obtained results with the formation of surface-active SDS/POBM complexes (aggregates) of the following structure (Figure 14):


**Figure 14.** Chemical structure of plant oil-based monomer (**A**), surfactant (**B**) and schematic of POBM solubilization by SDS molecules (**C**). Reprinted from Ref. 32, Copyright (2019), with permission from Elsevier.

The formation of a water-hydrocarbon layer of the spherical micelle leads to the localization of the acrylic groups of the POBM molecule at the interface. This opens up new possibilities for the formation of "core–shell" morphology, providing ability of POBM to undergo polymerization.

Chemical composition of plant oil-based monomer and SDS molecules is similar. They both have polar "head" and long hydrophobic "tail" with in average 17 (POBM) and 12 (SDS) carbon atoms. The obtained results indicate that SDS molecules solubilize sparingly soluble in water plant oil-based monomer (POBM) counterparts, thus facilitating formation of mixed (SDS/POBM) micelles. It was assumed that intermolecular interactions occur through physical association of both molecular "heads" and "tails" in water. The data show that surface activity of a surfactant/monomer mixture is generally higher than for SDS and varies by adding the POBM. Additionally, micellar parameters, size and structure, observed changes upon the addition of POBM.

## 6. Dual Role of Methyl-β-Cyclodextrin in the Emulsion Polymerization of Highly Hydrophobic Plant Oil-Based Monomers

The new acrylic monomers are also capable of complexation with cyclodextrins, which play a dual role in both enhancing POBM polymerizability as well as protecting against allylic termination chain transfer.

Amphiphilic oligosaccharide, methyl-β-cyclodextrin (M-β-CD), was used to improve the polymerizability of monomers from high oleic soybean and linseed oil in copolymerization with styrene. Using X-ray diffractometry and differential scanning calorimetry, interactions between the monomers and M-β-CD were confirmed, while the formation of 1:1 complex from oligosaccharide and each monomer molecules was demonstrated by mass spectrometry. In the presence of "host-guest" complexes, polymer yield increases as the coagulum amount drops during the emulsion polymerization of both plant oil-based monomers with styrene indicating their enhanced aqueous solubility. Remarkably, latex polymers with a consistently higher molecular weight were obtained in the presence of M-β-CD. The complex formation and incorporation of monomer molecules into the oligosaccharide cavities protect the fatty acid moieties and diminishes chain transfer. The latter assumption was quantitatively confirmed in $^{1}$H NMR spectroscopy by determining the number of protons of the alkyl carbon−carbon double bonds (–CH=CH–) and the bisallylic hydrogen atoms (–CH=CH–$CH_2$–CH=CH–) in the unsaturated fatty acid moieties of the latex copolymers. The observed effect is more pronounced for more unsaturated monomer from

linseed oil. Based on the obtained results, M-β-CD plays a dual role in both enhancing POBM polymerizability as well as protecting against allylic termination chain transfer.

These results are explained by the specific structures of M-β-CD having a hydrophobic cavity and a hydrophilic exterior, and the POBM molecule, possessing a long hydrophobic fatty acid chain; this results in the formation of an inclusion complex (Figure15).

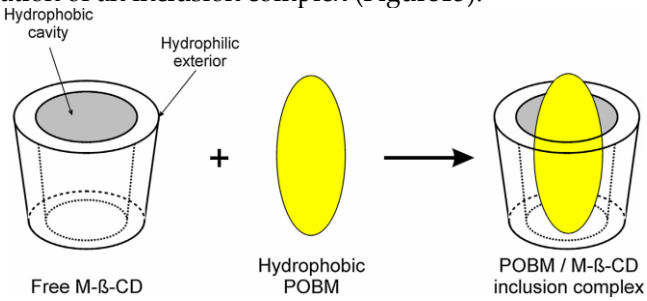


**Figure 15.** Schematic illustration of the association of free methyl-β-cyclodextrin and POBM to form a 1:1 inclusion complex. Reprinted from Ref. 35, Copyright (2018), with permission from Elsevier.

To confirm the formation of the inclusion complex, it was used Powder X-ray diffractometry (PXRD) which is a powerful technique to detect the cyclodextrin complexation of small molecules in a powder or crystalline state [36]. PXRD differentiates the formation of complexes due to clear alterations between the diffraction pattern superposition of the components and the diffraction pattern of the inclusion complex. The PXRD spectra of HSBM [monomer from hydrogenated (very low degree of unsaturation) soybean oil], M-β-CD, H-SBM/M-β-CD inclusion complex, and the physical mixture are shown in Figure 16A. The diffractogram of H-SBM displays numerous characteristic peaks due to its self-lattice arrangement, which indicates the crystallinity of the monomer. In contrast, M-β-CD is an amorphous substance thus its diffractogram shows two wide peaks related to the non-crystalline form. The diffraction pattern of the physical mixture of H-SBM and M-β-CD was just the superposition of the monomer and M-β-CD. This may indicate that there is no interaction between H-SBM and M-β-CD in the simple physical mixture [37]. Compared with the diffractogram of pure H-SBM and M-β-CD, the diffraction pattern of the inclusion complex is similar to that of the M-β-CD with increased intensity of the peak at 17.9° at 2θ scale and showed no characteristic peaks that pure HS-BM had. These results indicate that the self-lattice arrangement of H-SBM was changed from a crystalline to amorphous state, which can be attributed to the H-SBM inclusion into the M-β-CD cavity.

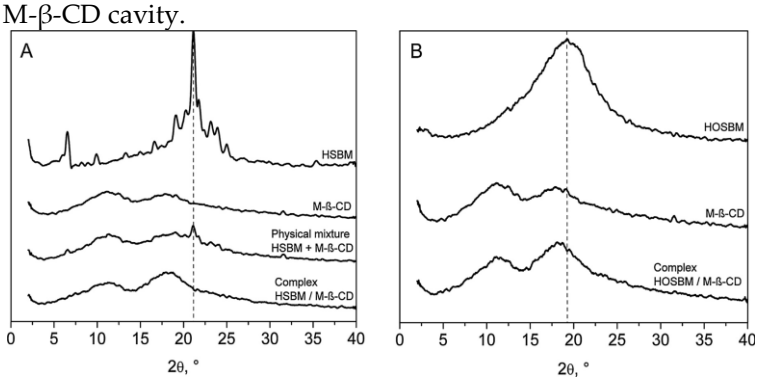


**Figure 16.** PXRD spectra of POBMs, methyl-β-cyclodextrin, their physical mixture and inclusion complexes (A – H-SBM, B – HO-SBM). Reprinted from Ref. 35, Copyright (2018), with permission from Elsevier.

The PXRD pattern of HO-SBM, M-β-CD, and HO-SBM/M-β-CD inclusion complex are presented in Figure 16B. HO-SBM is an oily viscous substance, and its diffractogram displays two wide peaks attributed to the non-crystalline form. Since both M-β-CD and HO-SBM are non-crystalline substances, the formation of HO-SBM/M-β-CD inclusion complex cannot be confirmed unambiguously by PXRD.

The inclusion of a guest molecule into a cyclodextrin can also be studied using differential scanning calorimetry, as cavity alters the boiling and melting points of the initial substances by shifting or suppressing them [38]. The DSC thermograms of H-SBM, M-β-CD, H-SBM/M-β-CD inclusion complex, and the physical mixture are shown in Figure 17. The DSC curve of H-SBM shows two sharp endothermic peaks corresponding to the melting of the monomer. The DSC thermogram of M-β-CD shows a broad endothermic band at 110°C due to the dehydration process. The endothermic peaks of H-SBM were observed in the thermogram of the physical mixture of H-SBM and M-β-CD. These results indicate that the complexation has not occurred, and the initial substances are simply mixed together. However, no peak in the melting range of H-SBM was detected in the DSC curve of H-SBM/M-β-CD samples prepared using the thin films method. This indicates that the monomer molecules are completely included into the M-β-CD cavities, monomer appears in an amorphous state, and H-SBM/M-β-CD inclusion complex forms.

The DSC thermogram of HO-SBM (data not shown) exhibited an endothermic peak at around 17°C corresponding to the melting point of the monomer. However, no peak in the melting range of HO-SBM was detected in the DSC curves of HO-SBM/M-β-CD inclusion complex and their physical mixture. This may imply that there was some interaction between the pure components. A plausible explanation is that unlike HSBM, HO-SBM is an oily liquid and, thus, monomer molecules might be able to penetrate into the M-β-CD cavities when the two substances are mixed together. In principle, this procedure is similar to the kneading method, which is used for the synthesis of cyclodextrin-guest complexes when a liquid guest component is added to a slurry of cyclodextrin and kneaded thoroughly in a mortar [39].

Although PXRD and DSC analyses indicate the changes from a crystalline to amorphous state of H-SBM upon its interaction with M-β-CD, these techniques can neither unambiguously confirm whether inclusion complexation (especially, for HO-SBM) occurs nor determine the complex stoichiometry. To this end, electrospray ionization–mass spectrometry (ESI–MS), which is an extremely sensitive and specific analytical technique, capable of providing the molecular masses within a sample and determination of molecular association of non-covalent bonding [39], was used in this work to monitor the formation of POBM/M-β-CD inclusion complexes. The feasibility of ESI to maintain the non-covalent structure upon the transition of inclusion complexes from the liquid to gas phase has been widely applied to investigate the complexation of cyclodextrins with various organic substances [40].

Figure 17 shows the ESI mass spectra of inclusion complexes of the POBMs with methyl-β-cyclodextrin. In the spectrum of H-SBM/M-β-CD (Figure 17A), ions detected at m/z 1665, 1679, 1693, 1707, and 1721 correspond to sodium adducts of complexes of stearate-H-SBM with M-β-CD having 9, 10, 11, 12, and 13 methyl groups, respectively. The ESI mass spectrum of the HO-SBM/M–β–CD inclusion complex is depicted in Figure 17B. Ions that correspond to the inclusion of oleate-HO-SBM by $M_{10\text{-}13}$-β-CD (sodium adducts) are detected at m/z 1677, 1691, 1705, and 1719. It is worth noting that stearate-H-SBM and oleate-HO-SBM are the main components of H-SBM and HO-SBM, respectively; M-β-CD is a mixture of β-cyclodextrins in which 9–13 hydroxyl groups are substituted with methyl groups. For that reason, these above-mentioned inclusion complexes are the most pronounced in the ESI spectra.

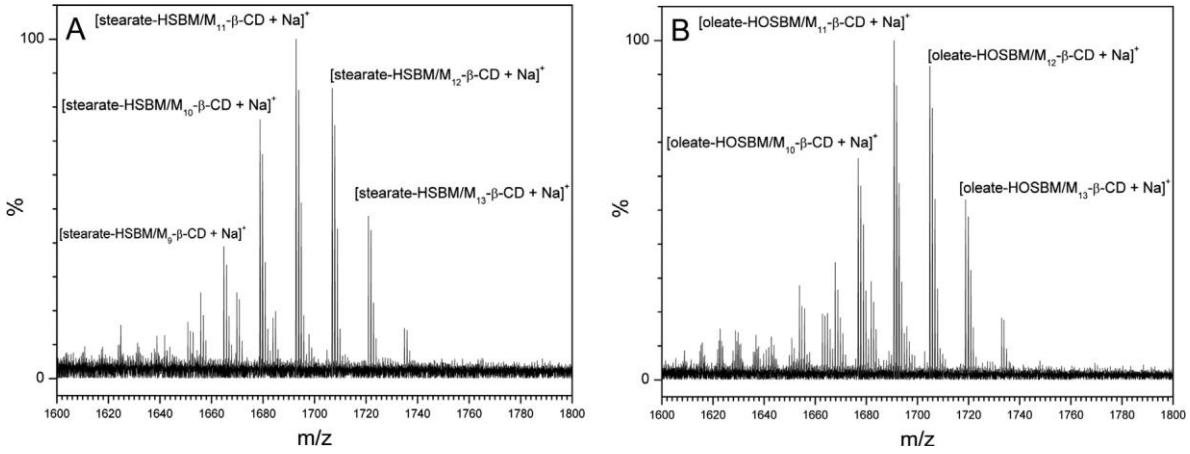


**Figure 17.** ESI mass spectra of H-SBM/M-β-CD (A) and HO-SBM/M-β-CD (B) inclusion complexes. Reprinted from Ref. 35, Copyright (2018), with permission from Elsevier.

Hence, the ESI–MS data directly confirmed the methyl-β-cyclodextrin complexation of POBM molecules (both H-SBM and HO-SBM) resulting in the 1:1 complex formation (Figure 15).

It was shown that the emulsion copolymerization of POBMs with styrene in the presence of M-β-CD allows for the protection and preservation of both fatty acid double bonds (–CH=CH–) of the monomers and the bisallylic hydrogen atoms (–CH=CH–$CH_2$–CH=CH–) in the case of latex polymers from LSM and styrene and fatty acid double bonds when HO-SBM is copolymerized with styrene. These results are consistent with previous reported literature on the cyclodextrin complexation of unsaturated fatty acids, reflecting protection of the latter against oxidation even in pure oxygen [41] due to burying the fatty acid double bonds into the CD cavity [42]. Thus, in the presence of M-β-CD, the latex polymers with a consistently higher molecular weight can be obtained evidently because of the incorporation of POBM molecules into the M-β-CD cavities that protects the fatty acid moieties and therefore decreases the chain transfer and addition of the fatty acid double bonds to growing radicals.

Furthermore, in the presence of M-β-CD during the emulsion polymerization, the polymer yield increases and the coagulum amount decreases. The obtained data imply the dual role of M-β-CD in the emulsion polymerization of POBMs, that is the enhanced aqueous solubility of highly hydrophobic monomers and their availability for the emulsion process as well as diminishing monomer chain transfer reactions due to "host-guest" complex formation.

A series of latexes from high oleic soybean- and linseed oil-based monomers was synthesized using emulsion copolymerization with styrene. In the presence of methyl-β-cyclodextrin, latex polymers with a consistently higher molecular weight were obtained from both HO-SBM and LSM (this effect is more pronounced for more unsaturated LSM). Moreover, the emulsion copolymerization adding M-β-CD resulted in an increased polymer yield and latex solid content accompanied by reduced coagulum formation. It was hypothesized that the incorporation of POBM molecules into the methyl-β-cyclodextrin cavity diminishes the chain transfer contribution by protecting the allylic moiety of the POBM fatty acid fragments and simultaneously enhances the aqueous solubility and availability of POBMs in the emulsion polymerization process. Consequently, a higher molecular weight of latex polymers from highly hydrophobic POBMs can be obtained with higher monomer conversion and lower coagulum formation.

## 7. Conclusions

Monomers based on various plant oils were synthesized through a two-step procedure. A one-step process for the synthesis of new vinyl monomers by the reaction of direct transesterification of plant oil triglycerides with N-(hydroxyethyl)acrylamide was recently patented. The features of **homopolymerization** kinetics for the POBMs were determined. The reactivity of the plant oil-based monomers was studied by radical **copolymerization** with vinyl monomers. The Alfrey−Price Q (0.41−0.51) and e (0.09−0.28) parameters are close for all POBMs and do not essentially depend on

the monomer structure. The unique molecular structure of the plant oil-based acrylic monomers is that they simultaneously have a $CH_2$=CH–C(O)–NH–$CH_2CH_2$–O–C(O)– polar (hydrophilic) fragment capable of electrostatic interactions and a hydrophobic fatty acid chain (C15–C17) capable of van der Waals interactions. This opens up new opportunities for formation of micelles from the complexes of highly hydrophobic plant oil-based monomers with sodium dodecyl sulfate and new approaches to conducting heterophase polymerization.

Preparation of polymeric coatings from the plant oil-based monomers through the incorporation of the hydrophobic fatty acid chains into the macromolecules of latex polymers allows for formation of polymer networks with a controlled cross-linking density along with enhancing the water resistance of the coatings. The copolymers based on the olive and soybean monomers enable the formation of coatings with low surface energy and water-repellent properties. The copolymers based on the olive and soybean monomers enable the formation of coatings with low surface energy and water-repellent properties.

The formation of inclusion complexes upon the interaction between the molecules of the plant oil-based acrylic monomers and methyl-β-cyclodextrin leads to a higher molecular weight of latex polymers from highly hydrophobic POBMs with higher monomer conversion and lower coagulum formation.

An analysis of the literature shows a rapid development of a new branch in polymer science related to the chemistry of aliphatic and aromatic biobased monomers from renewable plant sources. The synthesis of such monomers allows for producing fully biobased polymers with biocompatible and biodegradable properties which do not pollute the environment. Copolymerization of the biobased monomers with commercial monomers enables formation of copolymers with controlled physical, chemical, and mechanical properties.

## 8. Patents

Biobased Acrylic Monomers US 10,315,985 B2 June 11th, 2019.

Biobased Acrylic Monomers and Polymers Thereof US 10,584,094 B2 March 10th, 2020.

**Author Contributions:** Conceptualization, A.K., S.V. and A.V.; methodology, Z.D., V.K., K.K. and O.S.; investigation, A.K., Z.D., V.K., K.K. and O.S.; writing—original draft preparation, A.K., V.K. and S.V.; writing—review and editing, S.C. and A.V.; project administration, S.C. and A.V.; funding acquisition, A.V. All authors have read and agreed to the published version of the manuscript.

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