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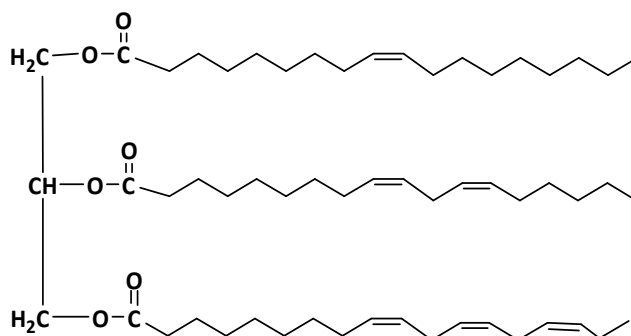


Polymerization of Soybean Oil with Superacids

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1. Introduction

Soybean oil is a triester of glycerol (triglyceride) with saturated and unsaturated fatty acids, 80-85% being unsaturated fatty acids (Fig.1). The iodine value of soybean oil, a direct measure of double bond content, is in the range of 125-132 gI₂/100g. Soybean oil has around 4.6 double bonds and all the double bonds are in the "cis" configuration. The saturated fatty acids are palmitic (C16:0) and stearic (C18:0) and the unsaturated fatty acids are oleic (C18:1), linoleic (C18:2) and linolenic (C18:3). The average molecular weight of soybean oil is M=874 (Ionescu, 2005). From the point of view of macromolecular chemistry, soybean oil having 4.6 double bonds/mol is a polyfunctional monomer (SCHEME I).



Scheme I. Structure of soybean oil

The fatty acid composition of soybean oil is presented in Table 1.

Unfortunately, the internal 1,2 disubstituted nonconjugated double bonds are of low reactivity and polymerize with difficulty (Petrović, 2008). There are two methods for polymerization of soybean oil on a larger scale, both methods being radical initiated processes: thermal polymerization and air blown polymerization. Thermal polymerization (called heat bodied polymerization) is carried out by simple heating of soybean oil at very high temperatures of 290-330 °C with or without catalysts such as anthraquinone (Erhan, 1994, 1998, Wang, 1999, Powers, 1950, Whereleer 1969). Viscous liquid polymers of soybean oil are formed with the yield of 75-80% and a loss of 20-25% of volatile organic compounds resulting from thermal degradation (Bernstein, 1946). The second process also used in industry for "air blown oils" (Christianson 2007, Geiger, 2006) consists of bubbling air through soybean oil at temperatures of 100-110 °C for a relatively long time (30-50 hours), resulting in viscous liquid polymers. Unfortunately, in this process many undesired organic groups are formed as a result of oxidation of fatty acid chains with air oxygen such as:

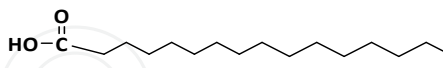
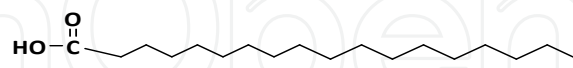
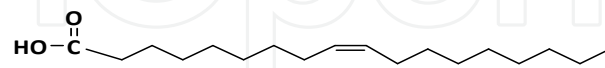
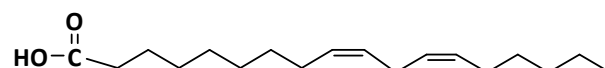
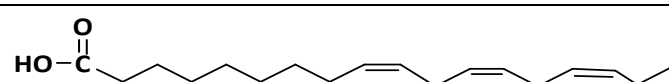
No.	Fatty acid	Percentage in soybean oil, %	Number of C atoms: Number of double bonds	Structure of fatty acid
1	Palmitic acid	10-11	C16:0	
2	Stearic acid	4-6	C18:0	
3	Oleic acid	23-25	C18:1	
4	Linoleic acid	50-55	C18:2	
5	Linolenic acid	6-9	C18:3	

Table 1. Fatty acid composition of soybean oil

hydroxyl, carboxyl, aldehydes, ketones, hydroperoxides. Because of the 1,2 substitution with electron releasing substituents (the alkyl fragments of fatty acid chains) the internal double bonds of soybean oil are rich in electrons and as a consequence are susceptible to the attack of electron deficient species such as organic radicals and cations. Cationic polymerization of soybean oil is an old process. Cationic polymerization of natural oils is described in two old patents. One describes polymerization of soybean oil at 130 °C, in the presence of 2.8% of BF_3 as a catalyst (Uloth, 1944). Liquid polymers of soybean oil with viscosity 5 times higher than those of initial soybean oil are obtained. The second patent (Eichvald, 1939) describes the polymerization of soybean oil at 70 °C in the presence of 2% BF_3 as a catalyst during 50-80 hours. Cationic homopolymerization of soybean oil and cationic copolymerization of soybean and other natural oils (fish oil, tung oil etc.) with vinyl monomers, such as styrene, divinyl benzene, norbornene, dicyclopentadiene, were carried out by Larock at Iowa State University (USA) (Li & Larock, 2000, 2001a,b, Li et al 2000 a,b, 2001, Larock & Li, 2000, Larock & Hanson 2001). They used the following conditions: 4-7% of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst and 110 °C to obtain solid polymers with some interesting properties. The cationic polymerization of soybean oil initiated by 2% $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 110-140 °C in supercritical carbon dioxide was developed successfully at the institute NCAUR from Peoria (USA), by the group of Sevim Erhan (Liu, 2007).

As a general observation, in the mentioned patents and papers the catalyst used for cationic polymerization of soybean oil was without exception boron trifluoride or its complex with diethylether. Cationic polymerization of fatty acids or of fatty acid methyl esters, by using the same BF_3 as a catalyst, was described in the literature (Turner, 1990, Croston, 1952, Ghodssi, 1970). The cationic oligomerization of fatty acids to dimeric and trimeric acids catalyzed by acidic clays at higher temperatures (230-240 °C) is described in several patents (Hayes 1986, Conroy 1972, Milks 1969, Vreswijk 1990, Wheeler 1969, Hayes 1986, Difranco, 2000). The present chapter describes a new process for cationic polymerization of soybean oil catalyzed by superacids (HBF_4 , $\text{CF}_3\text{SO}_3\text{H}$, HSbF_6 etc.), in mild reaction conditions

(temperature around 80-100 °C, atmospheric pressure, at 1% catalyst concentration, during several hours) and in practically quantitative yield (Ionescu & Petrović 2009). In 4-6 hours of cationic polymerization liquid polymers, of viscosity 100-260 times higher than those of initial soybean oil are formed. Reaction times longer than 6 hours result in solid polymers. We studied the effect of various parameters on the cationic polymerization of soybean oil with superacids, we propose a new reaction mechanism for this kind of unconventional cationic polymerization reaction of soybean oil and we characterized the resulted polymers. Our main objective was to obtain liquid viscous polymers, in high yield, by cationic polymerization of soybean oil with superacids, as an economical alternative to the high energy consumption and modest yield of heat bodied oils.

2. General procedure for cationic polymerization of soybean oil with superacids

A 1L glass reactor is charged with 500-600g of standard RBD soybean oil (Refined, Bleached, Deodorized) and about 9.5g of 54% solution of HBF_4 in diethyl ether (1% of pure HBF_4). The oil/catalyst mixture is stirred at room temperature for 20-30 minutes under protective atmosphere of nitrogen. In this interval of time the color of the reaction mass changed from the initial yellow color of soybean oil to dark brown, due to the formation of cationic active centers-conjugated allyl cations. The temperature is increased to 90 °C and is maintained at 88-92 °C for about six hours. In the first 3-4 hours the viscosity of the reaction mass increases slowly, but after 4 hours a marked increase of viscosity occurs. After about 6 hours of cationic polymerization viscosity rises to 8-16 Pa.s at 25 °C, which is 100-260 times higher than those of soybean oil (viscosity of soybean oil is around 0.06 Pa.s at 25 °C). After 6 hours the reaction is stopped and the polymerized oil containing the superacid catalyst is purified. The purification consists of the removal of catalyst and of some volatile compounds by treating the product with 3% (w% against the oil) of powdered calcium hydroxide for 1 hour at 50-60 °C. The dark brown color of polymerized oil changes to yellow after about 10-15 minutes of contact with solid $\text{Ca}(\text{OH})_2$. The color change is probably explained by the decomposition of cationic active centers as a consequence of the neutralization of the superacid catalyst. The reaction mass in the form of yellow suspension is filtered under pressure (about 70 p.s.i.) at 60-70 °C. The filtered oil is a transparent viscous liquid of orange color. The volatile compounds, especially diethyl ether from the catalyst and water resulted from catalyst neutralization, are eliminated in a rotary evaporator, under vacuum of 1-5 mmHg and 110-120 °C, for 60 minutes. The final product is a viscous orange liquid with viscosity of 8-16 Pa.s at 25 °C, a high content of oligomers and an acid number of 1.5-3 mg KOH/g. The number average molecular weight is in the range $M_n=1800-2100$, the weight average molecular weight in the range 20,000-50,000 and the molecular weight distribution index M_w/M_n is about 11-15 indicating a broad molecular weight distribution. If the filtration is difficult, especially with very viscous products, around 25% toluene is added before filtration. The solvent is removed together with diethyl ether and water in vacuum distillation step. If the polymerization reaction is continued for more than 6 hours, solid polymers dispersed in liquid polymers are formed. Eventually the entire reaction mass becomes a solid polymer. Our objective was to synthesize liquid viscous polymers as alternative to heat bodied oils by cationic polymerization of soybean oil.

3. General description of cationic polymerization of soybean oil with superacids

A superacid is any acid stronger than 100% sulfuric acid (Hall & Conant, 1927). The superacids are 10^{12} - 10^{16} times stronger than sulfuric acid 100%. (Olah, 2009) The most common superacids are triflic acid ($\text{CF}_3\text{SO}_3\text{H}$), tetrafluoroboric acid (HBF_4), hexafluoroantimonic acid (HSbF_6), hexafluorophosphoric acid (HPF_6), fluoro-sulfonic acid (FSO_3H), perchloric acid (HClO_4) and complexes of Lewis acids with a superacid acids such as SbF_5 - FSO_3H (Magic acid) or SbF_5 - $\text{CF}_3\text{SO}_3\text{H}$. Generally the strength of an acid is characterized by pKa [Olah, 1968, 1985, 2009] of the acid or by Hammett constant of acidity H_o (Hammett, 1932). Thus if the pKa of sulfuric acid 100% is pKa=-3, a superacid such as triflic acid has pKa=-14, FSO_3H has pKa= -15 and HClO_4 has pKa=-10. The Hammett constant of acidity of sulfuric acid 100% is H_o = -12, the superacids such as triflic acid has H_o =-14.5, tetrafluoroboric has H_o = -15.5, hexafluoroantimonic H_o = -28 and "Magic acid" (SbF_5 - FSO_3H) has H_o = - 25 (Olah, 1985, 2009). The superacids which have a true catalytic activity for cationic polymerization of soybean oil are: tetrafluoroboric acid (HBF_4 as solution in diethylether), triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) and hexafluoroantimonic (HSbF_6). Sulfuric acid and all the acids with acidity comparable or lower than those of sulfuric acid 100% such as methanesulfonic acid, nitric acid, phosphoric acid and all the organic acids-do not have any catalytic activity for soybean oil polymerization. As a general rule, only the superacids in pure form or as a solution in organic nonprotic solvents are catalytically active for soybean oil polymerization. Many superacids are delivered in the form of aqueous solutions. All the water solutions of superacids are catalytically inactive for cationic polymerization of soybean oil. The reason is very simple, water destroys the carbocations, the active species involved in any cationic polymerization. One of the best catalysts for soybean oil polymerization is tetrafluoroboric acid available as 54% solution in diethylether. Tetrafluoroboric acid is one of the cheapest superacids available commercially, and was used in the present study. Figures 1 and 2 show the gel permeation chromatograms (GPC) of the reaction mass during polymerization of soybean oil catalyzed by tetrafluoroboric acid (1 wt% against the oil) at 90 °C. Four GPC columns were specially adapted for the analysis of low molecular weights. The observed marked increase in oligomer and polymer content of soybean oil is direct evidence that cationic polymerization of soybean oil takes place. Around 28-30% of initial soybean oil remains unreacted, probably due to the triglycerides containing fatty acids without double bonds (palmitic and stearic acids) and with only one weakly polymerizable double bond (oleic acid).

Figure 3 presents the formation of oligomers during cationic polymerization of soybean oil. The increase of high molecular weight species with time is evident. After around 300 minutes of polymerization, the oligomer content is in the range of 68-72%. The monomer (the initial soybean oil) content decreases continuously and after 250-270 minutes of polymerization goes to a constant value of around 28-30% in polymerized oil.

The increase of viscosity during the cationic polymerization of soybean oil is small in the first 3-4 hours of reaction but very strong after 4-6 hours. Figure 4 shows the viscosity increase during the polymerization of soybean oil with tetrafluoroboric acid (1% concentration against soybean oil calculated as pure HBF_4), at 90 °C.

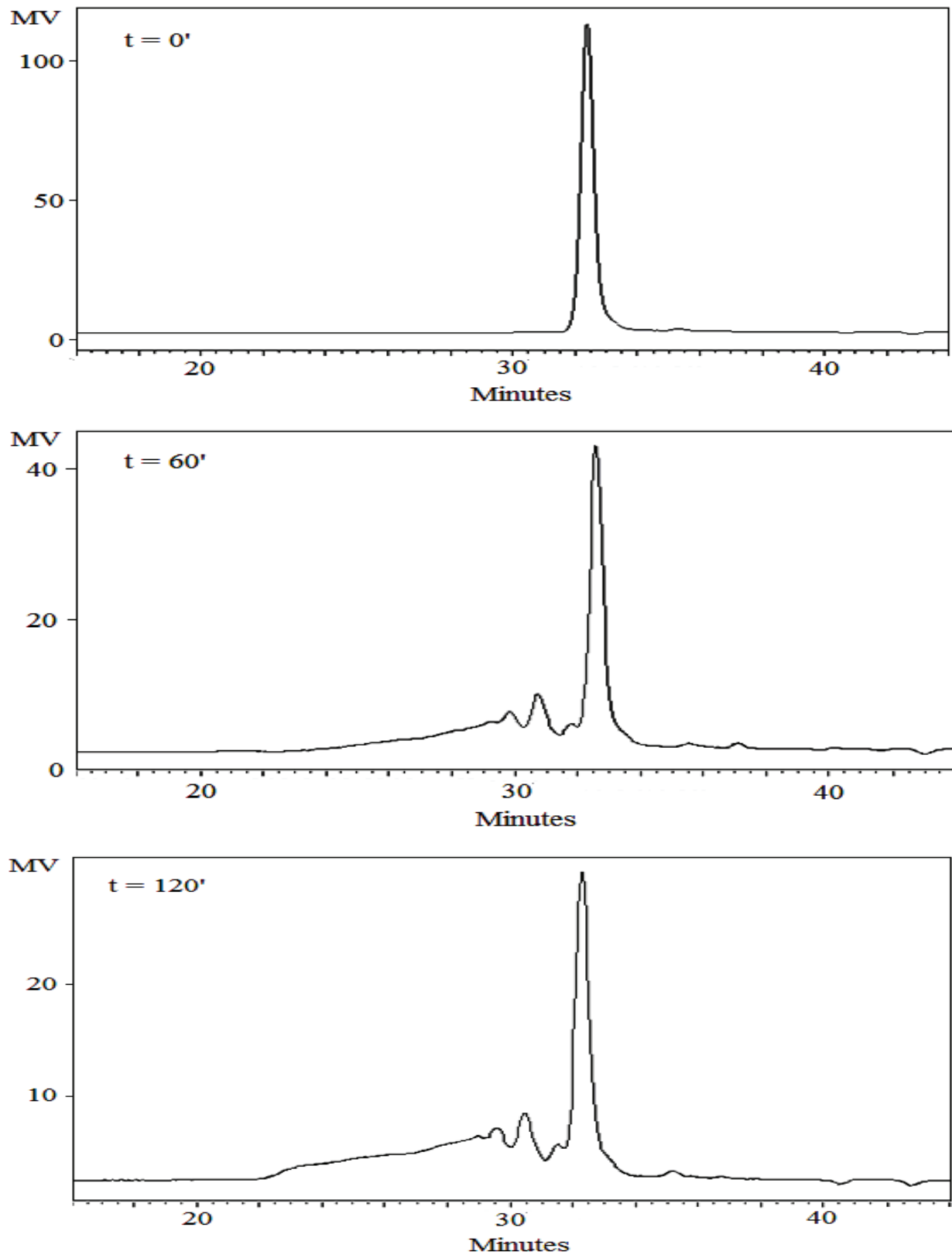


Fig. 1. GPC of initial soybean oil ($t=0$) and of the reaction mass after 60 minutes and 120 minutes of cationic polymerization. Temperature: 90 °C; tetrafluoroboric acid concentration: 1%.

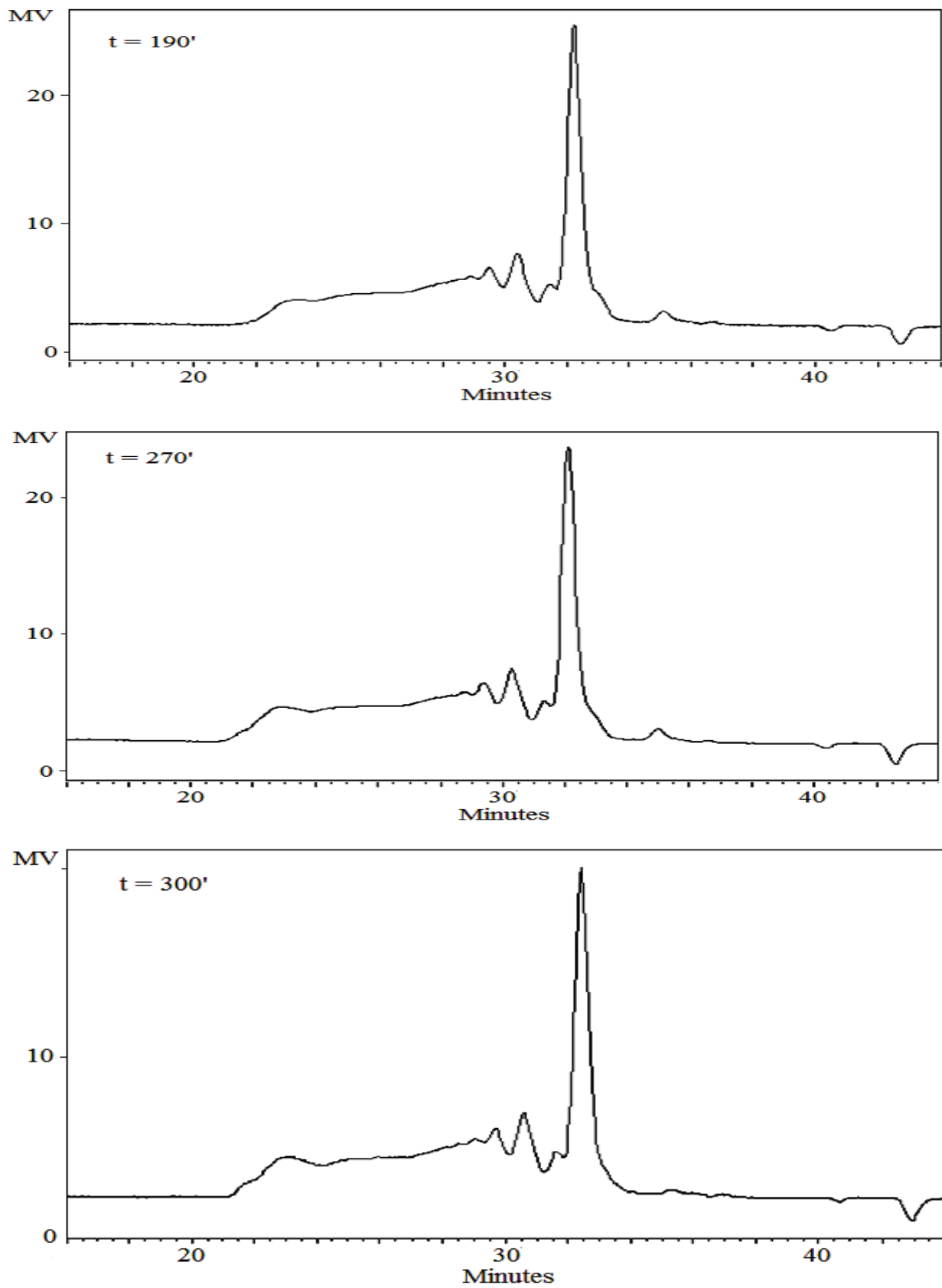


Fig. 2. GPC of the reaction mass after 190, 270 and 300 minutes of cationic polymerization of soybean oil. Temperature: 90 °C; tetrafluoroboric acid concentration: 1%.

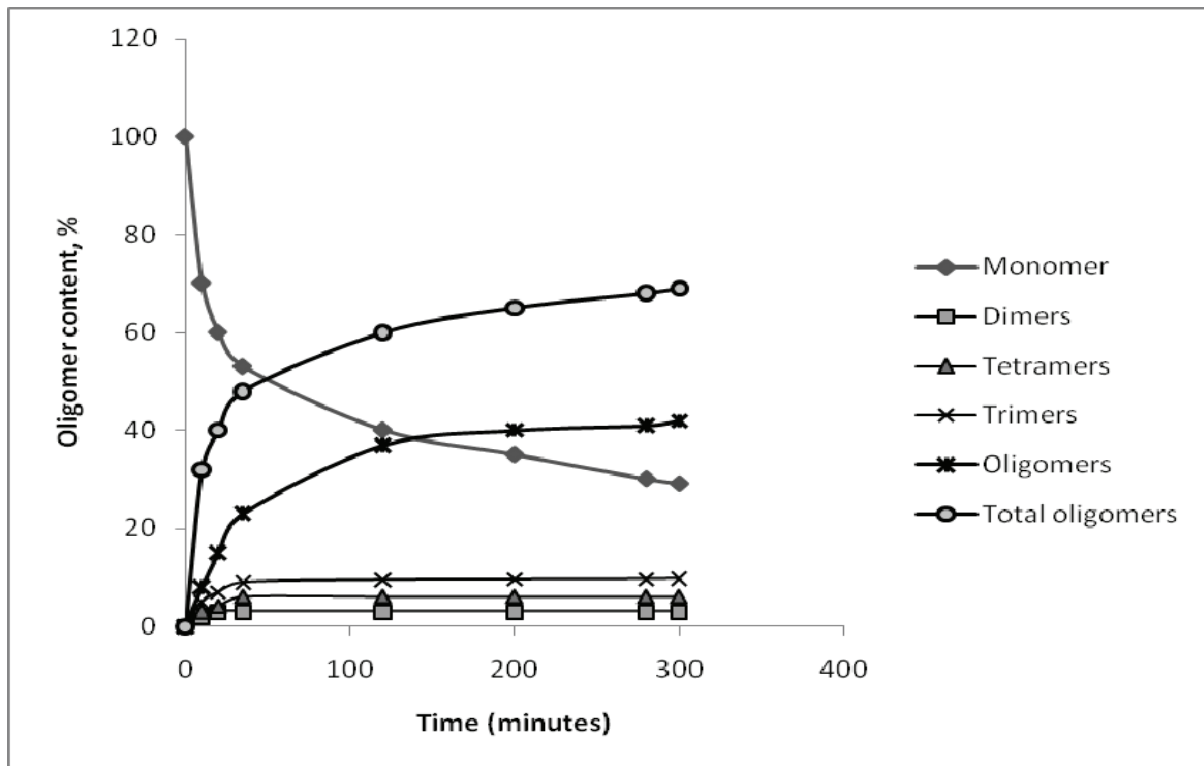


Fig. 3. The effect of time on monomer, dimers, trimers and oligomer content during cationic polymerization of soybean oil

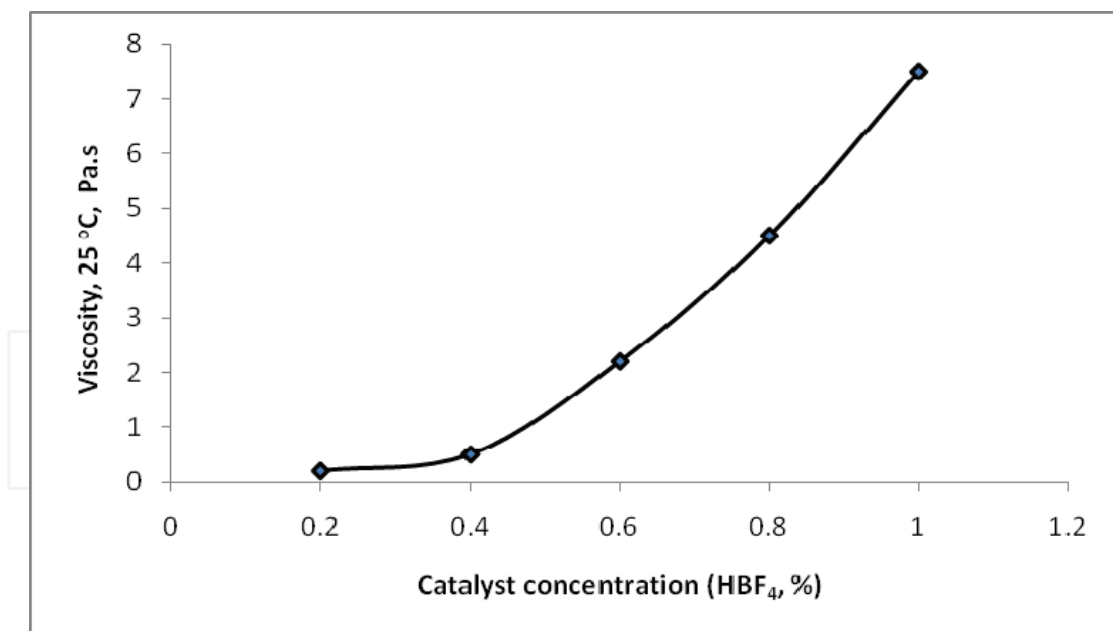


Fig. 4. Effect of time on viscosity during cationic polymerization of soybean oil with tetrafluoroboric acid (1%) at 90 °C.

The increase of viscosity with time is a direct measure of the efficiency of the process used for cationic polymerization of soybean. Figure 5 displays the effect of catalyst nature on viscosity of the reaction mass during cationic polymerization of soybean oil at the same catalyst concentration.

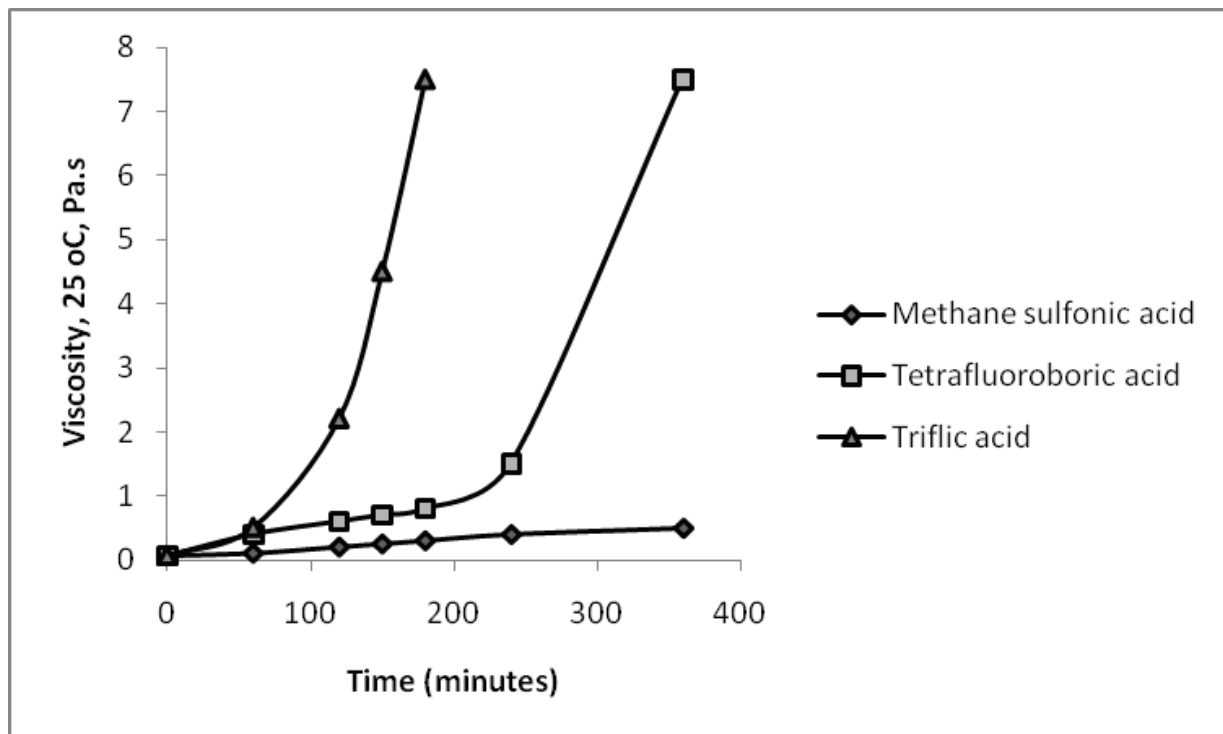


Fig. 5. Effect of catalyst nature on viscosity during cationic polymerization of soybean oil.

Three different catalysts were compared: two superacids (tetrafluoroboric acid and triflic acid) and methanesulfonic acid, with an acidity comparable with those of sulfuric acid. It is clearly observed that triflic acid is more efficient than tetrafluoroboric acid and methanesulfonic acid does not have any notable catalytic activity. The relative efficiency of these catalysts in cationic polymerization of soybean oil is presented below:

Triflic acid > Tetrafluoroboric acid >> methanesulfonic acid

Of course, the catalyst concentration has a strong effect on the viscosity increase during cationic polymerization of soybean oil. Figure 6 shows the effect of tetrafluoroboric acid concentration on viscosity after 5 hours of reaction. Temperature of polymerization has a strong effect on the reactivity of soybean oil in cationic polymerization. At temperatures below 70 °C the polymerization rate is very low. At 70-80 °C a small increase of viscosity is observed. After 6 hours of polymerization viscosity reached 2-5 Pa.s at 25 °C. Temperature of 90 °C leads to a strong increase of viscosity, reaching 14-16 Pa.s after 6 hours of polymerization, in a very controllable manner. Temperatures of 100-110 °C lead to a very rapid increase of viscosity, which is difficult to control, producing solid polymers suspended in a liquid. As mentioned before, our objective is to obtain high viscosity liquid polymers, as an alternative to heat bodied oils. This is the reason for selecting 90 °C as optimal temperature, which leads to high viscosity in a reasonable reaction time without formation of solids. Figure 7 presents the effect of temperature on viscosity of the reaction mass during cationic polymerization of soybean oil. As an interesting experimental observation, the oils containing linolenic acid polymerize more rapidly to high molecular weight polymers. Thus linseed oil having 53-55% linolenic acid leads easily to much higher viscosities of polymerized oil (in fact to much higher molecular weights) as compared with soybean oil, under the same reaction

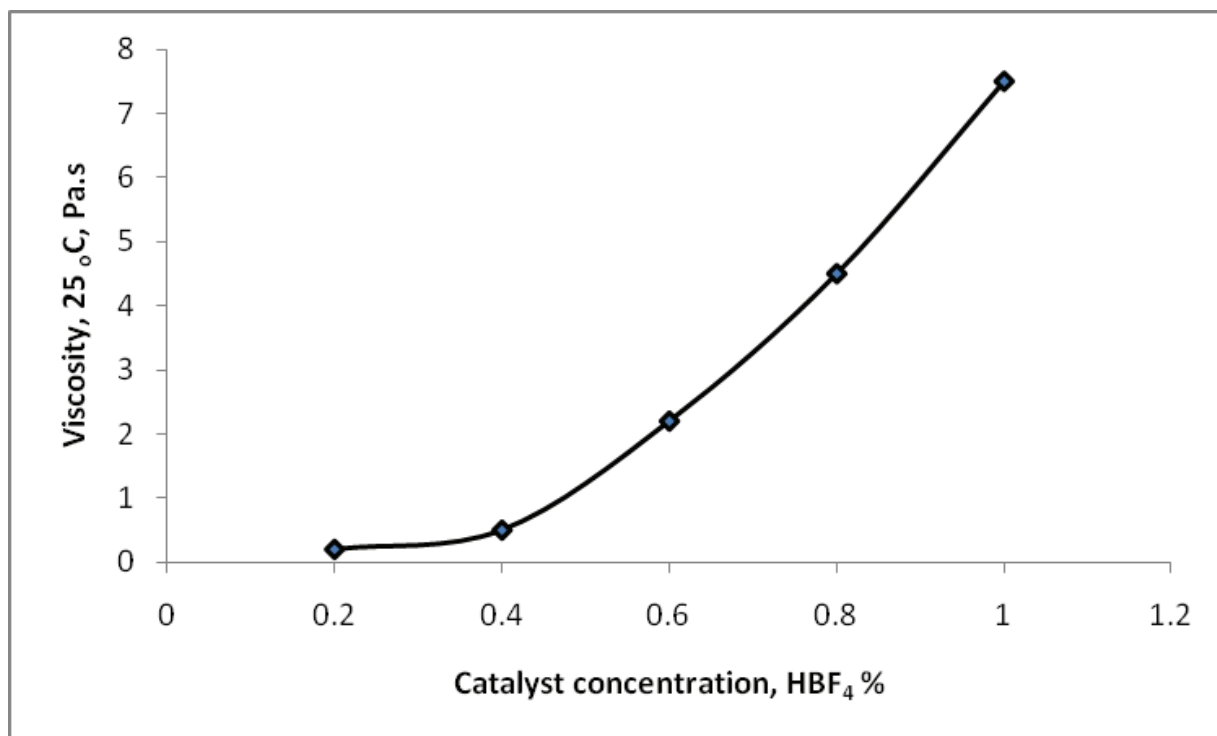


Fig. 6. Effect of catalyst concentration on viscosity of the reaction mass after 5 hours of polymerization of soybean oil at 90 °C.

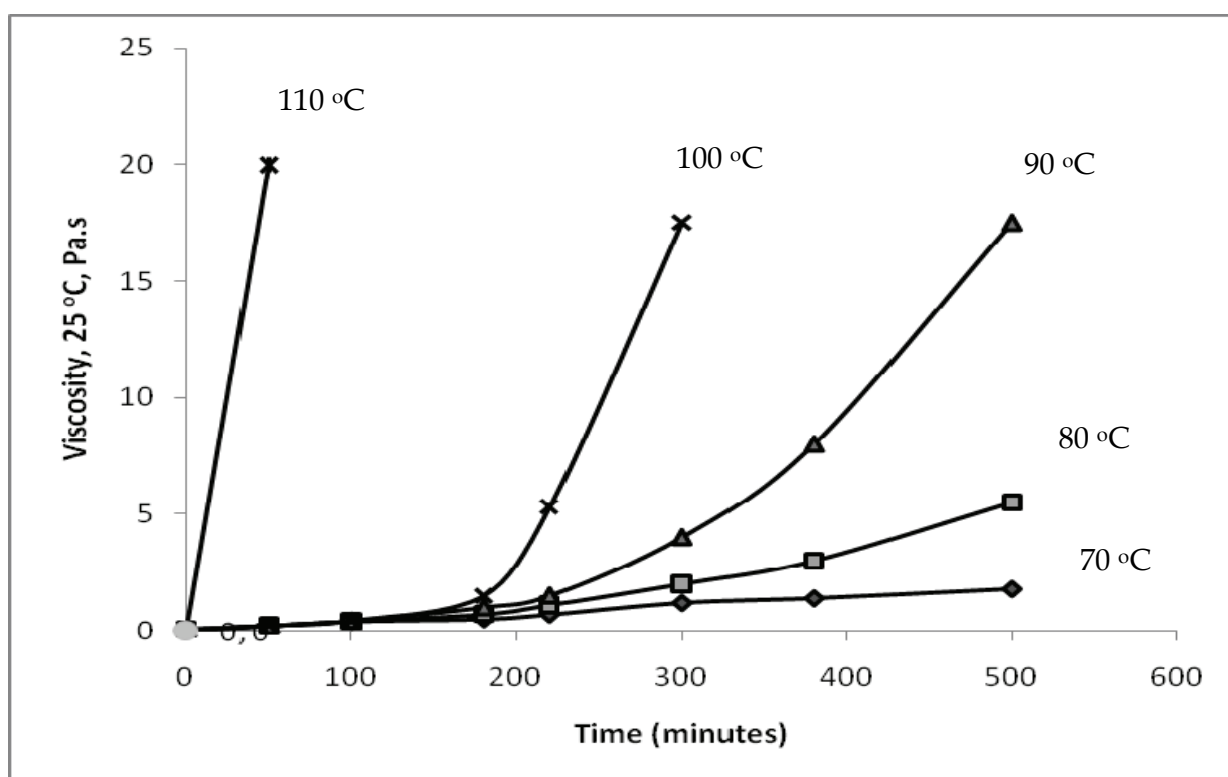


Fig. 7. Effect of temperature on viscosity of the reaction mass during of cationic polymerization of soybean oil. Catalyst HBF₄ 1%.

conditions (the same reaction time, temperature and catalyst concentration). Contrary, the vegetable oils with high content of linoleic acid but with very small content of linolenic acid (corn oil, safflower oil, sunflower oil), polymerize cationically, but in a lesser extent than soybean oil, to much lower viscosity polymers. Copolymers between these oils with low content of linseed oil (20%) polymerize cationically very efficiently proving the important role of linolenic acid to obtain highly viscous polymers. The oils having conjugated double bonds (tung oil, calendula oil, dehydrated castor oil etc.) are extremely reactive in conditions of cationic polymerization of soybean oil with superacids mentioned before. In less than 5 minutes, in a violent polymerization reaction, solid polymers are obtained from tung oil in the form of very dark-brown solid powders.

The increase of the viscosity of soybean oil in the presence of superacids is a consequence of cationic polymerization involving double bonds which are consumed during the reaction. Figure 8 illustrates the decrease of iodine value (IV), which is a direct measure of the double bond content, with time, during the cationic polymerization of soybean oil. At the beginning, a sharp decrease of IV is observed followed by a very slow decay in the last hours of polymerization. The final iodine value of polymerized soybean oil after 5-6 hours of polymerization is relatively high, being around 95-110 gI₂/100g. This relatively high value is very important for applications in printing inks, paints, varnishes, since double bonds are available for further crosslinking reactions.

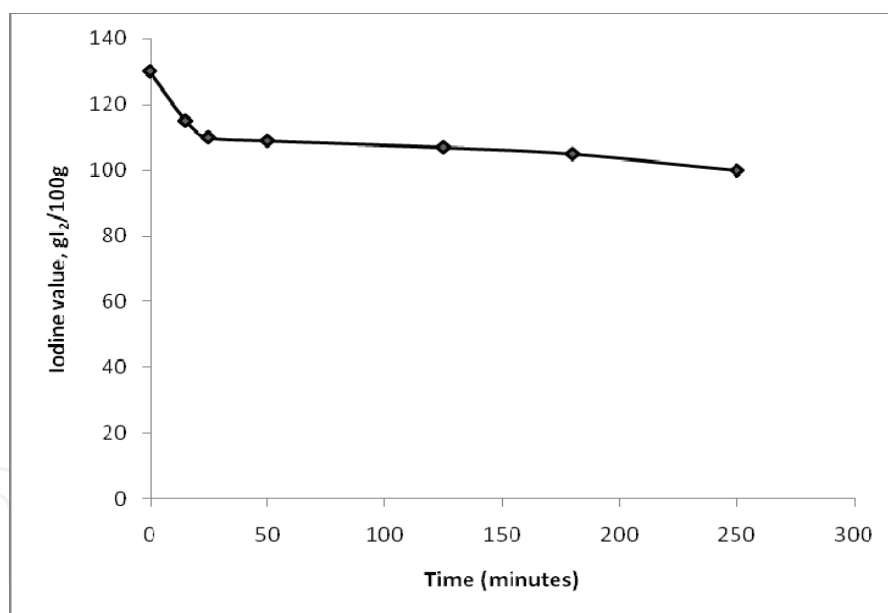


Fig. 8. Variation of iodine value with time in cationic polymerization of soybean oil catalyzed by HBF₄ (1%) at 90 °C.

Figures 9 and 10 show the FT-IR spectra of initial soybean oil and polymerized soybean oil after 6 hours of reaction, respectively. Both spectra show the bands characteristic of the carbonyl of ester bonds (at 1746 cm⁻¹), of double bonds at 3008-3009 cm⁻¹, of various C-H from CH₂ groups, CH groups and CH₃ groups (2925 cm⁻¹, 2854 cm⁻¹, 1163-1463 cm⁻¹). It is interesting that the polymerized soybean oil displays the absorption characteristic of "trans" double bonds at 967 cm⁻¹, proving that the rearrangement of some initial "cis" double bonds of soybean oil to "trans" double bonds occurs in the presence of superacids.

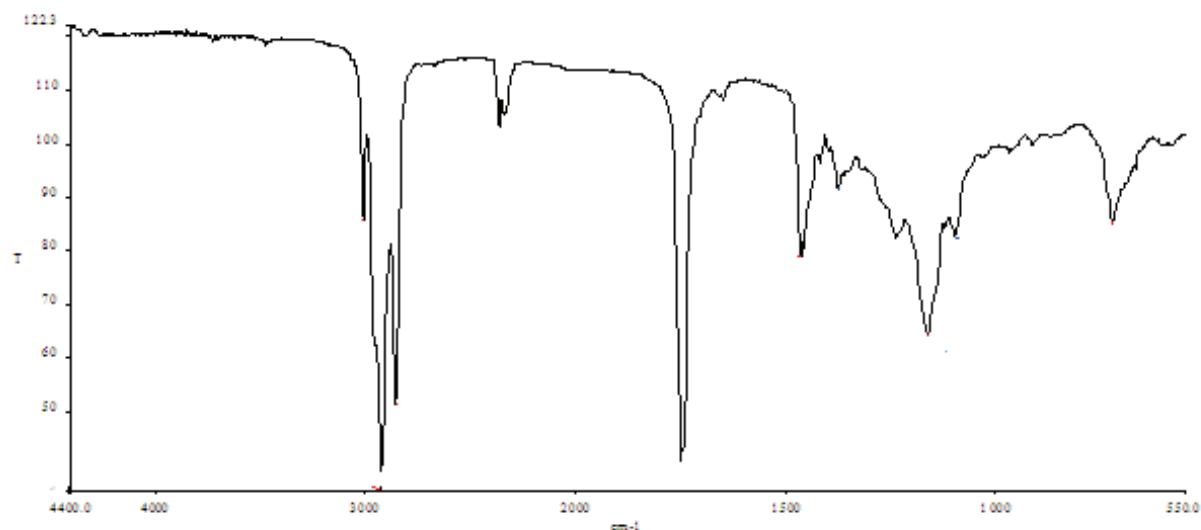


Fig. 9. FT-IR spectrum of soybean oil

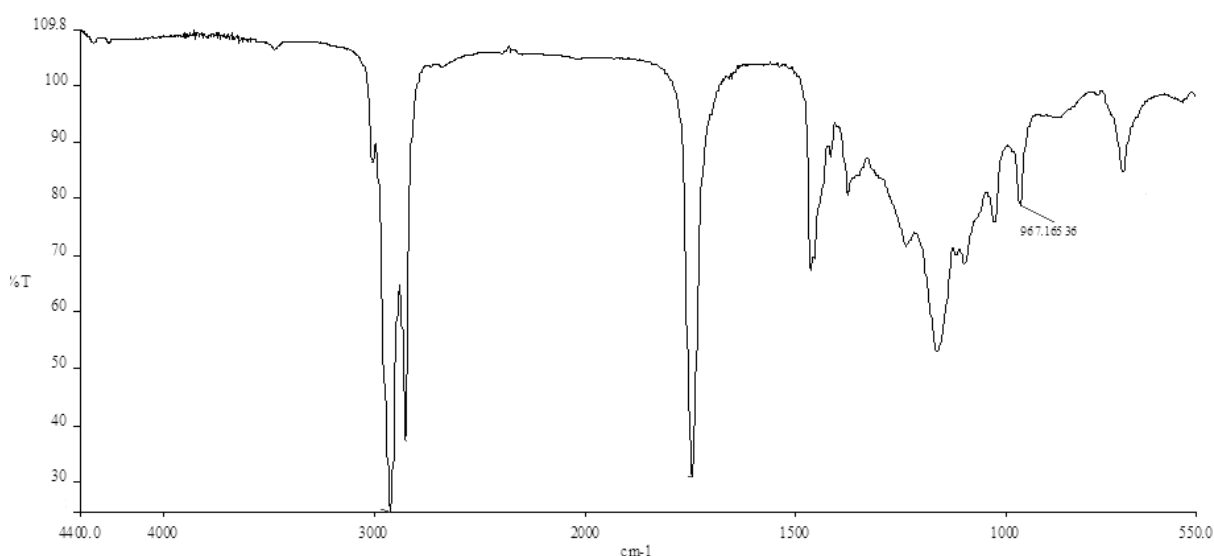


Fig. 10. FT-IR spectrum of cationically polymerized soybean oil after 6 hours of reaction. Catalyst: HBF_4 1%; temperature: 90 °C.

Figures 11 and 12 show ^1H NMR spectra of initial soybean oil and of cationically polymerized soybean oil after 6 hours of the reaction. They give important information on the possible mechanism of cationic polymerization soybean oil.

The decrease of double bond content at chemical shift of 5.42 ppm is evident. A strong decrease of mono-allyl (2.16 ppm) and bis-allyl (2.63 ppm) hydrogen atom concentrations observed in polymerized soybean oil suggests that they play an important role in the cationic polymerization. The mono-allyl and bis-allyl positions in fatty acids of soybean oil are displayed in Figure 13. Mono-allyl hydrogens are attached to a carbon atom linked to a double bond and bis-allyl hydrogen atoms are linked to a carbon atom between two double bonds. Thus, oleic acid has two mono-allyl positions, linoleic acid has two mono-allyl and one bis-allyl positions and linolenic acid has two mono-allyl and two bis-allyl positions.

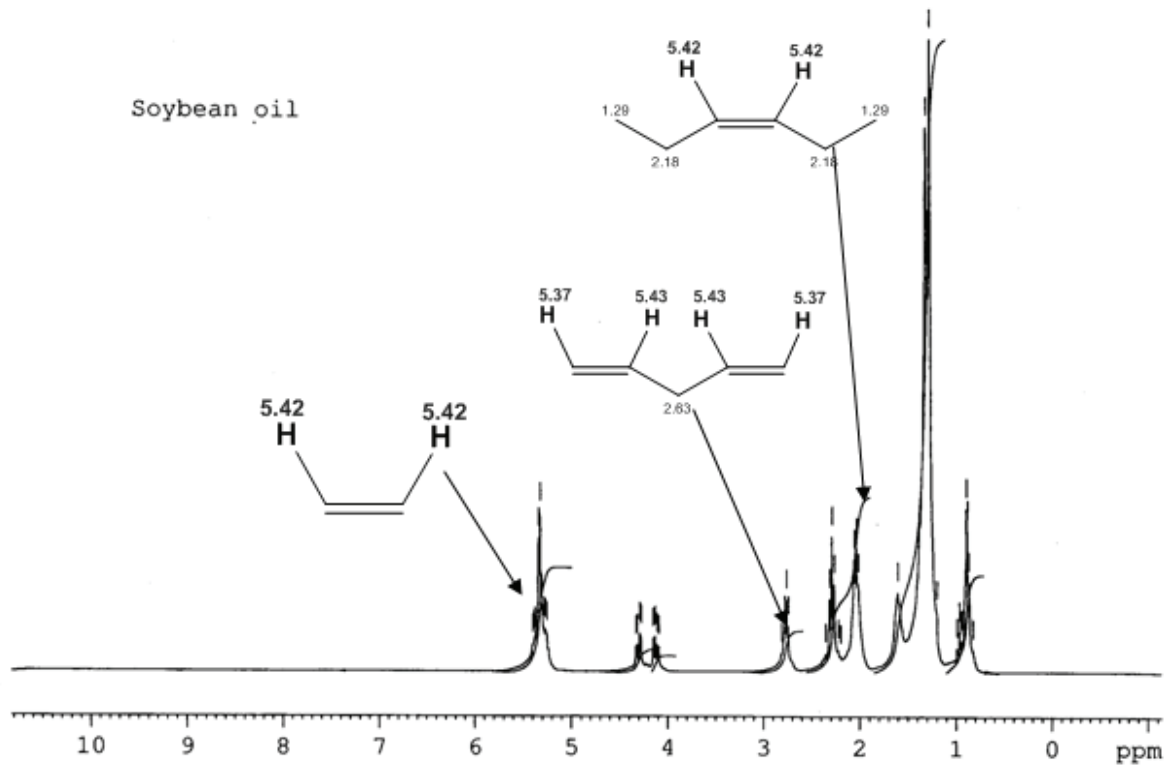


Fig. 11. ¹H NMR spectrum of initial soybean oil

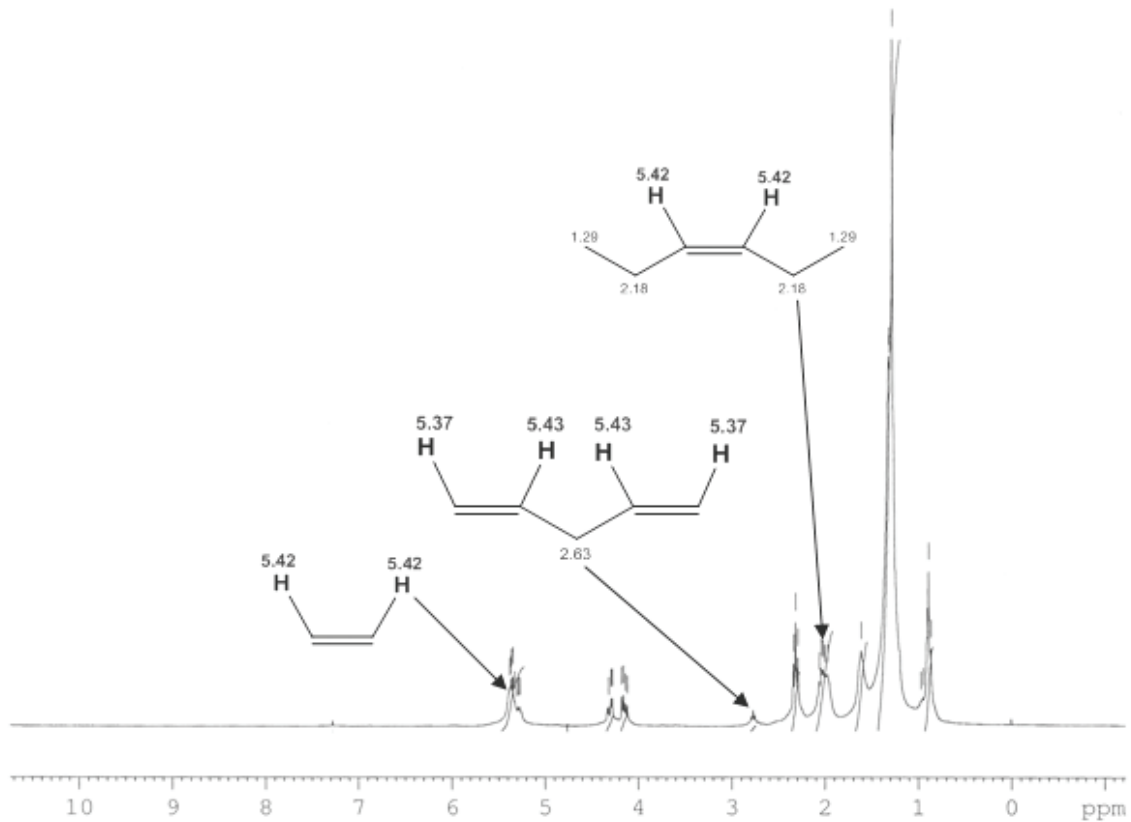


Fig. 12. ¹H NMR spectrum of polymerized soybean oil after 6 hours of reaction. Catalyst: HBF₄ 1%; temperature 90 °C.

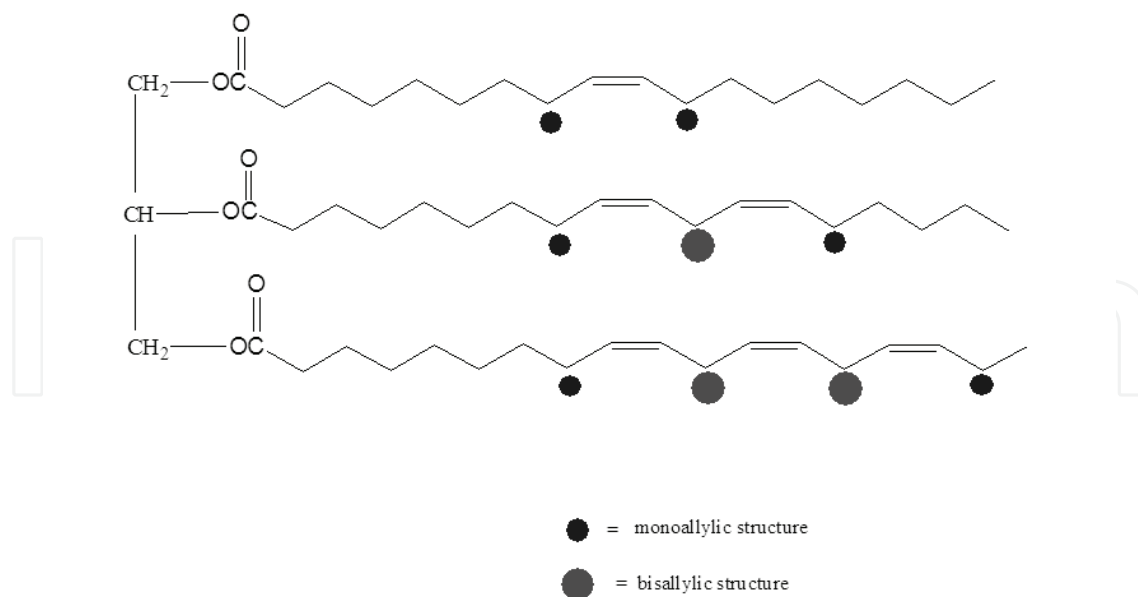
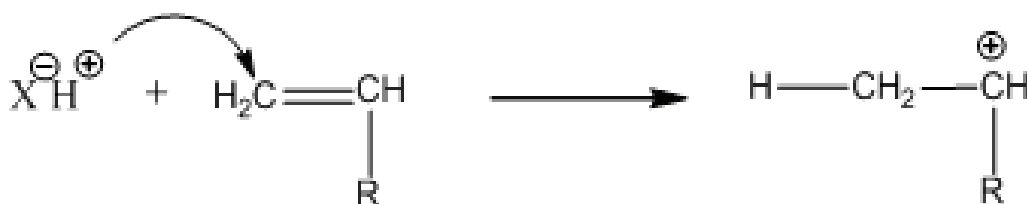


Fig. 13. The mono-allyl and bis-allyl positions in fatty acids of soybean oil.

4. The proposed mechanism for cationic polymerization of soybean oil

Based on the data presented, we propose a mechanism of cationic polymerization of soybean oil, which proved to be unconventional and different from the classical cationic polymerization of olefins.

The classical cationic polymerization of olefins activated by electron releasing substituents (vinyl ethers, isobutylene, vinyl carbazol etc) starts with the formation of carbocations resulting from the reaction of acid catalysts with double bonds of a monomer (SCHEME II).

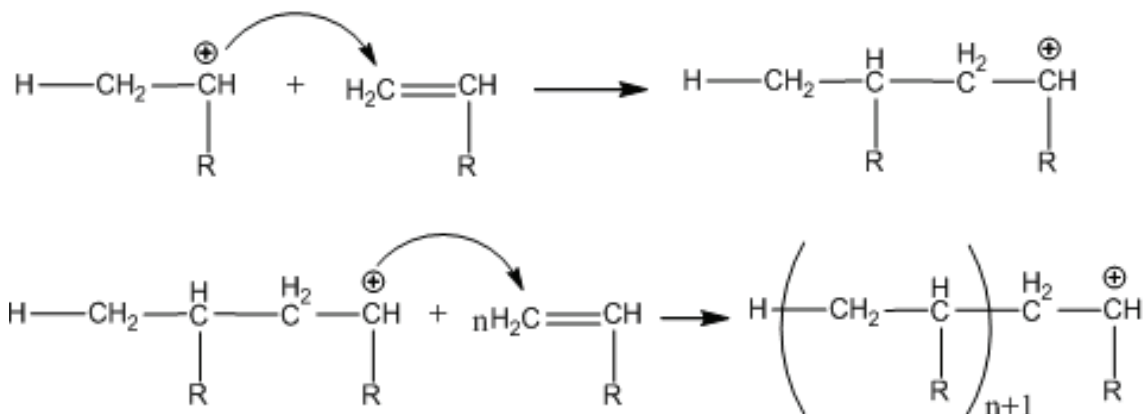


Scheme II. Formation of a carbocation by the attack of a proton on the olefin double bond

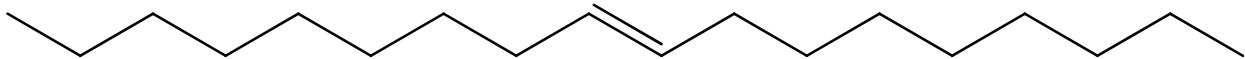
The formed carbocations attack double bonds, step by step, generating macrocations (polymers terminated with a carbocation active center) as shown in SCHEME III.

Internal 1,2 disubstituted double bonds are of much lower reactivity in cationic polymerization and do not follow the classical pathway presented in SCHEME II and SCHEME III. To prove that, we carried out the cationic polymerization of 9-octadecene, a model compound having an internal 1,2 disubstituted double bond (SCHEME IV).

Gel Permeation Chromatograms of initial 9-octadecene and after 6 hours of cationic polymerization are presented in Figure 14. The catalyst was triflic acid as the best superacid for soybean oil polymerization, at 90 °C. Surprisingly no oligomers or polymers were formed after 6 hours of reaction. The initial monomer was recovered unchanged.



Scheme III. Cationic polymerization of activated olefins



Scheme IV. Structure of 9-octadecene.

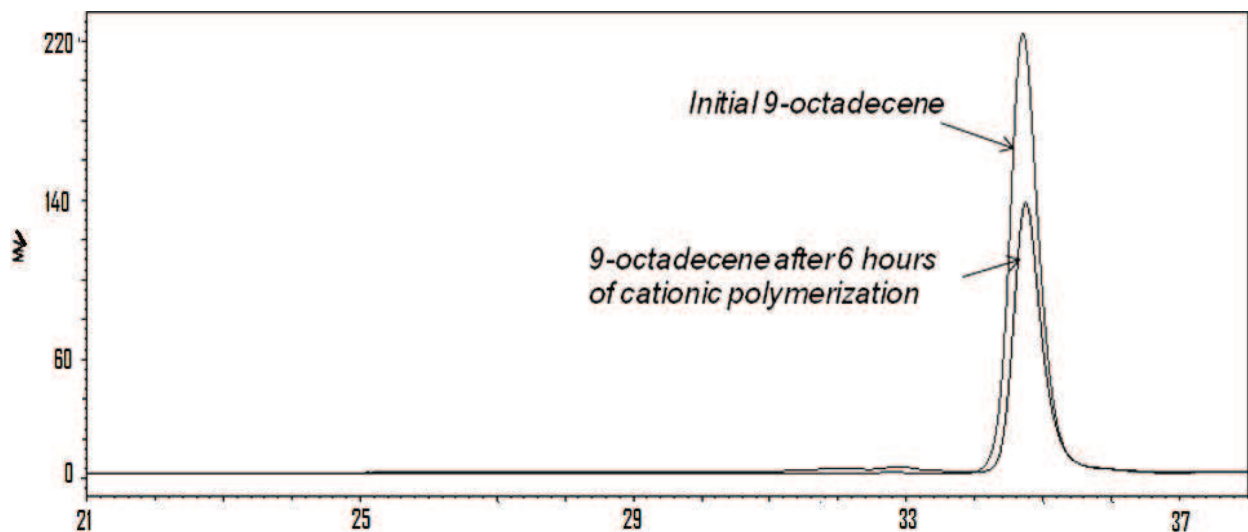
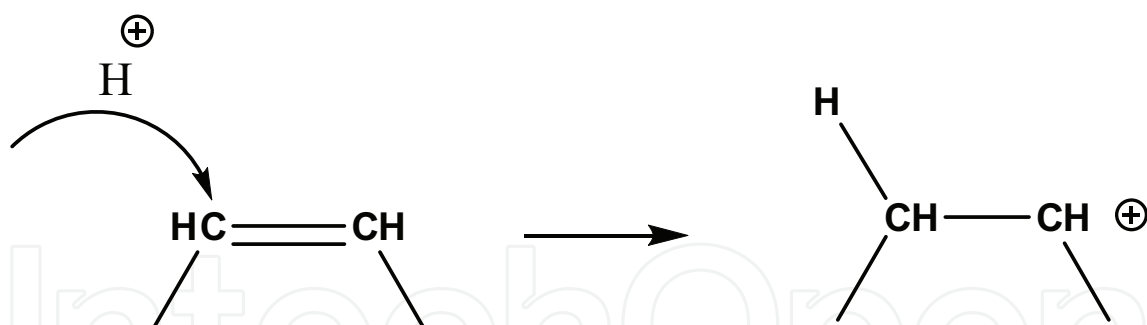


Fig. 14. GPC of the initial 9-octadecene and of 9-octadecene after 6 hours of cationic polymerization.

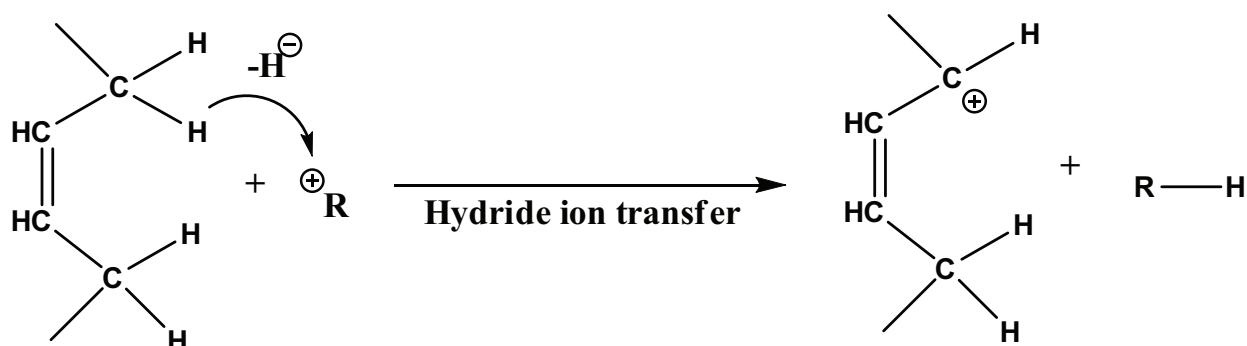
If other model compounds having an internal double bond such as methyl oleate or triolein (triglyceride of oleic acid) are used in the presence of superacids such as HBF_4 or triflic acid, no oligomeric or polymeric species are observed. These experiments lead to an important conclusion that fatty acids derivatives with one internal double bond (oleic acid) do not polymerize readily in the presence of superacids. Thus, the cationic polymerization of soybean oil is due to the fatty acids with two or three double bonds involving a totally different mechanism from that of the classical cationic polymerization of olefins.

We propose the following mechanism for the cationic polymerization of soybean oil. The first step of polymerization is undoubtedly the addition of protons of superacids to double bonds of oil (SCHEME V).



Scheme V. Formation of a carbocation in the reaction of a proton from superacids with the double bond of soybean oil

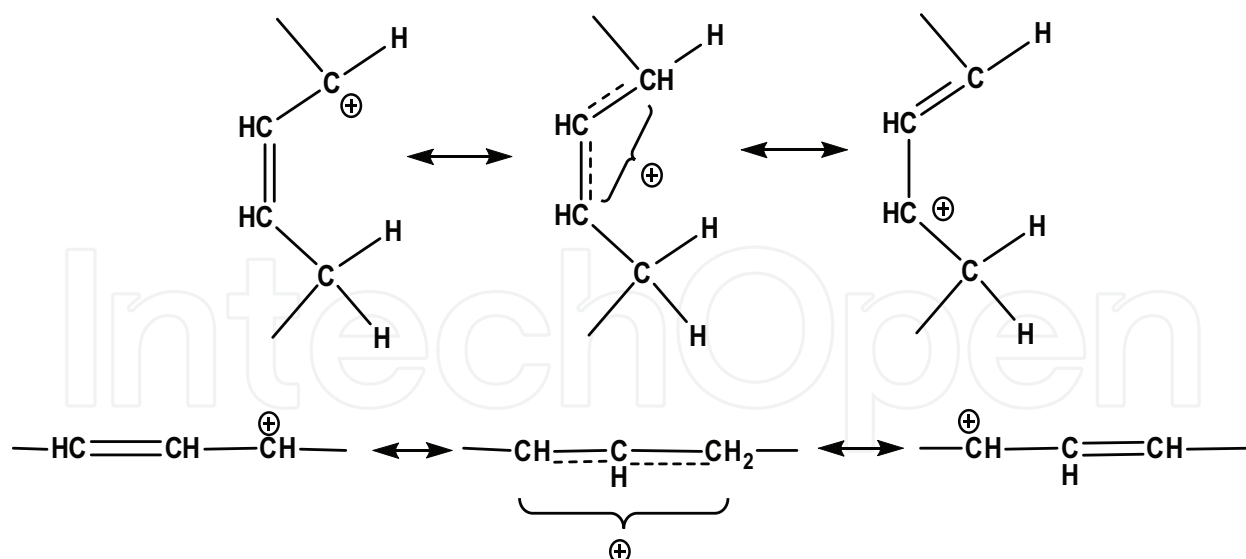
The next step is not the attack of the formed carbocation on a new double bond, but the transfer reaction of carbocations with hydrogen atoms from mono-allyl and especially from bis-allyl positions. The hydrogen atoms in allyl and bis-allyl positions are very labile and easily react with reactive carbocations forming allyl cations, which we consider to be the key species in cationic polymerization of soybean oil (SCHEME VI). The transfer reaction by abstraction by reactive carbocations of hydride anions from structures with labile hydrogen atoms (hydrogen atoms from allyl or benzyl positions) is a general reaction of carbocations.



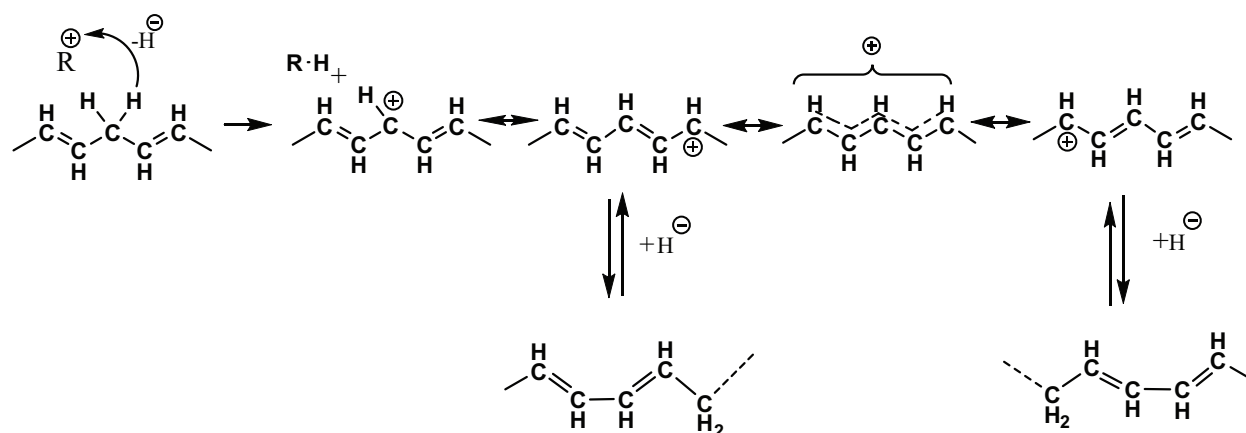
Scheme VI. Formation of allyl cations by transfer reaction of carbocations with the hydrogen atoms from allyl positions

Allyl cations are very stable due to the hybrid resonance, since practically the positive charge is distributed among 3 carbon atoms (SCHEME VII). As a consequence, the allyl cations have a much lower reactivity than the carbocations formed by addition of a proton to a double bond. This is the reason why the olefins having allyl positions do not polymerize cationically. Due to this transfer reaction, allyl protons disappear during cationic polymerization of soybean oil as was observed in ^1H NMR spectra. Thus, transfer reactions of carbocations with allyl protons play a major role in cationic polymerization of soybean oil.

The resonance structures formed in the case of transfer reactions with hydrogen atoms of bis-allyl position are more complicated in the case of linoleic acid, since the positive charge is extended to 5 carbon atoms as shown in SCHEME VIII. They lead to the formation of conjugated double bonds, which are around 4 Kcal/mol more stable than nonconjugated double bonds. Transfer reactions of these cations with other bis-allyl protons lead to other conjugated double bonds which participate in Diels Alder reactions, mainly with allyl cations.



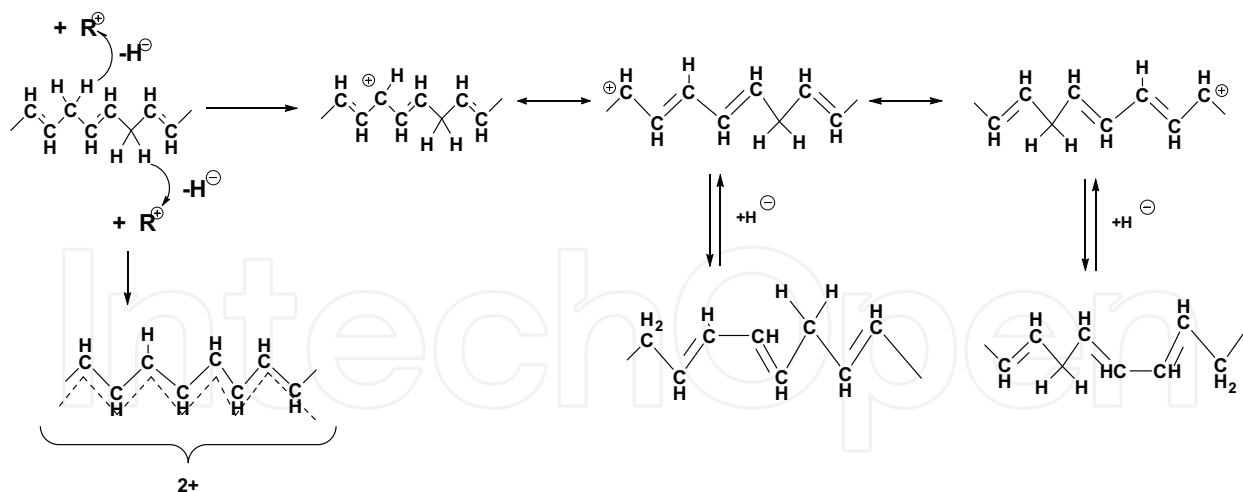
Scheme VII. Resonance hybrids of allyl cations



Scheme VIII. Transfer reactions of carbocations with bis-allyl protons of linoleic acid leading to the formation of conjugated double bonds.

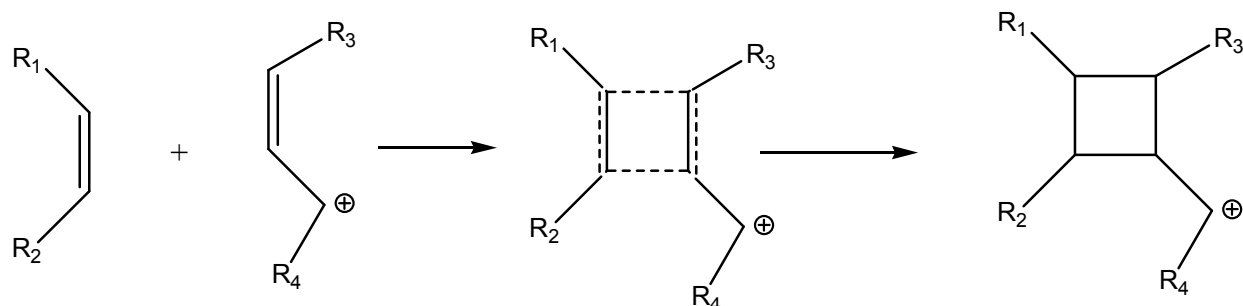
In the case of linolenic acid, the transfer reaction of hydrogen atoms from both bis-allyl positions can generate allyl cations with resonance structures having two positive charges distributed over 7 carbon atoms. Conjugated double bonds in linolenic structures are formed in a similar way as in linoleic acid. The resonance hybrids in the case of allyl cations derived from linolenic acid chains are presented in SCHEME IX.

One of the most important properties of electron deficient species such as allyl cations is to participate easily in Diels Alder reactions, which are a part of the group of pericyclic reactions characterized by a cyclic transition state. There is significant literature data on Diels Alder reactions of allyl cations (Beatriz de Pascual,1996, Gassman & Lottes 1986, Gassman &Becker 1992, Gassman 1992, Deno,1970). An allyl cation can react with an isolated double bond (e.g., from oleic acid) forming a cyclobutane ring ($2\pi+2\pi$ Diels Alder cycloaddition reaction), or to react an allyl cation with a 1,3 diene structure (conjugated double bonds) forming a 6-membered cycle ($4\pi+2\pi$ Diels Alder cycloaddition reaction), or to react an allyl radical with conjugated double bonds and form a seven-membered cycle ($4\pi + 3\pi$ Diels Alder cycloaddition reaction). This last Diels Alder reaction is recognized as a general



Scheme IX. Transfer reactions of carbocations with "bis" allyl protons of linolenic acid and the formation of conjugated double bonds

method for synthesis of 7 membered cyclic compounds. Schematically, these types of Diels Alder reactions of allyl cations are presented in the next SCHEMES X, XI and XII. It is well known that in Diels Alder reactions are two partners: one rich in electrons (for example dienes) and one deficient in electrons, in our case allyl cations. Of course allyl cations as any cationic species, are deficient in electrons with a big affinity for the species rich in electrons.

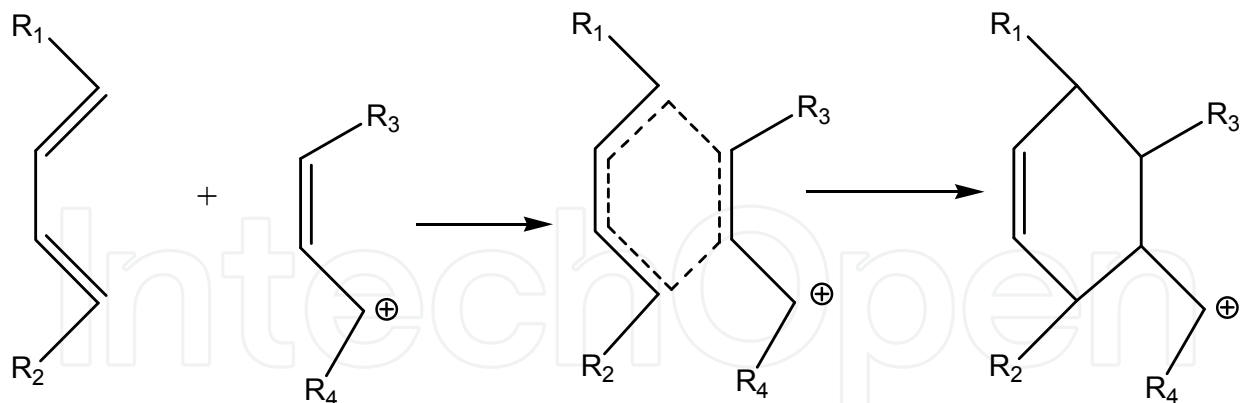
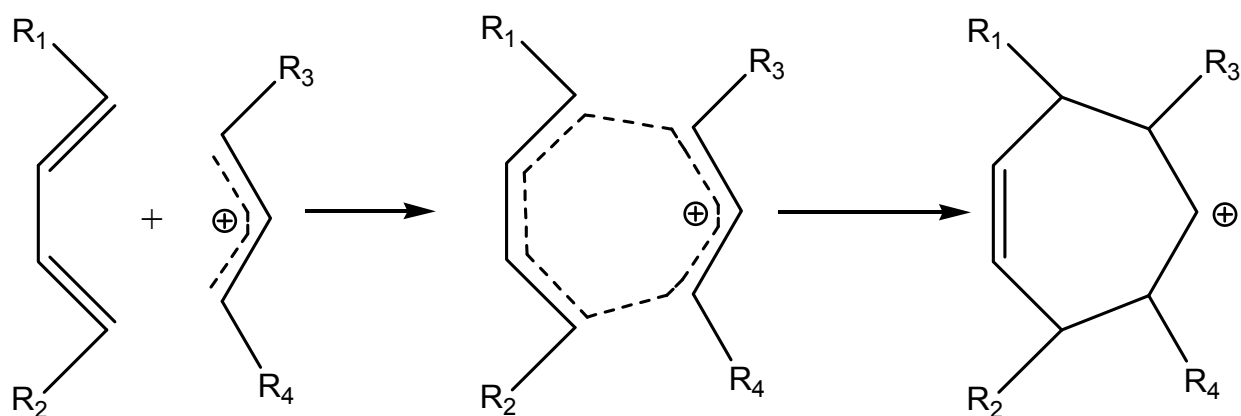
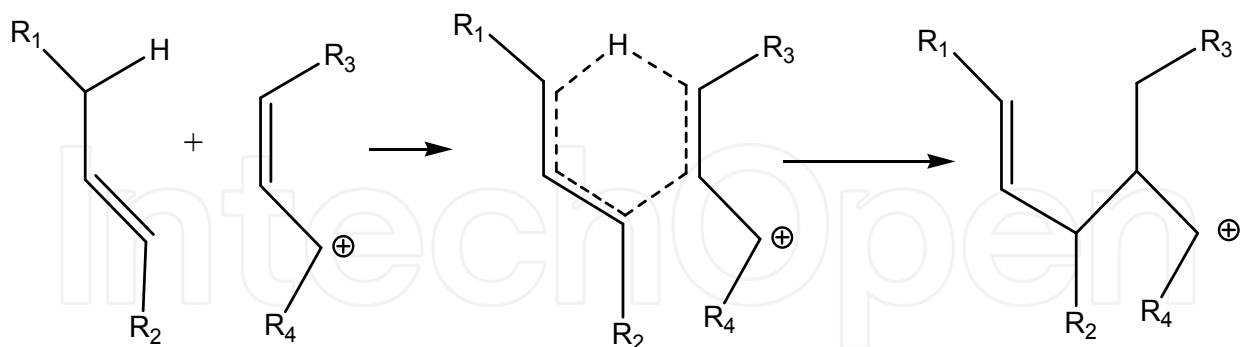


Scheme X. $2\pi+2\pi$ cycloaddition Diels Alder reaction of allyl cations

Diels Alder reactions with formation of cyclobutane rings are less probable (but not impossible) due to very high angular strain of cyclobutane ring and due to the lower reactivity of an isolated double bond as compared with conjugated double bonds in pericyclic reactions. Formation of cyclobutane rings was observed in cationic polymerization of oleic acid and derivatives with BF_3 as a catalyst (Ghodssi, 1970, Gassman & Lottes, 1992).

The new nonconjugated carbocations formed as a consequence of Diels Alder reactions are very reactive species and participate easily in transfer reactions with mono-allyl and bis-allyl hydrogen atoms.

Another possible reaction involving allyl cations called "ene" reaction, may be involved in the cationic polymerization of soybean oil. "Ene" reactions, another pericyclic reaction, are very similar with Diels Alder reaction, and are appreciated as a powerful way to generate C-C bonds (SCHEME XIII). The "ene" reaction, characteristic to isolated double bonds, probably is carried out in a lesser extent. In the cationic dimerization or trimerization of unsaturated fatty acids with acidic clays only 5-6% reaction products are formed as a consequence of "ene" reaction the rest being cyclic compounds (cyclic dimer and trimer acids) as a consequence of Diels Alder reactions, which are predominant reactions.

Scheme XI. $4\pi + 2\pi$ cycloaddition Diels Alder of allyl cationsScheme XII. $4\pi + 3\pi$ cycloaddition Diels Alder reaction of allyl cations

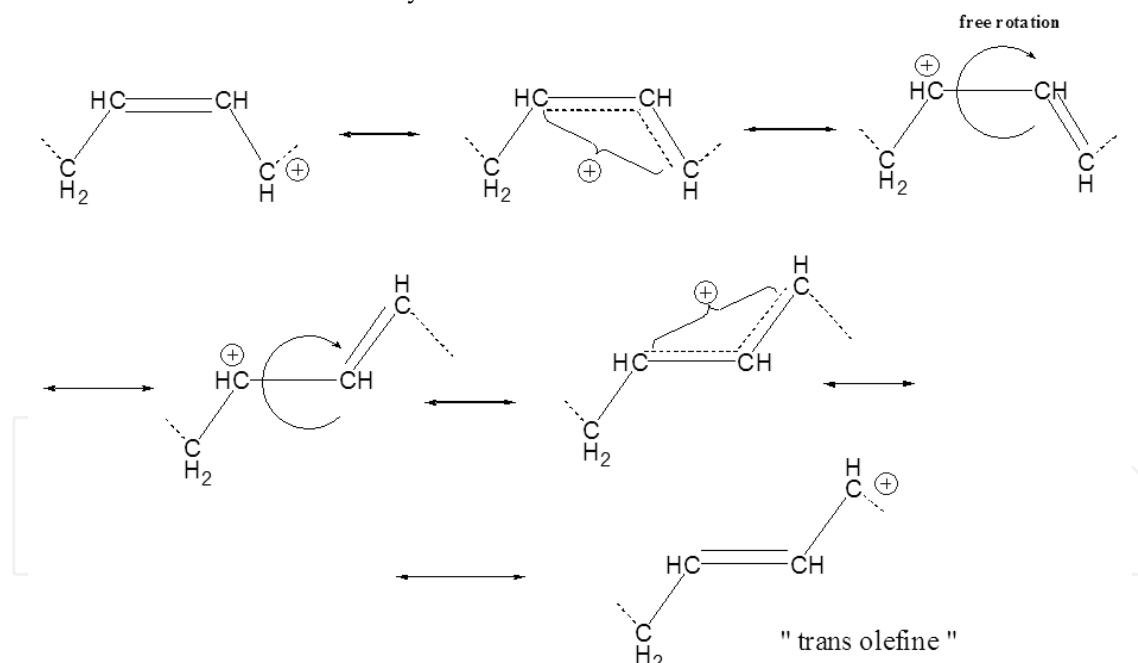
Scheme XIII. "Ene" reaction of allyl cations

In conclusion, the cationic polymerization of soybean oil is a reaction due to the allyl cations formed by transfer reactions of carbocations with mono-allyl and bis-allyl positions. The triglycerides structures are linked by various C-C bonds (in cyclic and acyclic forms), to branched oligomers and polymers as a consequence of Diels Alder and "ene" reactions of allyl cations.

Summarizing, the cationic polymerization of soybean oil has the following characteristic steps:

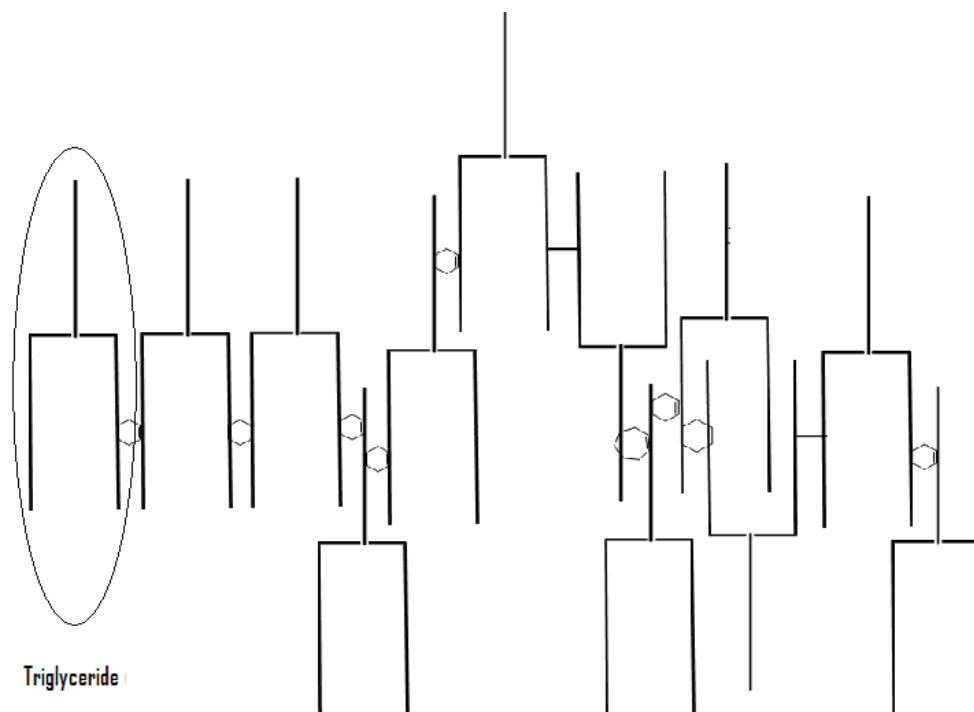
1. Formation of carbocations by addition of protons of superacids to double bonds of oil;
2. Transfer reaction of carbocations with the hydrogen atoms (hydride ion transfer) from mono-allyl and bis- allyl positions with formation of allyl cations, the "key" species in the cationic polymerization of soybean oil;
3. Diels Alder reactions of allyl cations with the double bonds and conjugated double bonds formed as a consequence of resonance hybrids of allyl cations in linoleic and linolenic structures. In that way the triglyceride fatty acid chains are linked by cyclic structures formed as a consequence of Diels Alder reactions;
4. In lesser extent, another pericyclic reaction of allyl cations, the "ene" reaction may take place, leading to a linkage between triglycerides chain by C-C bonds;
5. In parallel with polymerization reaction the rearrangement of "cis" double bonds of soybean oil to "trans" double bonds is carried out.

The rearrangement of "cis" double bonds to "trans" double bonds is possible due to the resonance hybrids of allyl cations too. In one resonance hybrid, the initial double bond becomes single bond, and it is permitted the free rotation around this bond (Deno et al 1970). The driving force of this free rotation is the repulsion between the alkyl substituent situated in "cis" position. Due to this free rotation are formed the "trans" isomer more stable than "cis" isomer (SCHEME XIV). As a general view of cationic polymerization of soybean oil, the formation of linkages between triglyceride units by Diels Alder and "ene" reactions and isomerization of "cis" double bonds to "trans" double bonds, all are a consequence of hybrid resonance structures of allyl cations.



Scheme XIV. Rearrangement of "cis" double bonds to "trans" double bonds in cationic polymerization of soybean oil

Based on the proposed mechanism, the probable structure of polymerized soybean oil is presented in the next SCHEME XVI. Cationic polymerized soybean oil is a highly branched polymeric structure constituted by triglyceride units linked by C-C bonds from cyclic rings, predominantly six or seven membered rings as a consequence of Diels Alder reactions or by simple C-C bonds as a consequence of "ene" reactions, all reactions involving allyl cations.



Scheme XVI. The structure of cationic polymerized soybean oil

Table 2 presents some characteristics of cationic polymerized soybean oil in comparison with heat bodied soybean oil and heat bodied linseed oil.

No.	Characteristic	Cationic polymerized Soybean oil	Heat bodied Soybean oil	Heat bodied Linseed oil
1	Mn	1900-3000	2300-2300	1800-2800
2	Mw	19000-42000	25000-35000	25000-75000
3	Mw/Mn	10-14	11-14	14-27
4	Monomer, %	26-31	11-18	21-30
5	Oligomers, %	68-72	77-78	68-75
6	Free fatty acids, %	<1	4-9	2-4
7	Iodine value, mgI ₂ /100g	105-110	65-95	103-110
8	Acidity, mg KOH/g	2-3	7-9	9-10
9	Viscosity, 25°C, Pa.s	7-16	6-10	5.6-17
10	Refractive index, n _D 25 °C	1.476-1.481	1.478-1.480	1.4896

Table 2. Characteristics of cationically polymerized soybean oil in comparison with heat bodied soybean oil and heat bodied linseed oil.

5. Conclusions

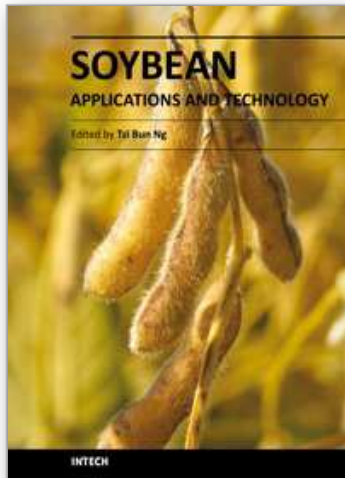
A new process for cationic polymerization of soybean oil, catalyzed by superacids such as tetrafluoroboric acid, triflic acid and hexafluoroantimonic acid, is presented. The high yield, practically quantitative process produces viscous liquid or solid polymers depending on the reaction time. The reaction is carried out in mild reaction conditions: 80-100 °C and atmospheric pressure. In comparison with the heat bodied oils, the current process is more

economical. In comparison with "air blown" oils, cationic polymerization of oils produces only triglycerides fatty acid hydrocarbon chains linked by various C-C bonds, without carboxyl, aldehyde, ketone or hydroperoxide groups. We proposed an unconventional mechanism for cationic polymerization of soybean oil involving pericyclic reactions of allyl cations (Diels Alder and "ene" reactions), allyl cations being the "key" cationic intermediates. The relatively high content of double bonds makes the cationically polymerized soybean oil suitable for further crosslinking reactions useful for printing inks and rubber modifiers, but also as lubricants, compressor fluids etc.

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