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Cooligomerization of dominant monomers of C_9 fraction of liquid pyrolysis products: comparison of heterogeneous catalytic approach with common methods

Research Article

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Abstract: Cooligomerization of liquid products of the C_9 fraction of diesel fuel pyrolysis to produce cooligomers of wide application is suggested to be carried out with silica-alumina catalysts, among which the activated bentonite clay seems to be optimal. Cooligomerization of the mixture simulating the C_9 fraction composition was studied to compare the suggested heterogeneous catalytic method with other methods of cooligomers production. Different methods have been compared in terms of yield of cooligomers and their properties, namely molecular weight and its distribution, density, unsaturation and colour. The ratio of monomer units in cooligomer has been determined and the monomers conversion degrees have been calculated for different cooligomerization methods. Reasons of structure and composition differences of cooligomers obtained by different methods are suggested.

Keywords: *Cooligomerization • C_9 fraction • Model mixture • Silica-alumina catalysts • Hydrocarbon resins*

1. Introduction

Gaseous olefins (ethylene, propylene and butylenes) are produced by pyrolysis of gasoline, diesel fuel, natural gas etc. Along with the target gaseous products, liquid pyrolysis products (by-products) are inevitably formed. Their yield ranges from 10 to 40% depending on the feedstock and the process conditions [1,2]. The C_5 and C_9 fractions are obtained as a result of the liquid products fractionation. Utilization of these petrochemistry by-products of is a problem of great economic and ecological importance. The C_5 and C_9 fractions are complex mixtures of saturated and unsaturated hydrocarbons of aliphatic (C_5) and aromatic or cycloaliphatic series (C_9). The most reasonable way of utilization of the C_5 and C_9 fractions is cooligomerization of their unsaturated components to produce cooligomers (so called hydrocarbon resins) which have wide applications. These cooligomers are used in paints and varnishes [1-3],in tackifiers [4], in hot melt [5], pressure sensitive [6] and solvent adhesives, in sealants, rubber compounding [7-9], papermaking [1,2], printing inks [1,2,10], corrosion-resistant coating [1,2], in pavement [1,11,12] and road marking [13], in woodworking and fibreboard production [1,2,14], in manufacturing of various building materials [1,2,15],in composite materials production [1,2,16], *etc*. Hydrocarbon resins production is important since such cooligomers substitute products being obtained from natural raw materials, *e.g*. plant oils, turpentine *etc*. The resins are not environmentally hazardous and not toxic to living organisms [17]. Recent publications report new high-technology applications of such cooligomers including polyelectrolyte membranes based on sulfonated hydrocarbon resin [18] and use of the resins in polypropylene/clay nanocomposites [19].

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The synthesis of cooligomers from the C_9 fraction of diesel fuel pyrolysis liquid products is the subject of our research.

Such cooligomers may be produced using thermal, initiated or catalytic cooligomerization [1,2]. The thermal cooligomerization requires high temperatures and long duration which results in high energy consumption. The initiated cooligomerization is also characterized by long duration while peroxide initiators used in this method are highly explosive, fire-hazardous and expensive. The most common method of producing the cooligomers is the homogeneous catalytic cooligomerization using either Friedel-Crafts [2,20-22] or Ziegler-Natta [23,24] catalysts. Although common, this process has a number of significant disadvantages. First of all, besides the proper cooligomerization , it includes stages of catalyst decomposition using alkaline solutions as well as washing off the salts formed. These additional steps produce approximately 6 t. of contaminated wastewater per 1 t. of the cooligomer obtained [1] and the catalyst is irreversibly lost. There is an additional cost related to drying the feed and corrosion protection of the equipment since highly corrosive mediums are formed upon expose to moisture. Finally the catalysts used in this process are unstable when stored and quickly lose their activity.

Our research is aimed at developing the efficient technology without aforementioned disadvantages. In addition, the technology should be environmentally safe and inexpensive. Our approach has been to synthesize the cooligomers by catalytic cooligomerization in the presence of heterogeneous acid-type catalysts of silica-alumina nature. The catalysts initiate oligomerization on the Brønsted active sites (predominantly surface silanol groups) present on their surface [25-27]. The use of such catalysts eliminates the stages of the catalyst decomposition and washing, since the catalyst can be easily separated by filtration or centrifugation. The problem of waste water is also solved and the manufacturing scheme is simplified. The silica-alumina catalysts are not only very cheap, but they also do not lose their activity when stored and do not create corrosion aggressive mediums [25-27].

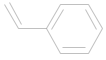
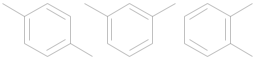
Both, homogeneous catalysts and initiators, are consumables, *i.e.*, they are irreversibly lost in the technological process, while the heterogeneous catalysts, after separation from the reaction mixture, can be recycled and used multiple times, though with decrease in the product yield. It has been found that the yield is less by almost a third when the catalyst is used for the second time, but in the further uses (from the third to the fifth) there is no observed decrease in the cooligomer yield [28].

The number of activated silica-alumina materials, including different zeolites and clays, has been previously studied as the C_9 fraction cooligomerization catalysts [29-31]. The activated bentonite clay has been found to be the optimal among the researched catalysts in terms of the cooligomer yield and properties [29], as well as itsprice (natural bentonite clay costs about 0.2 \$ kg^{-1}, activated one – about 0.4 \$ kg^{-1}, while the price for $AlCl_3$ is no less than 30 \$ kg^{-1}). The catalyst is efficient due to its high specific area [29] and high concentration of its active acid sites [30].

In this paper we compare differences in yield and properties of the cooligomers synthesized using our method of heterogeneous catalysis with other methods (homogeneous catalytic, thermal, initiated) used in industry. The main purpose of our research has been to determine the chemical structure features of the cooligomers synthesized from the same feed using different methods.

The C_9 fraction we researched contains about 58% by wt. of polimerizable hydrocarbons, including styrene (19 % by wt.), dicyclopentadiene (18% by wt.), vinyltoluenes (8% by wt.), α-methylstyrene (2% by wt.) and indene (2% by wt.). The content of any other polymerizable hydrocarbons is less than 1% by wt. Xylene is the main nonpolymerizable hydrocarbon of the C_9 fraction. However, the C_9 fraction composition may vary depending on the feedstock that had undergone pyrolysis and the pyrolysis conditions [1,2]. In order to obtain the results allowing for an objective comparison of the existing methods of the cooligomers synthesis, a mixture closely simulating the C_9 fraction composition (referred to as a model mixture) was studied. There has been no reproducibility problems found in the use of such a mixture. The results obtained for the heterogeneous catalytic cooligomerization of the model mixture are very similar to those obtained for the C_9 fraction cooligomerization carried out under the same conditions. The yields and properties of the cooligomer are very similar and the composition of the product synthesized from the model mixture conforms to the composition of the cooligomer obtained by heterogeneous catalytic cooligomerization of unsaturated hydrocarbons of the C_9 fraction. We have concluded that the model mixture satisfactorily represents the properties of the C_9 fraction and the comparison of different cooligomerization methods based on the results obtained for the model mixture is quite legitimate.

Table 1. The model mixture composition.

Substance name	Structure	Content, % by wt.	Source	Purity, % by wt.
Styrene		34	Aldrich	99
Dicyclopentadienee		24	Merck	95
Xylenes		42	Fluka	97

2. Experimental procedure

2.1. Materials

The model mixture used in our study had the composition given in Table 1. Xylenes and dicyclopentadiene were used as received, while styrene was distilled before it had been used.

Bentonite clay of Dashukivka deposit (Ukraine) was used for the preparation of the heterogeneous catalyst. The bentonite clay consists of 85% by wt of montmorillonite.

The liquid catalytic complex was prepared from anhydrous $AlCl_3$ (98% Aldrich), ethyl acetate (99.8% Aldrich) and toluene (99.8% Aldrich).

Benzoyl peroxide (75% Luperox A75) was used as an initiator in the radical initiated cooligomerization.

2.2. Catalysts preparation

The heterogeneous oligomerization catalyst,activated bentonite clay, was prepared as follows. The natural bentonite clay was treated with 13% by wt. sulphuric acid solution at 100°C for 6 h under intensive stirring. Afterwards the catalyst was filtered off, washed multiple times with water until the pH of the scourage was neutral and dried at 150°C until constant weight.

The $AlCl_3$/ethyl acetate/toluene liquid complex (hereinafter $AlCl_3$/EA/Tol) was used as a homogeneous cooligomerization catalyst; it has been reported to be one of the most efficient catalysts of the C_9 fraction monomers cooligomerization [20-22,32]. The homogeneous catalytic complex was prepared as follows. 15 g of aluminium chloride and 20.6 g of toluene were loaded into a thermally stabilized flask fitted with a stirrer and a condenser. The flask was continuously purged with argon. Afterwards 5 g of ethyl acetate was added dropwise over 30 min under intensive stirring at 35°C and the reaction mixture was stirred at 35°C for 1 more hour. As a result the $AlCl_3$/EA/Tol complex with a molar ratio of the components 1:0.5:2 was obtained.

2.3. Cooligomer synthesis

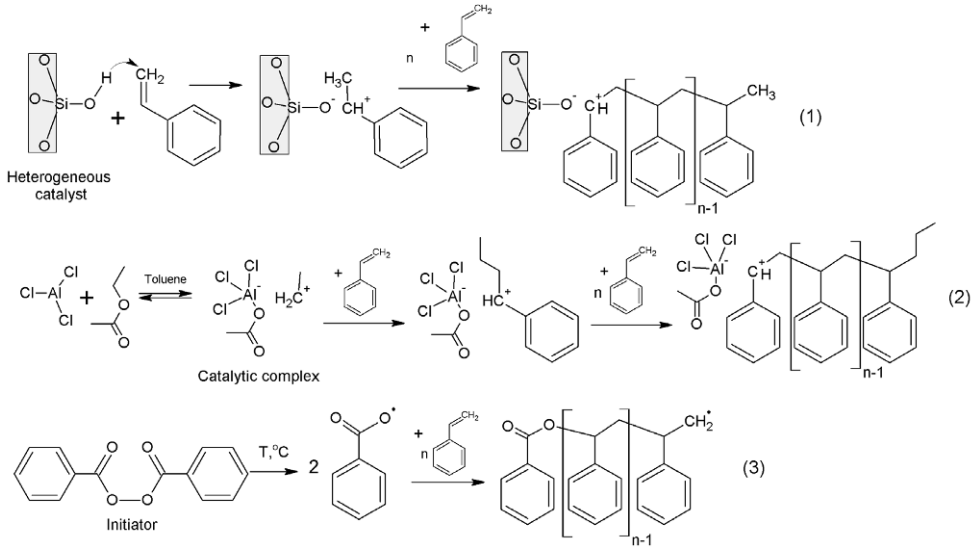
The heterogeneous catalytic cooligomerization was carried out in a three neck flask fitted with a stirrer and acondenser under argon atmosphere. The flask was placed in a thermostat heated to the process temperature. The process was carried out at 80°C for 3 hours under constant intensive stirring. There was 15% by wt. of the catalyst content in the reaction mixture. Before being used the catalyst was dried at 150°C for one hour. After the cooligomerization the catalyst was filtered off under vacuum.

The homogeneous catalytic cooligomerization was carried out the same way as the heterogeneous catalytic one, except for the catalyst isolation procedure. To deactivate the catalyst and remove it from the reaction mixture the latter was treated with 10% sodium hydroxide solution, settled and washed multiple times with water under intensive stirring until neutral pH. The water phase was separated from the hydrocarbon phase after each washing using a separatory funnel. The liquid catalytic complex was used in such an amount as to provide the concentration of $AlCl_3$ of l 3% by wt.

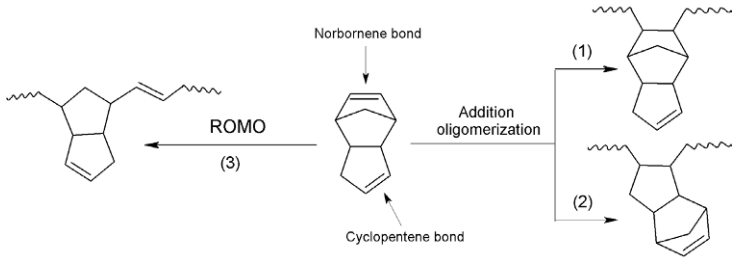
The thermal and the initiated oligomerizations were carried out at the temperatures over 100°C in 100 ml stainless steel ampoules. After the feed has been loaded the ampoules were purged with argon, hermetically sealed and placed in the thermostat. The concentration of the initiator was 1% by wt.

In all the methods the atmospheric and vacuum stripping were consecutively carried out to obtain the final product in the residue.

The cooligomer yield was calculated as the percent ratio of the final product weight to the weight of the feed (model mixture) taken for the synthesis, *i.e.*, the maximal possible yield was equal to the polymerizable components content in the model mixture (58% by wt.).



Scheme 1. Schemes of chain initiation and propagation when using different oligomerization methods.



Scheme 2. Possible DCPD oligomerization pathways.

2.4. Cooligomer properties determination

The colour of the cooligomer was determined by comparing its 10% benzene solution with the standard iodine scale [33].

The bromine number (unsaturation) was determined by iodometric back titration according to a common technique [34].

The cooligomer average molecular weight was determined by cryoscopic Beckmann method in benzene solution [35].

The molecular weight distribution of the cooligomers was determined by gel permeation chromatography (GPC). Chloroform was used as the eluting solvent with a flow rate of 1.0 mL min^{-1}. Four columns with MZ-SD-plus gel were applied. Each column was 300 mm in length, 8 mm in diameter, while the diameter of the gel particles was 5 μm, and the nominal pore widths 50, 100, 1000, and 10000 Å. The conventional calibration was performed using poly(methylmethacrylate) standards. Polymer Laboratories ELS-Detector PL-ELS 1000 was used for detection andthe GPC data were processed by the WinGPC Unity program.

The cooligomer density was defined by hydrostatic weighing [36].

Raman spectra were recorded on Bruker RFS 100/S in the range from 400 to 4000 cm^{-1}. The samples were prepared by pelleting of the comminuted cooligomer with KBr powder.

^{1}H-NMR-spectra were recorded on Bruker AV600 with operating frequency 400 MHz. The samples for NMR were prepared by dissolving the cooligomer (10 mg weighed very precisely) in deuterated chloroform (0.7 mL). Quantitative analysis was carried out based on the squares of the ^{1}H-NMR-spectra peaks, calculated by integration of the corresponding spectra regions using MestReC software.

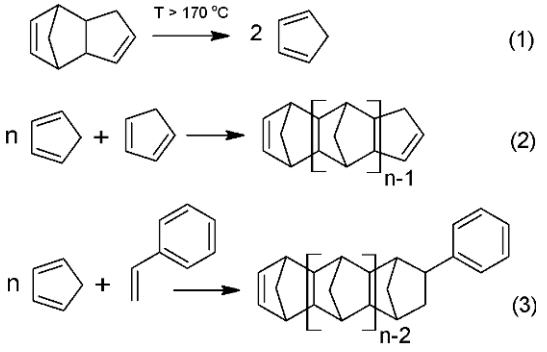
3. Results and discussion

Synthesis of the cooligomers from the model mixture was carried out by the thermal and the initiated cooligomerization, both proceeding by a radical mechanism, as well as by the homogeneous catalytic

and heterogeneous catalytic cooligomerization, proceeding by a cationic mechanism. Although the liquid catalytic complex does not form a true solution with the feed and the reaction mixture is more of a fine emulsion than a solution, we will call it "homogeneous catalysis" for the convenience and to distinct it from the solid silica-alumina catalyst.

In our opinion it will be useful for the further discussion of the results to first describe the possible reaction pathways for each method of synthesis.

The chain initiation and propagation for each case (in terms of styrene) are schematically represented in Scheme 1 (1 – heterogeneous catalytic, 2 – homogeneous catalytic, 3 – initiated). The thermal cooligomerization differs from the initiated one only by the source of the primary radicals.

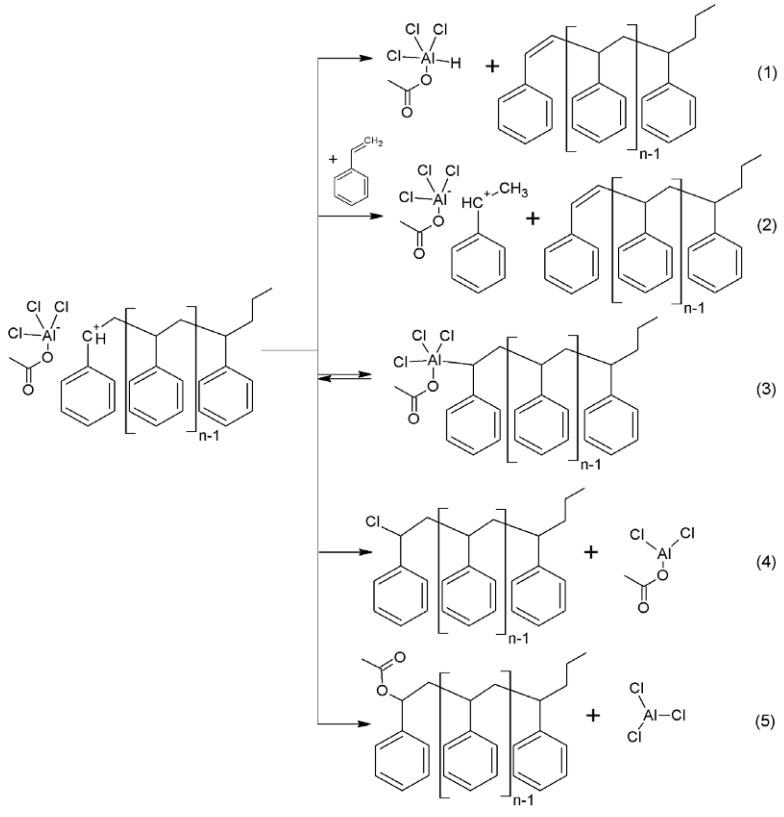


Scheme 3. Retro-Diels-Alder reaction of DCPD (1) and CPD oligomerization by Diels-Alder reaction.

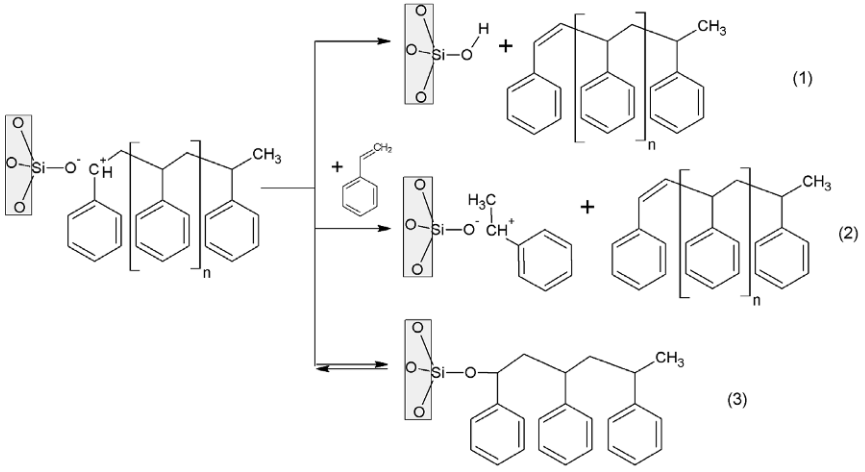
Dicyclopentadiene (IUPAC name [5.2.1.$0^{2,6}$]deca-3,8-diene) contains the strained ring and two double bonds (the norbornene and the cyclopentene ones) in its molecule (Scheme 2) and therefore it may oligomerize by two possible pathways (path (1) and path (2) on Scheme 2). Besides the addition oligomerization of dicyclopentadiene (DCPD), the ring opening metathesis oligomerization (ROMO) is also possible (Scheme 2 path (3)) [38].

Oligomerization of DCPD using both double bonds of the same molecule is theoretically possible during the homogeneous catalytic process, but it is impossible in case of the heterogeneous catalysis. Since the active sites are fixed on the surface, a DCPD molecule bound to the surface active site by one unsaturated bond cannot interact with another site using the other double bond.

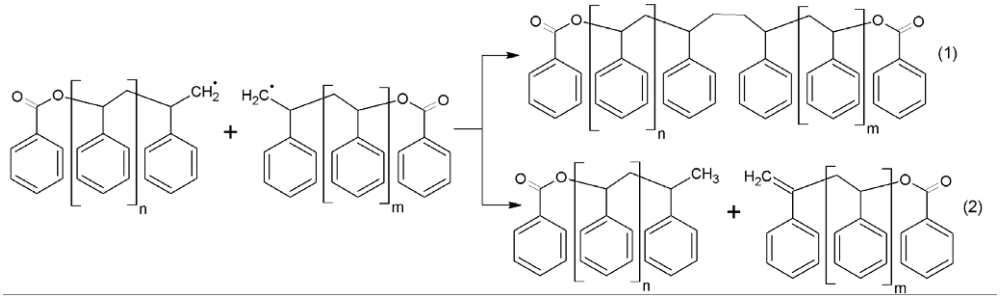
It is also known that at the temperatures over 170°C DCPD is converted into two molecules of cyclopentadiene (CPD) by retro-Diels-Alder reaction (Scheme 3(1)). The monomer of CPD can then participate in Diels-Alder reaction [2] resulting in oligocyclopentadiene as shown in Scheme 3(2).



Scheme 4. Schemes of chain termination in case of homogeneous catalytic cooligomerization.



Scheme 5. Schemes of chain termination in case of heterogeneous catalytic cooligomerization.



Scheme 6. Schemes of chain termination in case of initiated cooligomerization.

Styrene can also participate, as a dienophile, in Diels-Alder reaction with CPD (Scheme 3(3)). But all these reactions are possible only at temperatures higher than 170°C.

Chain termination is worth of thorough consideration as there are many possible pathways in each case. The greatest number of the chain termination pathways is possible for the homogeneous catalytic cooligomerization (Scheme 4).

Besides the pathways given in Scheme 4 the chain transfer to another cooligomer molecule or to the solvent are also possible.

When using a silica-alumina catalyst, the number of possible chain termination pathways decreases (Scheme 5).

In radical oligomerization the chain is terminated either by recombination (Scheme 6(1)) or by disproportionation (Scheme 6(2)).

Chain transfer on monomer or oligomer is also possible for a radical mechanism.

3.1. Cooligomer yield

All syntheses have been carried out at the optimal temperature and duration for the catalytic cooligomerization (both heterogeneous and homogeneous) (pale grey colour in Figs. 1,2,5-7). In addition, the thermal and the initiated cooligomerizations have been carried out at the conditions that are reported to be optimal for these processes (shades of dark grey colour in Fig. 1,2,5-7).

As seen in Fig. 1 our heterogeneous catalytic method allows achieving the product yield of 25.1% that is almost equal to the one obtained when using the initiator under the same conditions. The yield obtained in the cooligomerization without a catalyst under the same conditions is almost four times less. The cooligomer yield in the homogeneous catalytic process is about twice the yield obtained in the heterogeneous catalytic process. The thermal method under the optimal conditions (temperature increased by a factor of 2.5 while duration increased twice) gives the yield only 6.3% higher than in case of the heterogeneous catalytic process under the much milder conditions.

3.2. Properties of cooligomers

The average molecular weight indicates that the cooligomers obtained by our method are predominantly pentamers. The average molecular

weight of the cooligomers formed by the cationic mechanism (homogeneous and heterogeneous catalytic cooligomerization) is considerably lower than that of the products obtained under the same conditions by the radical mechanism (thermal and initiated cooligomerization) (Fig. 2). While increase of temperature of the thermal cooligomerization decreases the molecular weight of the product by half it has almost no effect on the molecular weight of the product obtained by the initiated cooligomerization.

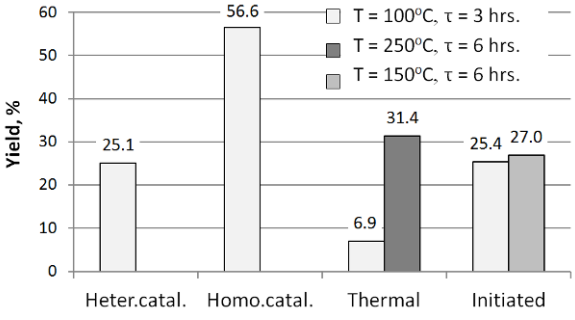


Figure 1. Yield of the cooligomers synthesized by different methods.

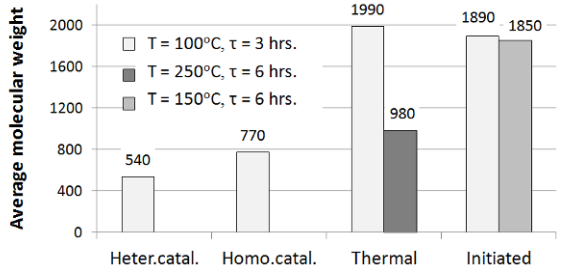


Figure 2. Average molecular weight of the cooligomers synthesized by different methods.

The molecular weight distribution determined by GPC varies significantly depending on cooligomerization method (Fig. 3).

In case of the heterogeneous catalysis the molecular weight of the product ranges from 150 to 4000 with a distinct prevailing of the cooligomer molecules of the molecular weight of 350-1500 (Fig. 3(1)). There is a rather similar curve in case of the homogeneous catalysis, though the main peak is broader (300-3000). The broadest molecular weight distribution (200-90000) is observed for the cooligomer obtained by the thermal method.

The cooligomers polydispersity index (PI) has been calculated based on the GPC data (Fig. 4).

Polydispersity is rather close for the products obtained by all the cooligomerization methods except the thermal one. The cooligomer synthesized by the heterogeneous catalytic cooligomerization has the lowest polydispersity. As could be foreseen, cooligomerization at high temperature results in a highly polydisperse product. As a rule, low polydispersity is preferable.

The cooligomers density has also been determined (Fig. 5). The following relationship between density and molecular weight has been determined: the product of lower molecular weight has higher density. It is probably because smaller molecules can be packed more closely.

An important characteristic of the cooligomers obtained from the C_9 fraction is their residual unsaturation. The high unsaturation is desirable because cooligomers with higher content of double bonds are able to cross-link, have stronger adhesion and, consequently, are better film-forming agents [1,3]. Additionally, high unsaturation enables further chemical modification of the cooligomer by its double bonds to obtain functional products of specific properties [1,37].

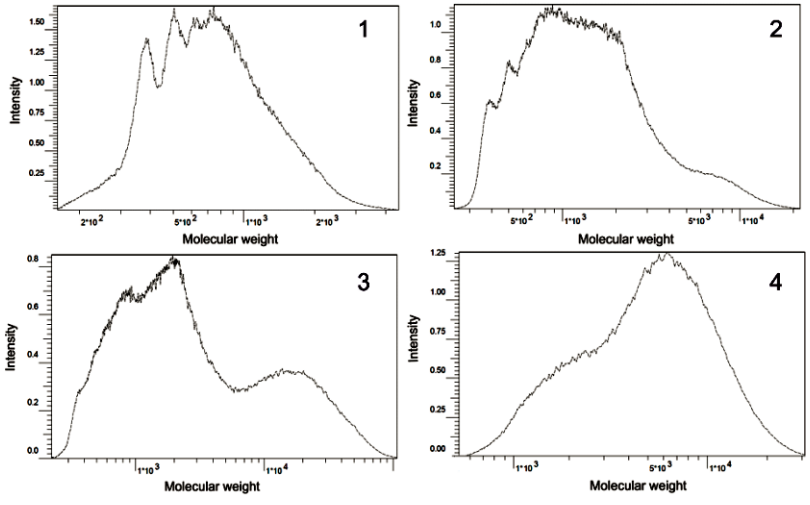


Figure 3. Molecular weight distribution of the cooligomers synthesized by: 1 – heterogeneous catalytic, 2 – homogeneous catalytic, 3 – thermal and 4 – initiated cooligomerization.

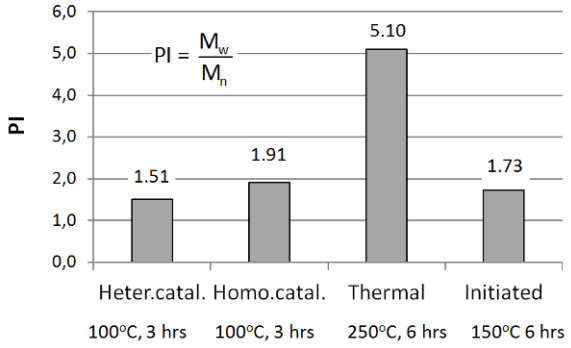


Figure 4. Polydispersity index of the cooligomers synthesized by different methods.

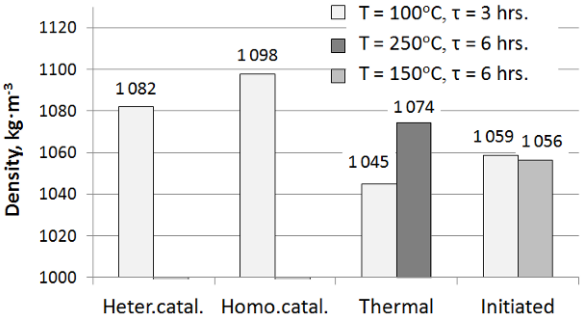


Figure 5. Density of the cooligomers synthesized by different methods.

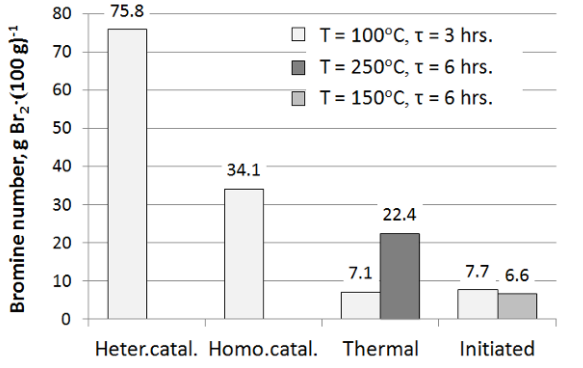


Figure 6. Unsaturation of the cooligomers synthesized by different methods.

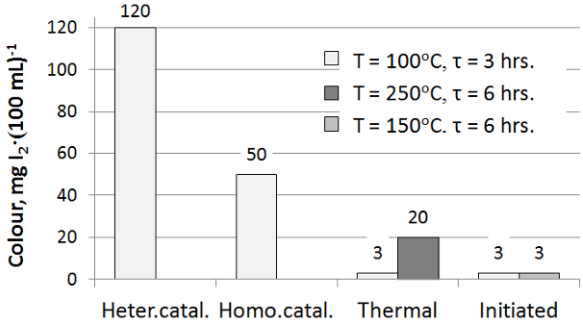
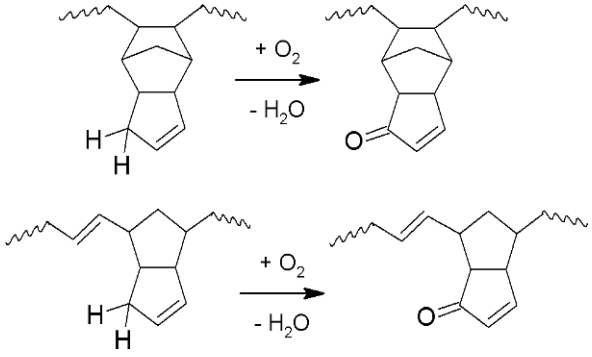


Figure 7. Colour of the cooligomers synthesized by different methods.



Scheme 7. DCPD units oxidation resulting in cooligomer intensive colouration.

The heterogeneous catalytic method developed by us allows achieving considerably higher unsaturation of the cooligomers in comparison with that obtained through other methods (Fig. 6). In case of the thermal cooligomerization unsaturation dramatically increases when rising the process temperature from 100 to 250°C.

Since the cooligomers obtained from the C_9 fraction are used as film-forming agents in paints and varnishes, colour is their important characteristic. Cooligomers are glassy transparent solids coloured from pale yellow to red-orange. The most coloured cooligomer is obtained in the heterogeneous catalytic cooligomerization while the least coloured in the initiated one (Fig. 7).

There is a clear relationship between the cooligomer unsaturation (Fig. 6) and its colour (Fig. 7): the higher the cooligomer bromine number the darker its colour. Generically, this agrees with the Chromophore-Auxochrome theory.

Another explanation is related to the cyclopentene ring of the DCPD units in the cooligomer. The methylene groups of these rings are very reactive and under the influence of light and atmospheric oxygen change to a fulvene-like structures (Scheme 7) [2].

The chromophore structures are characteristic of fulvenes and cause such structures to be intensely yellow, yellow-orange, or yellow-brown in colour. So the presence of even small quantities of this type of structures may have a considerable effect on the cooligomer colour. Thus, a higher content of the DCPD units in the cooligomer should lead to more intensive colour of the product.

In consideration of the model mixture composition, let us analyze the nature of all possible residual unsaturated bonds present in the final cooligomer product. The main source of unsaturation of cooligomers obtained from the model mixture (as well as those obtained from the C_9 fraction) is DCPD. Thus, when dicyclopentadiene (DCPD) oligomerization proceeds by the norbornene

double bond the corresponding monomer unit contains a residual cyclopentene double bond (Scheme 2(1)), and when DCPD oligomerizes by the cyclopentene bond the corresponding monomer unit contains a residual norbornene double bond (Scheme 2(2)). The monomer unit formed by ROMO (Scheme 2(3)) retains the cyclopentene double bond and the vinyl bond arises instead of norbornene one [38]. In case of ROMO of DCPD the number of double bonds is not reduced and consequently the most unsaturated product is obtained.

Styrene cannot be the source of the unsaturated bonds in the middle part of a macromolecule. However, it (as well as dicyclopentadiene) may be the source of the unsaturation at the end of the cooligomer chain. The terminal unsaturated bond arises in the cooligomer chain when it detaches from the active site with proton detachment and the active site regeneration (Scheme 4(1) and Scheme 5(1)) or when transferring the chain to the monomer (Scheme 4(2) and Scheme 5(2)). Regarding the above, it may be concluded that some part of the total unsaturation is caused by these terminal unsaturated bonds. And the contribution of these bonds to the total unsaturation is the greater, the smaller the cooligomer molecular weight. Since the product synthesized by the heterogeneous catalytic cooligomerization has the lowest molecular weight (Fig. 2), the terminal unsaturation may considerably influence the cooligomer total unsaturation.

3.3. Spectroscopy

To define the chemical nature of the differences found in the products obtained by different methods, the cooligomers have been investigated by Raman and ^{1}H-NMR spectroscopy. The Raman-spectra of the cooligomers are given in Fig. 8.

Raman-spectra of the cooligomers synthesized by the homogeneous and heterogeneous catalytic cooligomerization are very similar (Fig. 8). The main difference is the band at 1646 cm^{-1} corresponding to the stretching vibrations of the acyclic C=C bonds. It is present in the spectrum of the cooligomer obtained by the heterogeneous catalytic method, while in the spectrum of the product synthesized by the homogeneous catalytic cooligomerization only a very weak shoulder corresponds to this otherwise intensive peak (Fig. 8, scaled up section in the top). This testifies to the higher content of the double bonds in the cooligomer synthesized when using the heterogeneous catalyst. The shoulder at 1617 cm^{-1} corresponding to the cyclopentene double bonds is present in both cooligomers; however it is a bit more intensive in case of the heterogeneous catalytic cooligomerization. The weak signals at 919 and 1304 cm^{-1} corresponding to the deformation vibrations of the C–H bonds at the C=C bonds are present in the spectra of both products of cationic cooligomerization.

When comparing the spectra of cooligomers obtained by the heterogeneous catalytic and the initiated cooligomerizations (Fig. 8, scaled up section in the bottom) it becomes clear that there are almost no signals corresponding to the double bonds in the product obtained when using the initiator.

Raman-spectra of the products obtained by radical mechanism (thermal and initiated cooligomerization) are very similar (Fig. 8). However, very weak peaks corresponding to the double bonds can be detected in the spectrum of the thermal cooligomerization product, in particular the shoulder at 1617 cm^{-1}, unlike in the spectrum of the cooligomer synthesized by the initiated cooligomerization.

The signal in the range of 3100-3700 cm^{-1} is caused by the vibrations of the hydroxyl groups. So, we can conclude that the cooligomers synthesized by cationic cooligomerizations (both homogeneous and heterogeneous) contain some amount of hydroxyl groups. The hydroxyl groups, most probably, appear due to the oxidation of hot melt of the cooligomer with atmospheric oxygen when pouring the melt out from the distillation flask (distillation is carried out in the argon atmosphere). The hydroxyl groups are also present in the products of the initiated and thermal cooligomerizations but to a much lesser extent. The oxidation of the double bonds leads to the formation of the hydroxyl groups, while the oxidation of the methylene groups of the cyclopentene ring of DCPD units (Scheme 7) leads to the carbonyl groups formation. So, the higher the cooligomer unsaturation, the higher the number of the hydroxyl groups in the product.

In the ^{1}H-NMR spectra of the cooligomers three main sections may be distinguished (Fig. 9). The peaks in the range of 6.5-7.5 ppm correspond to the aromatic hydrogen atoms (except for the peak at 7.19 ppm which is the residual signal from the trace amount of $CHCl_3$ present in the solvent – $CDCl_3$). The broad group of intensive peaks in the range of 0-2.3 ppm corresponds to the hydrogen atoms of saturated aliphatic and cycloaliphatic hydrocarbons – the methylene units of the main chain. The peaks in the range of 2.3-3.5 ppm correspond to the hydrogen atoms of the cycloalkyl links present in the cooligomers due to DCPD oligomerization. The middle section of the spectra, 4.5-6.0 ppm, corresponds to the hydrogen atoms of the double bonds. The more intensive the peaks in this region are the more unsaturated the cooligomer is. There are two main peaks in this region: one at 5.6 ppm that corresponds to the hydrogen atoms

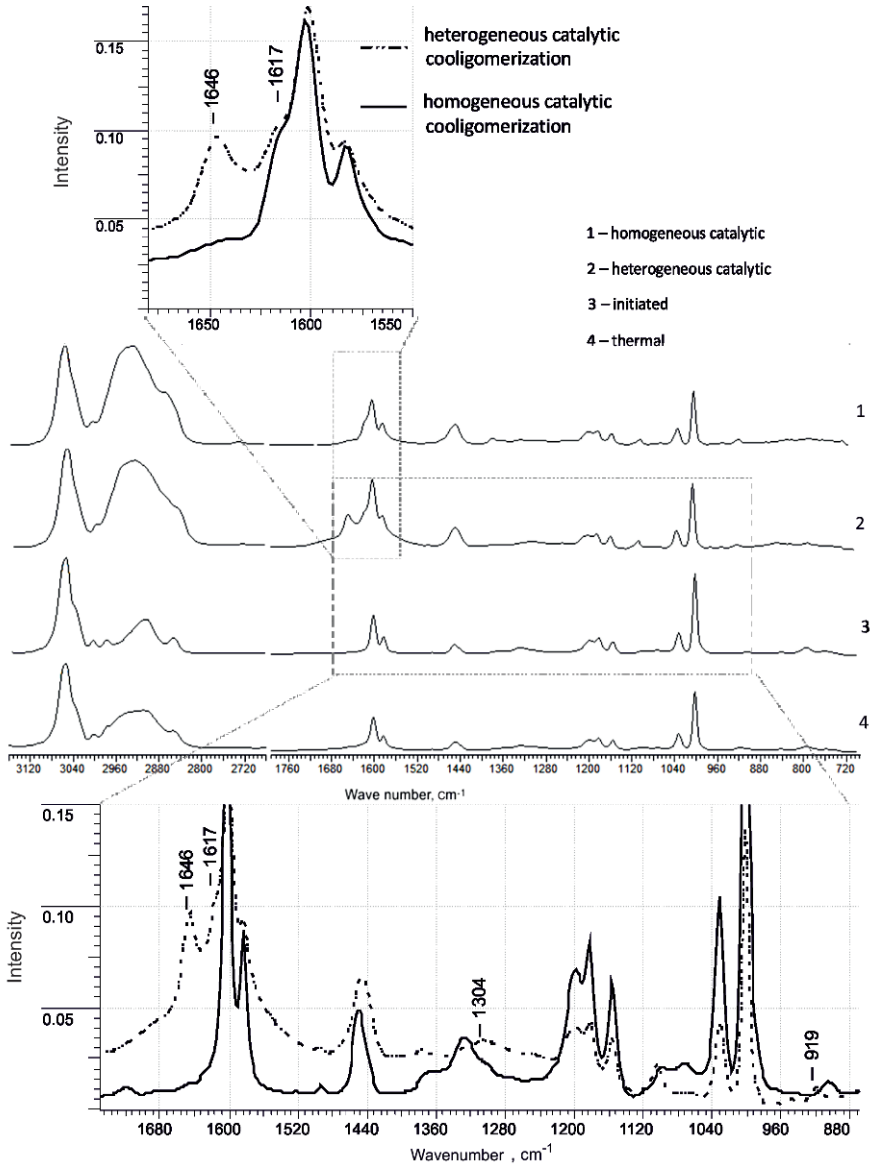


Figure 8. Comparison of Raman spectra of the cooligomers synthesized by different cooligomerization methods.

of the cyclopentene double bonds, and another one at 5.4 ppm which corresponds to the hydrogen atoms of the vinyl double bonds. Besides, in the spectrum of the cooligomer synthesized by the heterogeneous catalytic cooligomerization there is a very weak peak at 5.9-6.0 ppm which corresponds to the hydrogen atoms of the norbornene double bonds.

The total area of the ^{1}H-NMR-spectra peaks corresponding to the hydrogen atoms of the double bonds is an indicator of the cooligomer unsaturation. There is a strict conformity of this indicator with the corresponding bromine number values (Fig. 10), that supports the validity and accuracy of the both measurements.

The ^{1}H-NMR-spectra treatment allowed us to assess the ratio of different types of the double bonds in the cooligomers total unsaturation (Fig. 11). Almost half of the double bonds in case of the thermal and the homogeneous catalytic cooligomerization and more than a third in case of the heterogeneous catalytic process are aliphatic (vinyl). The sources of the aliphatic double bonds are ROMO of DCPD (Scheme 2(3)) and the cooligomer chain termination by the mechanisms given in Schemes 4(1) and 4(2) and Schemes 5(1) and 5(2) in the cationic cooligomerization and the chain termination by disproportionation (Scheme 6(2)) in radical cooligomerization.

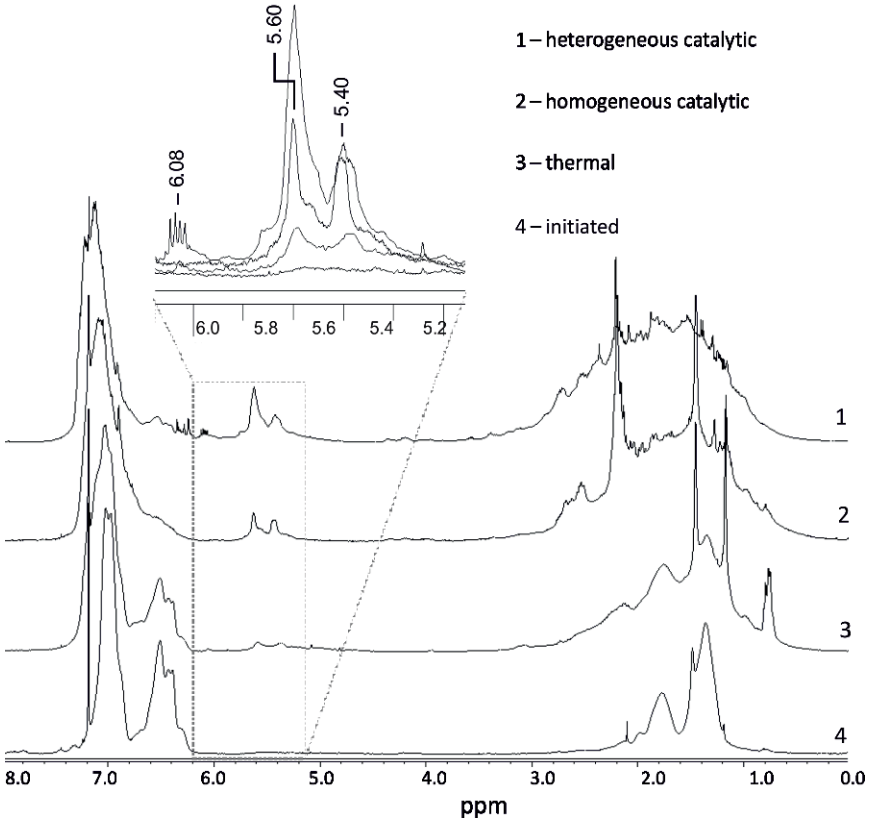


Figure 9. Comparison of ^{1}H-NMR spectra of the cooligomers synthesized by different cooligomerization methods.

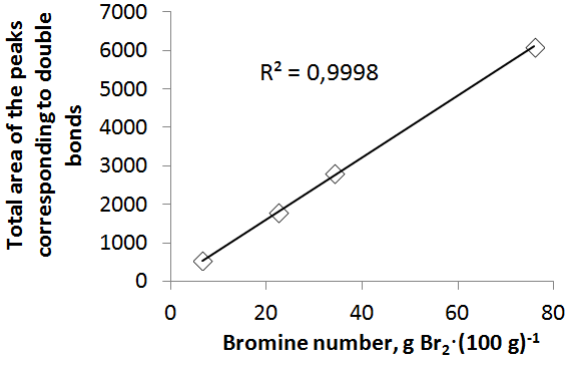


Figure 10. Correlation between bromine number and total area of ^{1}H-NMR peaks corresponding to hydrogen atoms at double bonds.

Thus, we can conclude that DCPD oligomerizes predominantly by the norbornene double bond (Scheme 1(1)) and by the ROMO mechanism (Scheme 1(3)) and practically doesn't oligomerize by the cyclopentadiene double bond (Scheme 1(2)). However, some small amount of the norbornene double bonds (Fig. 11) is present in the cooligomer synthesized by the heterogeneous catalytic method. It is not only because of DCPD oligomerization by the cyclopentadiene bond (Scheme 1(2)), but because some cooligomer molecules end by DCPD unit and, consequently, the terminal norbornene double bond appears at the end of a macromolecule when it detaches from the active site by the mechanisms leading to terminal unsaturation.

For the additional proof that DCPD oligomerizes by ROMO when using activated bentonite clay as a catalyst, DCPD was homooligomerized and the signals corresponding to the acyclic double bonds were found in the Raman-spectrum of the product. The only possible source of the acyclic double bonds in the oligo-DCPD is ROMO (Scheme 2(3)); the addition oligomerization (Schemes 2(1) and 2(2)) results in the oligomer with the cyclic double bonds only.

The ^{1}H-NMR spectrum of the cooligomer obtained by the initiated method allows us to state that there are no cycloalkyl links in it (no signals in both the 2.3-3.5 ppm region and at 5.6 ppm), and the synthesized product is the oligostyrene *per se*. So, DCPD is unable to undergo radical oligomerization. It is probably because DCPD interacts with free radicals by a very reactive methylene group of the cyclopentene ring, not by its double bonds. The spectrum of the thermally synthesized product indicates a very low content of the cycloaliphatic fragments. These results explain low unsaturation and

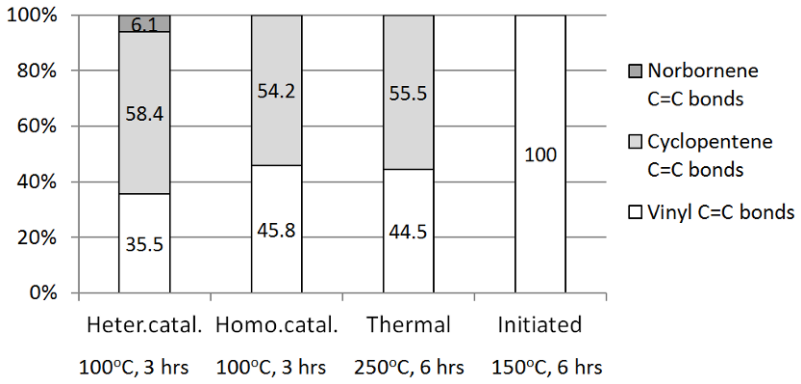


Figure 11. Contribution of double bonds of different types to the total unsaturation of the cooligomers synthesized by different methods.

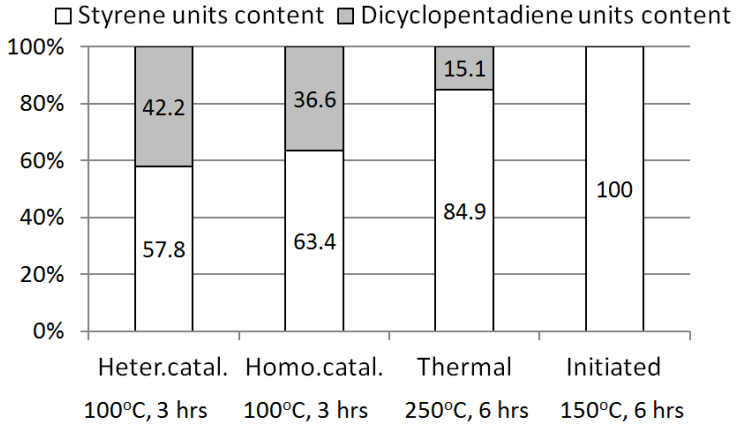


Figure 12. Composition of the cooligomers synthesized by different methods.

light colour of the cooligomers obtained by the radical mechanism.

In consideration of the fact that the product synthesized using the initiator consists of the styrene units only, the styrene/dicyclopentadiene units ratio in the cooligomers obtained by different methods has been calculated based on the area of the peaks corresponding to the hydrogen atoms in the aromatic rings (Fig. 12).

The cooligomer synthesized by the heterogeneous catalytic cooligomerization has the highest content of the DCPD units, though the cooligomer obtained by the homogeneous catalytic method has the similar composition.

DCPD doesn't oligomerize by the radical mechanism, but in case of the thermal cooligomerization under the higher temperature cyclopentene double bonds and cycloaliphatic fragments are present in the cooligomer. It is obviously because of CPD formation and its cooligomerization as shown in Scheme 3. So, the product obtained by the thermal method contains not the DCPD units but the CPD units (Fig. 12).

Taking into account the average molecular weight values (Fig. 2) we can conclude that the cooligomer synthesized by the heterogeneous catalytic cooligomerization consists on average of 3 styrene and 2 dicyclopentadiene monomeric units; the product obtained by the homogeneous catalytic method consists of 4-5 styrene and 2 DCPD units; the one synthesized by the thermal cooligomerization consists of 8 styrene and 4 CPD units; and the oligostyrene obtained when using benzoyl peroxide as an initiator consists on average of 17-18.

Having determined the styrene/dicyclopentadiene units ratio in the cooligomers (Fig. 12), as well as the yields (Fig. 1) and the initial model mixture composition, it is easy to calculate the degree of monomers conversion into the cooligomer (Fig. 13).

Based on the average molecular weight (Fig. 2) and bromine number values (Fig. 6), as well as the data of Fig. 11, the average total number of double bonds and number of double bonds of each type per a cooligomer molecule has been calculated (Table 2).

It is clear why the products obtained by the initiated and thermal cooligomerization are less unsaturated than those formed by the cationic mechanism, but the question remains: "What is the cause of such a big

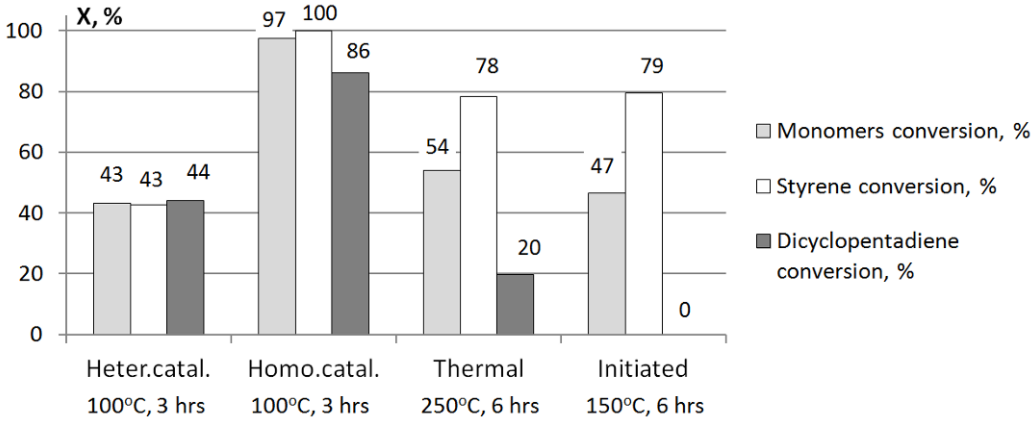


Figure 13. Monomers conversion when using different cooligomerization methods.

Table 2. Average number of double bonds per a cooligomer molecule.

Cooligomerization method	Average number of double bonds per molecule			
	Total	Vinyl C=C bonds	Cyclopentene C=C bonds	Norbornene C=C bonds
Heterogeneous catalytic	2.54	0.90	1.49	0.16
Homogeneous catalytic	1.65	0.76	0.90	0.00
Thermal	1.38	0.61	0.77	0.00
Initiated	0.76	0.76	0.00	0.00

difference in unsaturation of the cooligomers synthesized when using the homogeneous and the heterogeneous catalysts?" Since the styrene/DCPD ratio is almost the same in the products obtained by the catalytic methods (Fig. 12), there should be some differences in the cooligomerization mechanism resulting in a different unsaturation of the cooligomers.

In case of the homogeneous catalytic cooligomerization the chain termination may occur by various mechanisms (Scheme 4). Some of them result in a terminal double bond formation (Schemes 4(1) and 4(2)) and some of them don't (Schemes 4(3)-4(5)). In case of the heterogeneous catalytic cooligomerization all the chain termination mechanisms resulting in a cooligomer molecules formation without a terminal double bond are impossible (Scheme 5). The mechanism of the chain transfer to another cooligomer molecule is not possible in this case due to the steric hindrance. The mechanisms of the chain termination in which a catalyst fragment enters the cooligomer molecule (Schemes 4(4) and 4(5)) is also impossible because of the heterogeneous catalyst nature. In case of the chain termination by combination with the counterion the cooligomer molecules do not detach from the catalyst surface, remain in the used catalyst (Scheme 5(3)) and are removed from the reaction mixture along with it when filtering.

Thus, the chain termination in the heterogeneous catalytic cooligomerization proceeds predominantly by the mechanism resulting in formation of the product with terminal double bonds (Schemes 5(1) and 5(2)). In such case, the lower the molecular weight, the higher the bromine number of the cooligomer. The molecular weight of the product obtained by the homogeneous catalytic cooligomerization is half of that of the cooligomer synthesized when using the activated bentonite clay (Fig. 2). That is why the impact of the terminal double bonds may be of considerable influence on the total unsaturation.

4. Conclusions

The use of the activated bentonite clay as a catalyst enables achieving the same yield as in the thermal cooligomerization at much lower temperature and much shorter period of time. The same yield as in the initiated process is obtained under the same conditions when

using the heterogeneous catalyst which is 50 times cheaper than benzoyl peroxide. When comparing the heterogeneous and homogeneous catalytic methods, it is clear that the high product yield is not an advantage of our method, but this technology is more environmentally friendly and costs than the homogeneous catalytic one.

The heterogeneous catalytic cooligomerization, when using the activated bentonite clay as a catalyst, enables to obtain a highly unsaturated product: the bromine number is an order higher than in case of the initiated or thermal (at 100°C) cooligomerization and about twice as high as in case of the homogeneous catalytic cooligomerization and the high-temperature thermal cooligomerization. However, the product obtained by our method is intensively coloured, which is undesirable for paints and varnishes of light colours.

It has been confirmed that DCPD doesn't oligomerize by a radical mechanism when carrying the process out both thermally (below the temperature of DCPD monomerization by retro-Diels-Alder reaction) and in presence of the initiator.

The difference in unsaturation of the cooligomers synthesized by the homogeneous and heterogeneous catalytic cooligomerization is most probably caused by a different mechanism of chain termination.

Of course, some features of the process may vary depending on an initiator type and a catalyst type, however the general features of the cooligomerization methods are assumed to be the same for the investigated catalysts and the initiator.

Obtained results indicate that it is almost impossible to regulate the cooligomer properties by changing the initiated cooligomerization conditions (no changes in the properties of the product were recorded when the temperature was increased by a factor of 1.5 and the time of the process doubled). In case of the heterogeneous catalytic cooligomerization the cooligomer properties can be easily regulated by changing the process conditions [31,39], which is also an advantage of our method.

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