CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 8, No. 4, 2014 Chemistry

Zoriana Gnativ, Irena Nykulyshyn, Anna Rypka, Taras Voronchak and Zorian Pikh

STUDY OF AROMATIC AND TERPENIC HYDROCARBONS CATALYTIC COOLIGOMERIZATION REGULARITIES

Lviv Polytechnic National University
12, S. Bandera str., 79013 Lviv, Ukraine; rypka_ganna@ukr.net

Received: April 02, 2014 / Revised: April 18, 2014 / Accepted: September 30, 2014

Abstract. Regularities of cationic cooligomerization of C_9 fraction aromatic hydrocarbons of diesel fuel pyrolysis products and terpenic hydrocarbons of turpentine have been ascertained. New efficient catalyst of the process, namely homogeneous complex of aluminium chloride with ethyl acetate in the organic solvent (xylene), is suggested.

Keywords: C_9 fraction, turpentine, aromatic-terpenic resins, catalytic cooligomerization.

1. Introduction

Polyterpenic resins (PTR) is one of the products obtained as a result of turpentine processing *via* polymerization with acid-type catalysts. It is widely used in industry, especially abroad [1]. Depending on the raw material composition and production method the polymers with broad range of consistency (from viscous liquids to solid high-melting products) can be obtained. Such a broad range of physicochemical properties determines application area of the products.

Liquid PTR are used as a glass fiber oiling agent [2], in natural leather goods production [3], as well as antilumping additives for abrasive tools [4]. Besides, liquid PTR are used in various filming compositions, including insulating [5] and paint coatings [6]. In recent publications it is reported that liquid PTR may be applied as rubber compounding ingredients [7].

Solid PTR (with the softening point over 363 K by ring and ball method) are successfully applied as thermoplastic adhesive additives in hot-melt and pressure-sensitive adhesives, as well as in paint, sealing and insulating materials [8-10].

Hydrocarbon resins (HR) are cooligomers of unsaturated compounds of aliphatic and aromatic range. They are widely used in production of synthetic drying oils, oleoresinous varnishes, alkyd resins, as well as additives for various paint-and-lacquer formulations. Basically, liquid pyrolysis products (LPP) or products of cracking of secondary oil processing products are used as a raw material for HR production. LPP are the mixture of saturated and unsaturated hydrocarbons C_5–C_{14}. They include benzene, toluene, ethylbenzene, xylene, isoprene, dimethylbutadiene, various alkenes, cyclopentadiene, styrene, α-methylstyrene, vinyltoluene, indene, methylindene, *etc*. [1, 11, 12].

To obtain HR of different composition and different physicochemical properties different fractions of LPP and combinations thereof are used. Depending on the main unsaturated compound name, HR are called polyalkenic, polydienic, polycyclopentadienic, polystyrenic, polystyrenic-indenic, *etc*.

Depending on what raw material is undergone to oligomerization, it is possible to obtain the products of different chemical compositions and different physicochemical properties. This substantially broadens the area of resins application as substituents of natural products in various branches of industry. Synthesis of aliphatic-terpenic resins has been studied before [13]. The research results showed that aliphatic hydrocarbon resins had good properties, and the improvement thereof by terpenic monomers addition improved their physicochemical properties considerably. On this basis the combined cooligomerization of aromatic and terpenic monomers seems to be interesting and reasonable, and this is the aim of our further research.

2. Experimental

2.1. Research Object

In our research C_9 fraction – the by-product of diesel fuel pyrolysis, was used as a source of aromatic monomers. Dominant unsaturated hydrocarbons of the fraction include (wt %): styrene 18.93, allylbenzene 0.86, α-methylstyrene 1.97, vinyltoluenes 8.13, dicyclopentadiene 17.78 and indene 1.93.

A terpene oil – the turpentine obtained from barras by steam distillation or vacuum distillation was used as a source of terpenic hydrocarbons [14]. The terpene oil has been chosen because it has the highest content of unsaturated terpenic hydrocarbons, namely α-, *β*-pinenes (60–70 wt %) and Δ^3-carene (10–18 wt %), among different industrial samples of turpentine (obtained by steam, extraction, dry distillation or sulphate method).

2.2. Synthesis of the Catalytic Complex

The catalytic complex synthesis was carried out in a four-necked reactor fitted with a thermometer, backflow condenser, stirrer, dropping funnel and bubbler of inert gas – argon, under continuous stirring at 308 K. Reaction mixture is kept under given conditions for 1 h. As a result liquid $AlCl_3$/ethylacetate/xylene catalytic complex of molar ratio $AlCl_3$/EA/Xylene = 1:0.5:2 is obtained.

2.3. Synthesis of Resins

Cooligomerization of aromatic and terpenic monomers was carried out in a four-necked thermally stabilized flask fitted with a stirrer, thermometer, dropping funnel, backflow condenser and bubbler of argon. The reaction mixture was thermostated until the reaction temperature. Thermostating was carried out by a heat carrier supply into the reactor jacket from the thermostat. After the cooligomerization temperature has been reached the required amount of the catalytic complex was added through the dropping funnel. When cooligomerization is finished, a further contact of the catalyst with the reaction mixture is undesirable. That is why the cooligomerizate was neutralized followed by removing of the catalytic complex and neutralizing agent. To decompose and remove the catalyst the cooligomerizate was sequentially washed with water and 10 % sodium carbonate solution, settled and repeatedly washed with water until the neutral pH. Unreacted hydrocarbons were removed by atmospheric (pressure is 0.11 MPa, still temperature is 453 K) and vacuum (residual pressure is 3–4 kPa, still temperature is 423 K) stripping of the cooligomerizate.

2.4. Analysis of Resins

The following characteristics were determined for obtained aromatic terpen resins (ATR): ***bromine number*** of ATR as described in [16]; ***molecular weight*** by a cryoscopic method in benzene [17, 18]; ***colour*** of ATR by a visual comparison of 10% benzene solution of the resin with a standard iodine scale according to standards [19]; the ***softening point*** by ring and ball method [19]. In addition the ***cooligomerizate density*** was determined by an areometer according to [15].

3. Results and Discussion

Based on our earlier research results [12, 13] the process was carried out under the following conditions: duration – 3 h, temperature – 343 K, the catalytic complex concentration – 1 wt % (in terms of aluminium chloride).

The first stage of the research was aimed at the optimum ratio of turpentine to C_9 fraction determination. The components ratio (turpentine : C_9 fraction) in the initial mixture varied from 10 : 90 to 50 : 50 (w/w).

The turpentine chemical composition is strongly dependent on the tree species and age, geographic location and the overall procedure used to isolate it. In general, however, the major components are a few unsaturated hydro- carbon monoterpenes ($C_{10}H_{16}$) namely, α-pinene and *β*-pinene with smaller amounts of other monoterpenes (Fig. 1) [20-22].

Abundant terpenes constitute the logical precursors to polyterpenic materials destined for bulk applications. In this context, pinenes, readily isolated on an industrial scale from turpentine, are obvious candidates. Although less abundant than α-pinene, *β*-pinene is by far the most studied homologue because of the higher reactivity of its exo- cyclic double bond in the cationic polymerization. A considerable number of other monoterpenes has been tested as polymer precursors, using different polymerization mechanisms.

The influence of the turpentine : C_9 fraction ratio on the cooligomerizate density and bromine number, as well as yield, colour, molecular weight, bromine number and softening point of the aromatic-terpenic resins are represented in Figs. 2-3 and 5-6. The obtained results show that the increase of the turpentine content in reaction mixture results in the cooligomerizate density decrease from 927 kg/m^3 to 903 kg/m^3 and in the ATR yield decrease from 25 to 18 wt %. This may be explained as follows: when the turpentine content in the reaction mixture increases, the considerable amount of liquid diterpenes is formed during cooligomerization and these diterpenes are removed from the target product when stripping.

Since α-pinene is the dominant polymerizable hydrocarbon of turpentine (its content is 54.95 wt %), it is clear that α-pinene polymerization has the key impact on the physicochemical properties of ATR obtained.

Based on the earlier researches we suppose that α-pinene (I) polymerization with Friedel-Krafts catalysts occurs by the mechanism schematically shown in Fig. 4.

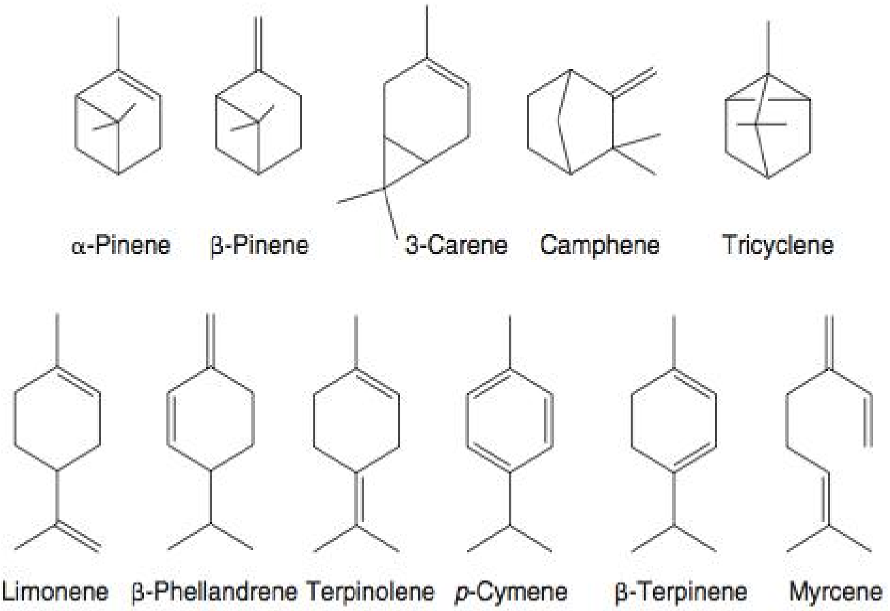


Fig. 1. Chemical structures of the most common turpentine monoterpene components

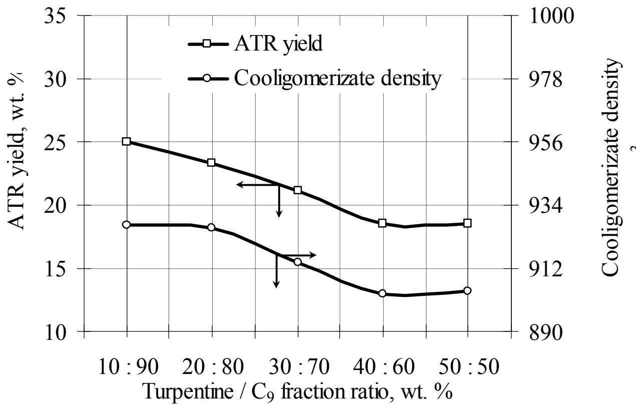


Fig. 2. ATR yield and cooligomerizate density dependences on the turpentine : C_9 fraction ratio at unsaturated aromatic and terpenic hydrocarbons cooligomerization

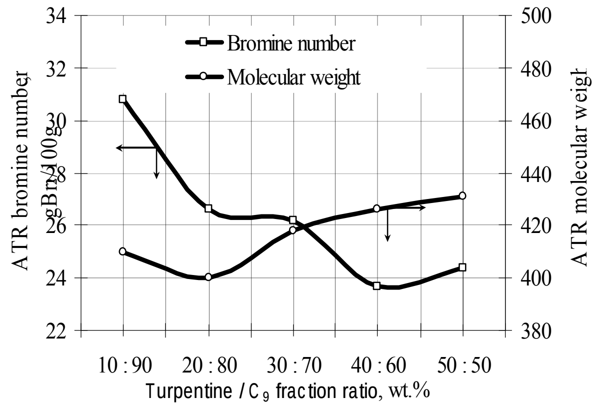


Fig. 3. ATR bromine number and molecular weight dependences on the turpentine : C_9 fraction ratio at unsaturated aromatic and terpenic hydrocarbons cooligomerization

$T = 343$ K, $\tau = 3$ h., $C_{cat.} = 1$ wt % (in terms of aluminium chloride)

The initial attack of the double bond of molecule (I) by the initiator leads to formation of the “hidden” cyclic carbocation (II), capable of rearrangement attended by the opening of the four-ringed structure resulting in a sterically favoured tertiary carbocation (IV) formation. However, further growth of the chain from (I) is sterically hindered because a double bond of the molecule (I) of bicyclic structure is situated in one of the rings. As a result polymerization of (I) is accompanied by the formation of the great amount of diterpenes (DT) of different structures including both bicyclic and monocyclic fragments corresponding to the ion structures (III, V and VI). The same structure of DT is suggested by the authors of [23-26] based on spectrometry data.

Polyterpenes (PT) are formed as a result of the chain growth involving a tertiary carbocation corresponding to the structure (VI) formed as a result of its sterically hindered analog (V) rearrangement (Fig. 4). The suggested mechanism is also proved by NMR-spectra of high-melting PTR synthesized by cold polymerization of (I) with Friedel-Krafts catalysts [26]. The spectra showed that PTR consists mainly of the repeated units of monocyclic cyclohexane-like structure with the insignificant content of bicyclic pinene-like structure.

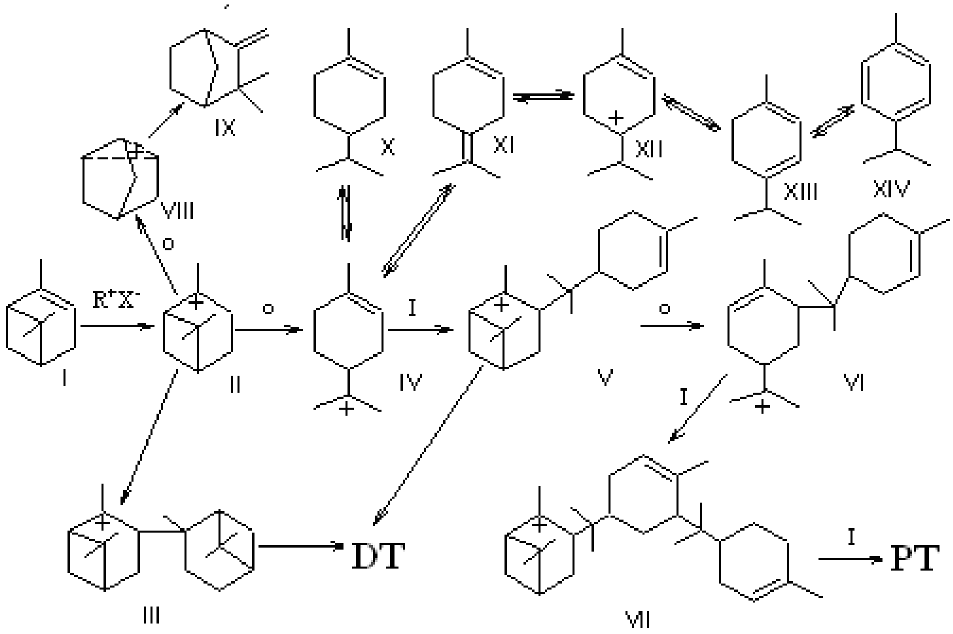


Fig. 4. Scheme of α-pinene oligomerization with Friedel-Krafts catalysts

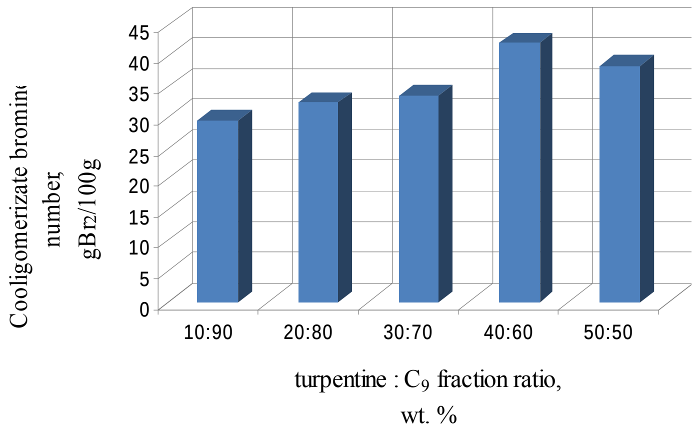


Fig. 5. The cooligomerizate bromine number dependence on the turpentine : C_9 fraction ratio at unsaturated aromatic and terpenic hydrocarbons cooligomerization

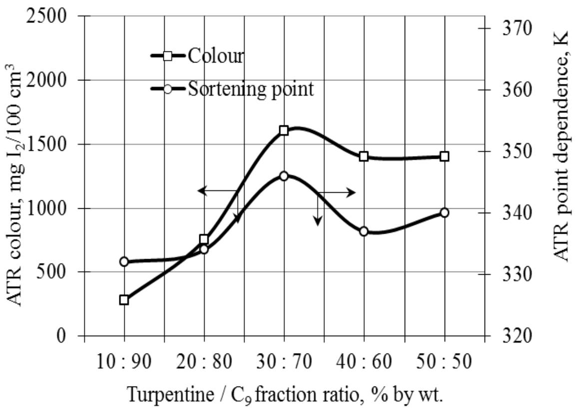


Fig. 6. ATR colour and softening point dependence on the turpentine : C_9 fraction ratio at unsaturated aromatic and terpenic hydrocarbons cooligomerization

T = 343 K, τ = 3 h., $C_{cat.}$ = 1 wt % (in terms of aluminium chloride)

Increase of the turpentine content causes decrease of ATR unsaturation (bromine number of ATR decreases from 31 to 24 g Br_2/100 g) and slight increase of ATR molecular weight (from 391 to 431). Probably, the increase of turpentine content in the reaction mixture leads to formation of considerable amount of polyterpenes along with diterpenes. And the presence of polyterpenes influences the mentioned characteristics.

When raising the turpentine : C_9 fraction ratio from 10 : 90 to 30 : 70 (w/w), ATR softening point increases from 332 to 346 K. However, when the turpentine : C_9 fraction ratio increases further, the softening point decreases to 337 K (at 40 : 60 w/w ratio) and to 340 K (at 50 : 50 w/w ratio). It is probably because in case of lower content of turpentine monomers in the reaction mixture the cooligomers with prevailing of aromatic hydrocarbon units (monomers of the C_9 fraction) in the chain are formed, and such cooligomers are solid materials. Unsaturation of the cooligomerizate and final cooligomer product increases when raising the turpentine : C_9 fraction ratio to 40 : 60 and 50 : 50 (w/w). (Figs. 5 and 6). It is known that the dominant terpene of turpentine – α-pinene under given conditions easily isomerizes into camphene, dipentene and terpinolene each involving reactive double bonds [27, 28]:

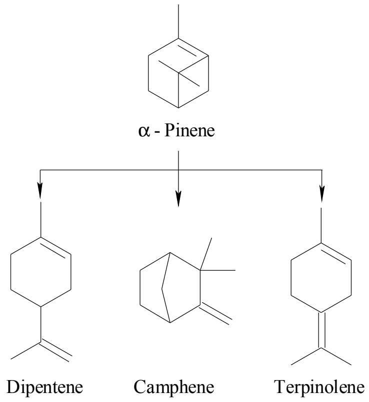


Fig. 7. α-Pinene isomerization routes

It is also known that polyterpenes, in composition of which α-pinene is quantitatively dominant, are liquid products [1]. So, when raising the turpentine content in the reaction mixture to 40 and 50 wt % gradual "softening" of the obtained resins is observed, and these resins have good adhesive behavior.

One of the key characteristics determining the application area of a hydrocarbon resin is its colour. Analyzing the obtained results concerning the components ratio influence on the resins colour (Fig. 6) we can conclude that the increase of the turpentine : C_9 fraction ratio from 10 : 90 30 : 70 (w/w) results in gradual deterioration of the product colour (from 280 to 1600 mg I_2/100 cm^3), that is undesirable because it makes the resins application in paints and varnishes impossible.

Taking into account a satisfactory yield of ATR (25 wt %), sufficiently high unsaturation of the products (31 g Br_2/100 g), enabling their further modification, and the best colour (280 mg I_2/100 cm^3), we can state that the turpentine : C_9 fraction ratio equal to 10 : 90 wt % is optimal for aromatic-terpenic resins synthesis.

Further research was aimed at determination of the catalytic complex optimal concentration for C_9 fraction monomers and turpentine monomers cooligomerization. As a catalyst we used homogeneous catalytic complex of aluminium chloride with ethyl acetate in xylene [$AlCl_3$: C_2H_5–O–CO(CH_3) : $(CH_3)_2C_6H_4$], which has been determined to be the most effective in C_9 fraction monomers cooligomerization [12], as well as in C_5 fraction and turpentine monomers cooligomerization [13].

Xylene was chosen among other possible hydrocarbons because it is the main component of atmospheric distillate (37.49 wt %) obtained in HR production from C_9 fraction. Hydrocarbon constituent of the catalytic complex – xylene is an aromatic compound existing as three isomers: *ortho*-, *metha*- and *para*-xylene. Since relative activity of xylene isomers in substitution reactions decreases in the range [29]:

metha-xylene > *ortho*-xylene > *para*-xylene

Metha-xylene was used for the catalytic complex synthesis.

The catalytic complex concentration used for aromatic-terpenic resins synthesis varied from 1.0 to 3.0 wt % (in terms of $AlCl_3$, to the amount of the feedstock undergone cooligomerization). The influence of the catalytic complex concentration ($C_{cat.}$) on ATR yield and physicochemical properties was studied at the turpentine : C_9 fraction ratio equal to 10 : 90 (w/w). Obtained results are shown in Figs. 8-9 and 12-13.

As is clear from the obtained experimental data, raise of $C_{cat.}$ from 1.0 to 3.0 wt % has a positive impact on the cooligomerization reaction as it results in increase of the cooligomerizate density (from 921 to 970 kg/m^3) and ATR yield (from 25 to 38 wt %) (Fig. 8). Such a result is quite expected, because the increase of a catalyst amount facilitates initiation and growth of a polymeric chain.

Scheme of α-pinene transformations catalyzed by $AlCl_3$/ethyl acetate/toluene complex is shown in Fig. 10. First, α-pinene combines with $C_2H_5^+$ cation dissociated from the catalytic complex and forms a pinanyl cation. Then, the pinanyl cation rearranges by ring-opening to form isobornyl cation and by ring-enlargement to form *p*-menthenyl cation. Finally, most of the cations formed by both mechanisms initiate polymerization forming polymers; a small part of them forms isomers.

Although α-pinene is readily protonated to form a tertiary carbocation, which can then rearrange to an unsaturated *p*-menthane isomer (Fig. 11), the attack of the endocyclic double bond on the isopropenyl cationic site is limited by a steric hindrance.

This fact explains a molecular weight increase (from 409 to 652) when raising the catalytic complex concentration from 1.0 to 2.0 wt % (Fig. 9). ATR bromine number, however, increases from 29 to 36 g Br_2/100 g when raising $C_{cat.}$ from 1.0 to 2.0 wt , afterwards it decreases by about 3 g Br_2/100 g (at $C_{cat.}$ equal to 2.5 and 3.0 wt %). The softening point of ATR increases from 332 to 346 K when raising $C_{cat.}$.

Although the raise of the catalyst concentration results in slight increase of ATR softening point, it also leads to the resins colour deterioration (from 400 to 520 mg I_2/100 cm^3, Fig.13). That is why the catalyst concentration increase over 3 wt % is unreasonable and physicochemical properties of ATR may be improved by cooligomerization conditions adjustment.

Presence of oxygen in the system retards cooligomerization and causes deterioration of HR colour due to the oxidation reaction [30]. Composition of hydrocarbon fractions also affects the products darkening. Dicyclopentadiene (DCPD) (content in C_9 fraction is 17.78 wt %) and indene (1.93 wt %) are considered to be the main polymerizable hydrocarbons of the feed causing darkening of the resins.

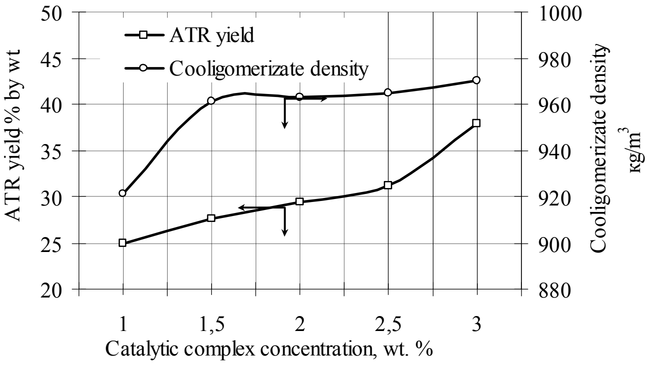


Fig. 8. Cooligomerizate density and ATR yield dependence on the catalytic complex concentration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

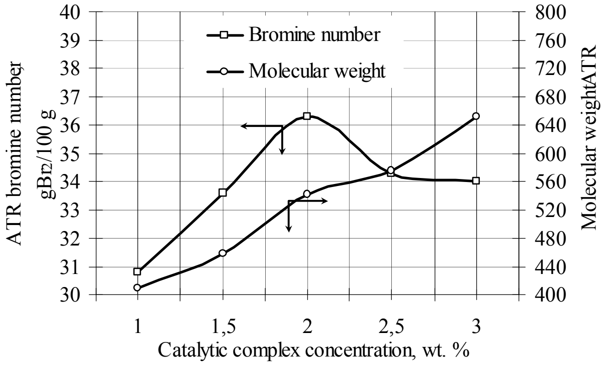


Fig. 9. ATR bromine number and molecular weight dependence on the catalytic complex concentration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

T = 343 K, τ = 3 h., turpentine : C_9 fraction ratio = 10 : 90 % (w/w)

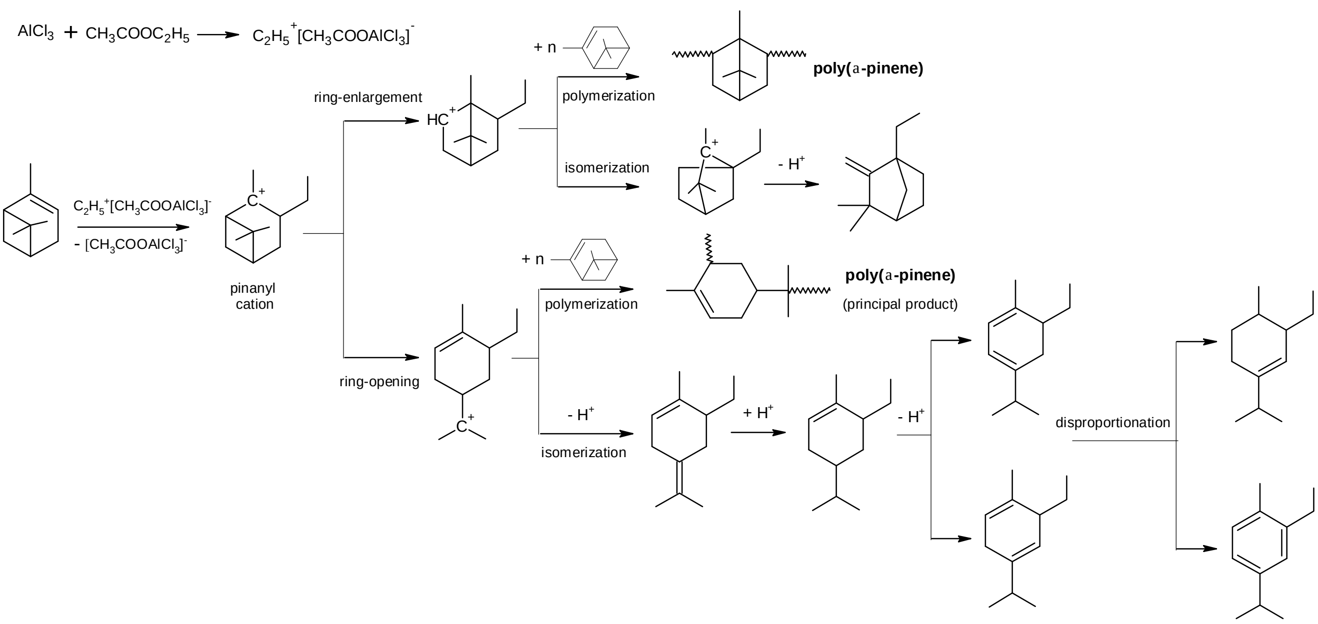


Fig. 10. General mechanism of the cationic polymerization of α-pinene catalyzed by $AlCl_3$/ethyl acetate/toluene catalytic complex

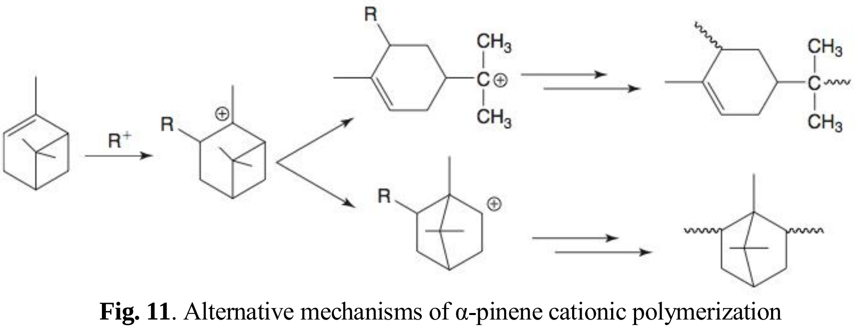


Fig. 11. Alternative mechanisms of α-pinene cationic polymerization

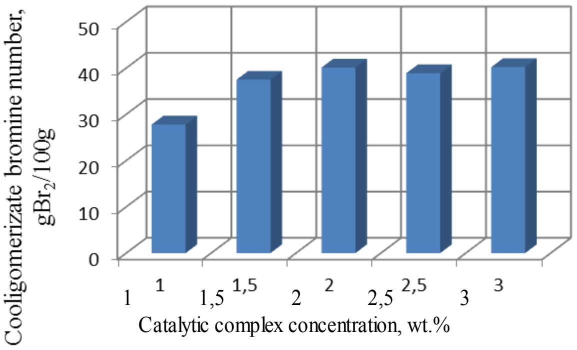


Fig. 12. Cooligomerizate bromine number dependence on the catalytic complex concentration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

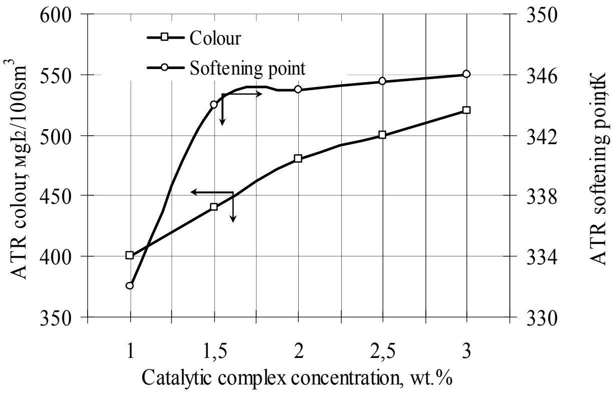
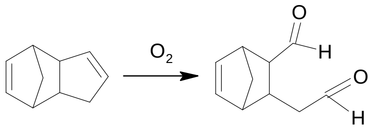


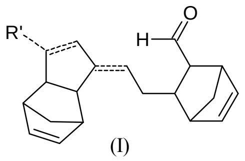
Fig. 13. ATR colour and softening point dependence on the catalytic complex concentration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

T = 343 K, τ = 3 h., turpentine : C_9 fraction ratio = 10 : 90 % (w/w)

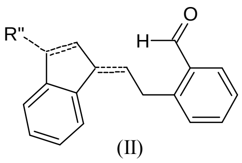
DCPD and indene transformation under the influence of oxidizer occurs by the following scheme (in terms of DCPD) [31]:



The oxidized molecules interact with polymer chain units forming fulvene-like structures:



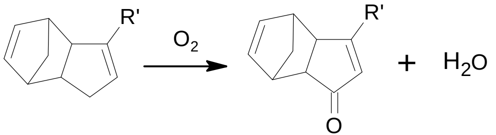
(I)



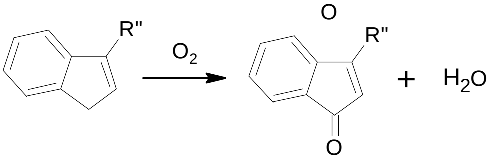
(II)

where R' – polycyclopentadiene fragment and R" – polyindene fragment.

Due to the high reactivity of DCPD methylene group and indene caused by a vicinal double bond of the five-membered ring, this methylene group can also be oxidized:



(III)



(IV)

So, dark colour of the resins is caused (when oxygen is present in the reaction system) by fulvene Carmody structures I and II, and DCPD III and indene IV structures, each containing three conjugated bonds. Due to high polarity of C=O groups structures III and IV are more intensively coloured than structures I and II much less affecting the resins darkening.

With regard to above-said, the cooligomerization is carried out in the inert atmosphere – argon, to prevent oxidation.

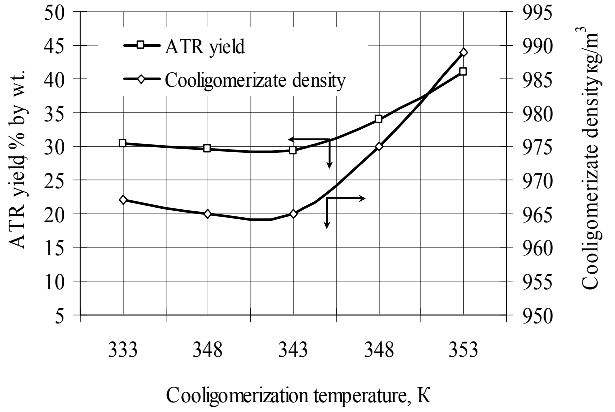
Based on the obtained results it was determined that the optimum concentration of catalytic complex is 3.0 wt % (in terms of $AlCl_3$). At this concentration the aromatic-terpenic resin obtained is characterized by: yield – 38 wt %; bromine number – 34 g Br_2/100 g; molecular weight – 652; colour – 520 mg I_2/100 cm^3; softening point – 346 K.

The research results concerning temperature and duration influence on the catalytic cooligomerization of aromatic and terpenic monomers are represented in Figs. 14-19. The results show that the increase of temperature and duration leads to the increase of the cooligomerizate density, ATR yield, molecular weight and softening point and to the decrease of bromine number and colour of ATR.

As is clear from the experimental data (Fig. 14) that ATR yield increases (from 30.5 to 41.1 wt %) when the temperature increases from 333 to 353 K and the maximum yield of the final product (41.1 wt %) is reached at the cooligomerization temperature equal to 353 K.

ATR molecular weight increases when raising the cooligomerization temperature and reaches 1124 at 353 K. The cooligomerization temperature raise from 333 to 353 K improves resin colour (from 900 to 220 mg I_2/100 cm^3) (Fig. 16).

It has been determined (Figs. 17 and 18) that the increase of the cooligomerization duration up to 3 h results in the increase of the cooligomerizate density (up to 986 kg/m^3), ATR yield (up to 41.1 wt %), molecular weight (up to 1124) and softening point (366 K). Further increase of duration (up to 4 h) results in practical invariability of ATR yield, cooligomerizate density and softening point. However, molecular weight and colour deteriorate up to 873 (molecular weight) and 400 mg I_2/100 cm^3 (colour) (Fig. 19). It is known that in case of turpentine terpenes cooligomerization in 45 min after the reaction beginning such by-products as mirzene, α-, γ-terpinene, tricyclene, *etc.* begin accumulating in the system [27]. In 1.5 h their content reaches 13.0–15.0 wt %. So, it can be assumed that in the case of turpentine terpenes cooligomerization with C_9 fraction these by-products (which are distilled off during sripping) accumulation takes place too. So, this fact is obviously the cause of the yield decrease (to 28.8 wt %) and deterioration of main physicochemical properties of the cooligomers (Figs. 17 and 18).



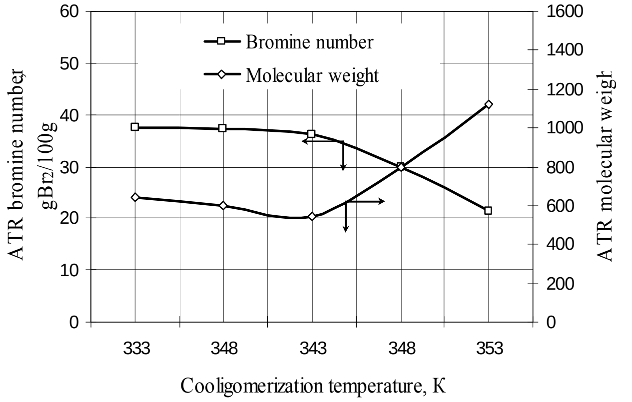


Fig. 14. ATR yield and cooligomerizate density dependence on the cooligomerization temperature at unsaturated aromatic and terpenic hydrocarbons cooligomerization

Fig. 15. ATR bromine number and molecular weight dependence on the cooligomerization temperature at unsaturated aromatic and terpenic hydrocarbons cooligomerization

Turpentine : C_9 fraction ratio = 10 : 90 % (w/w), $C_{cat.}$ = 3 wt % (in terms of aluminium chloride), τ = 3 h

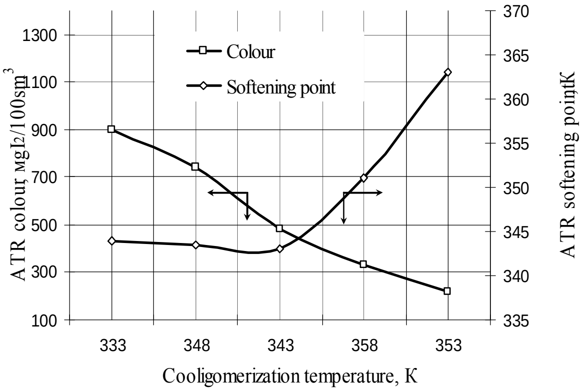
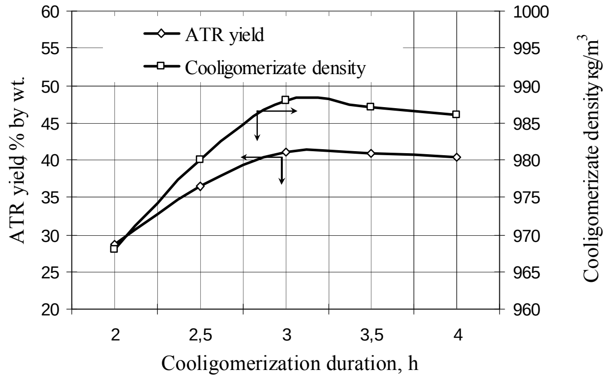


Fig. 16. ATR colour and softening point dependence on the cooligomerization temperature at unsaturated aromatic and terpenic hydrocarbons cooligomerization. Turpentine : C_9 fraction ratio = 10 : 90 % (w/w), $C_{cat.}$ = 3 wt % (in terms of aluminium chloride), τ = 3 h



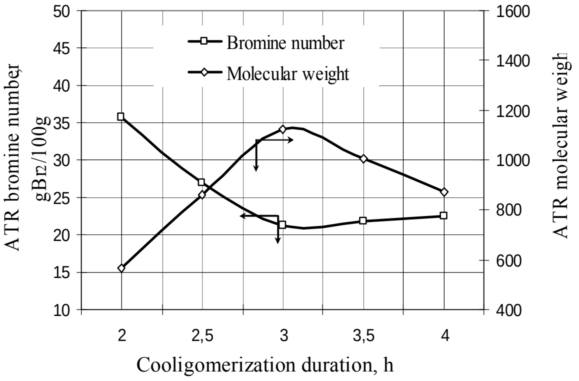


Fig. 17. ATR yield and cooligomerizate density dependence on the cooligomerization duration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

Fig. 18. ATR bromine number and molecular weight dependence on the cooligomerization duration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

Turpentine : C_9 fraction ratio = 10 : 90 % (w/w), $C_{cat.}$ = 3 wt % (in terms of aluminium chloride), T = 353 K

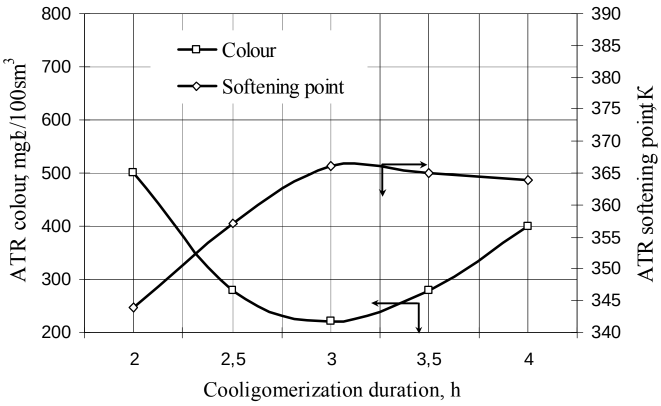


Fig. 19. ATR colour and softening point dependence on the cooligomerization duration at unsaturated aromatic and terpenic hydrocarbons cooligomerization

Turpentine : C_9 fraction ratio = 10:90 % (w/w), $C_{cat.}$ = 3 wt % (in terms of aluminium chloride), T = 353 K

Based on the obtained results we can conclude that cooligomerization duration over 3 h is unreasonable and the optimum duration is 3 h.

Under these conditions cooligomerizate density is 988 kg/m^3 and the resin yield is 41.1 wt %. ATR obtained is characterized by bromine number – 21.3 g Br_2/100 g; molecular weight – 1124; colour – 400 mg I_2/100 cm^3 and softening point – 364 K.

4. Conclusions

As a result of the research done: principal regularities of the catalytic cooligomerization of turpentine and C_9 fraction monomers have been studied; the influence of the initial feedstock composition (turpentine : C_9 fraction ratio) on the process has been ascertained; the effect of main factors (temperature, duration, catalyst concentration) on ATR yield and physicochemical properties has been studied.

References

[1] Radbil B., Zyrinova T. and Starostina E.: Khimiya Rast. Syrja, 2004, **4**, 39.

[2] Titova K., Vojcehovich N., Kosterina N. *et al.*: Otkrytija. Izobretenia, 1983, **2**, 99.

[3] Lypjan L., Movsik F., Shylman L. *et al.*: Otkrytija. Izobretenia, 1985, **20**, 106.

[4] Sokolov V., Rajt V., Nechaeva T. *et al.*: Otkrytija. Izobretenia, 1982, **35**, 63.

[5] Jaroshevskij S., Kokoshkina N., Panchenko N. *et al.*: Otkrytija. Izobretenia, 1983, **25**, 89.

[6] Lamotkin A., Gyrjan B. and Petrashel I.: Otkrytija. Izobretenia, 1983, **27**, 111.

[7] Lesuk E., Hydolej M., Soboleva S. *et al.*: Konferencija po Kaychyky i Rezine. Russia, Moscow 2004, 144.

[8] Gonzenbach C., Jordon M. and Junick R.: Encyclop. Polymer Sci. & Techn., 1970, **13**, 575.

[9] Nesterova E. and Starostina E.: Gidrolizacia i Lesokhim. Prom., 1970, **4**, 11.

[10] Ruckel E. and Orit Jr.: Naval Stories Rev., 1984, **1**, 1.

[11] Dymskij Yu., No B. and Bytov G.: Khimia i Technologiya Neftepolimernykh Smol. Khimia, Moskwa 1999.

[12] Mokryj J., Nykulyszyn I. and Budzan B.: Dopovidi Acad. Nauk Ukrainy, 1994, **5**, 134.

[13] Nykulyszyn I., Rypka A., Pich Z. and Urbaniak W.: Recykling 05. Poland, Poznan 2009, **5**, 23.

[14] Vasechkin V.: Tehnologia Ekstraktivnykh Veshzestv Dereva. Goslestehizdat, Moskwa 1944.

[15] Proskuriakov V. and Drabkin A. (Eds.): Khimia Nefti i Gaza. Khimia, Moskwa 1989.

[16] Odobaszjan G. and Shvec V.: Laboratornyi Praktikum po Khimii i Technologii Organicheskogo Neftekhimicheskogo Sinteza. Khimia, Moskwa 1992.

[17] Sorokin N. and Lyashko N.: Praktukum po Khimii i Technologii Plenkoobrazujushzikh Veshzestv. Khimia, Moskwa 1971.

[18] Isagulianc V. and Egorova G.: Khimia Nefti. Naukova dumka, Moskva 1956.

[19] Kakjakina M.: Ispytanie Lakokrasochnych Materialov i Pokrutij. Khimia, Moskwa 1988.

[20] Belgacem M. and Gandini A. (Eds.): Monomers, Polymers and Composites from Renewable Resources. The Boulevard, Langford Lade, Kidlington Oxford, UK 2008.

[21] Derfer J. and Traynor S.: [in:] Zinkel D. and Russel J. (Eds.), Chemistry of Turpentine. Pulp Chemical Association, New York 1989, 225-260.

[22] Cascaval C., Ciobanu C., Rosu L. and Rosu D.: Mater. Plast., 2005, **42**, 229.

[23] Popov A., Starostina E. *et al.*: Sovershenstvovanie Proizvodstva Kanifolno-Skipidarnykh Produktov. Nauka, Gorkij 1986.

[24] Soboleva S.: PhD thesis, Siberian State Technological University, Krasnojarsk 2001.

[25] Higashimura T., Lu J., Kamigaito M. *et al.*: Macromol. Chemie – Macromol. Chem. and Physics, 1993, 3441.

[26] Dymskij Yu., Berenc A. *et al.*: Neftepolymernye Smoly. CNIITEneftechim, Leningrad 1983.

[27] Zhuravljov P.: Polucenie Proizvodnykh Skipidara: Ekspress-inform.: Zharub. Opyt. VNIIPIlesprom, Moskwa 1983.

[28] Nikitin O.: Vysokomol. Soed.A, 1984, **26**, 208.

[29] Dumskij U., Berenc A. and Kozodoj L.: Neftepolymernye Smoly. CNIITEneftechim, Leningrad 1983.

[30] Ruckel E., Arlt H.: [in:] Zinkel D. and Russel J. (Eds.), Polyterpene Resins. Pulp Chemical Association, New York 1989, 510-530.

[31] Satoh K., Sugiyama H. and Kamigaito M.: Green Chem., 2006, **8**, 878.

ВИВЧЕННЯ ЗАКОНОМІРНОСТЕЙ КАТАЛІТИЧНОЇ КООЛІГОМЕРИЗАЦІЇ АРОМАТИЧНИХ ТА ТЕРПЕНОВИХ ВУГЛЕВОДНІВ

Анотація. *Встановлено основні закономірності перебігу катіонної коолімеризації ароматичних вуглеводнів, які містяться у фракції C_9, що одержується піролізом дизельного палива, та терпенових вуглеводнів скипидару. Запропонований новий ефективний каталізатор процесу – гомогенний комплекс хлориду алюмінію з етилацетатом в органічному розчиннику (ксилолі).*

Ключові слова: *фракція C_9, скипидар, ароматично-терпенові смоли, каталітична коолігомеризація.*