

## MODIFICATION OF AROMATIC PETROLEUM RESIN

Vladimir G. Bondaletov, Lyudmila I. Bondaletova\*, Nguyen Van Thanh, Tatyana A. Prokopyeva

*Institute of Natural Resources, Tomsk Polytechnic University, Russia*

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### Abstract

One of the directions of quality improvement of petroleum resin obtained from petrochemical by-products is their functionalization. The petroleum resins, synthesized by thermal, initiated and ionic polymerization, have been modified using peracetic acid, prepared *in situ*. This process leads to the epoxy, carbonyl and hydroxyl group introduction into the resin composition. It has been shown that at a high oxidant concentration and long process duration the petroleum resin oxidation process proceeds in parallel with the epoxidation process.

**Keywords:** liquid pyrolysis products; C<sub>9</sub> fraction; petroleum resin; modification.

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### 1. Introduction

The rational use of by-products and wastes of petrochemical production is the basic strategy of industrial development. The pyrolysis of hydrocarbon raw materials of different origin is the most common method for the lowest olefins producing. 20-40 % by-products with higher molecular weight, i.e. pyrolysis liquid products are formed along with the main products (ethylene, propylene) in the pyrolysis process. As pyrolysis production power increases, the by-products quantity grows continuously. The rational use of them is an urgent problem in respect of both resource conservation and environmental protection [1-2].

Liquid pyrolysis products are the feedstock for production of a petroleum resin (PR) that are well-known and widely used as a substitute for the costly and limited products of wood processing and vegetable oil processing. PRs are used in the paint, furniture, pulp-and-paper, rubber industry, in the manufacture of printing inks, artificial leather, anticorrosive and protective coatings, in the construction and various compositions. In recent decades, PRs are becoming more widely used in the manufacture of polymer concrete with high strength and frost-resistance and low permeability to water, in the production of construction mastic for walls and roofs, for waterproofing and adhesive compositions. The combinations of PR and bitumen or phenolic resin are used to prepare high-strength asphalt. PR properties such as low softening temperature (50-150°C), light resistance, chemical firmness, heat resistance, water tightness, good solubility in organic solvents, as well as good compatibility with synthetic film formers and oxidized oils determine the areas of their use [3-7].

The composition of polymerizable components of the liquid pyrolysis products can change within quite wide limits depending on both the raw materials subjected to pyrolysis and pyrolysis conditions [3, 8-9]. The chosen mechanism of polymerization (radical or ion) has an influence on the composition of a polymeric chain. For example, resins obtained by ionic polymerization are copolymers comprising styrene links, vinyl toluene, indene, and dicyclopentadiene. Styrene is the main link in the structure of resin synthesized by a radical mechanism [3]. PR obtained by polymerization of C<sub>9</sub> fractions unsaturated components are typically aromatic oligomer or copolymer resin.

Certain problems during the work with PR are connected with their limited variety and insufficient compatibility with many materials due to the absence of functional groups in a PR struc-

ture. The processes of oxidation, maleinization, the introduction of monomers with polar groups (carboxyl, anhydride, ester,) in the initial fraction are the most common methods of functionalization [8, 10].

Unsaturated compounds can be converted into 1,2-epoxides and 1,2-glycols by various oxidizing agents effect. The air in the presence of silver, hypochloric acid, alkaline solution of hydrogen peroxide, hydrogen peroxide in the presence of aliphatic alcohols, hydrogen peroxide in the presence of acids and acid salts of heavy metals group (for example, tungsten) of the Periodic system are widely used for oxidation (epoxidation) of the lowest olefins. The last oxidants belong to the group of reactions with participation of the obtained *in situ* peracids [11-13]. The effective method of oxygen-containing group introduction is the epoxidation process discovered by N. A. Prilezhaev. The reaction of organic peracids with the double bonds of unsaturated compounds (the Prilezhaev reaction) has a great industrial importance for epoxy compounds obtaining [14]. The reactivity of unsaturated compounds when reacting with peracids depends both on the nature of the used peracid and on the nature and amount of sub-stitutes located near a double bond.

The processes of epoxy group introduction in PR are studied insufficiently fully for technological problems solving. The resins, modified by hydrogen peroxide by the Prilezhayev reaction, which has been obtained on the basis of C<sub>5</sub> and dicyclopentadiene fractions, are described in works [15-16]. The reactions proceed in mild conditions and result in forming modified resins suitable for the preparation of compositions with bitumen or oxidized vegetable oils.

The C<sub>9</sub> fraction of liquid pyrolysis products, which is most often used, is a mixture of aromatic and unsaturated hydrocarbons: styrene,  $\alpha$ -methylstyrene, vinyl toluene, indene, dicyclopentadiene. P. R obtained by these monomers polymerization is called aromatic resin (PR<sub>C9</sub>). The purpose of this work is to carry out the process of oxidation of aromatic petroleum resin obtained by radical and ionic polymerization of C<sub>9</sub> fractions by the Prilezhaev method and study their properties.

The research of influence of oxidative system composition on the properties of PR<sub>C9</sub> oxidation products and oxidation process duration was carried out to achieve that goal. Standard titrimetric and spectral methods were used to perform the research.

## 2. Experimental

### 2.1. Objects of research

The C<sub>9</sub> fraction of liquid pyrolysis products of hydrocarbons with a boiling temperature of 110-190°C was used as a raw material for obtaining petroleum resin (PR<sub>C9</sub>). PR obtained by radical and ion polymerization of C<sub>9</sub> fraction unsaturated compounds was used as an object of the research (initial resin).

Thermal radical polymerization was carried out at a temperature of 230-280°C, pressure up to 1.0 MPa for 4-8 hours. The samples of resin (PR<sub>C9\_T</sub>) had been got at the plant «Slantsy» (St. Petersburg).

Initiated radical polymerization was carried out at a temperature of 70-130°C, pressure up to 0.1-0.2 MPa for 5-30 hours depending on the applied initiator. The samples of resin (PR<sub>C9\_IN</sub>) had been got at the plant LLC «Omsk-Polimer» (Omsk).

Ionic polymerization of C<sub>9</sub> fraction unsaturated components was carried out under the following conditions: the catalyst system – TiCl<sub>4</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl, TiCl<sub>4</sub> concentration – 2 %, TiCl<sub>4</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl – the equimolar ratio of components, temperature – 80 °C, duration – 2 hours, pressure – 0.1 MPa. The TiCl<sub>4</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl catalyst system was deactivated by using propylene oxide at the end of the reaction and products of the reaction remained in the resin composition (PR<sub>C9\_ION</sub>) [17].

The modification of PR obtained by radical polymerization was carried out in 30 % toluene solution, and modification of resin obtained by ionic mechanism – in a unreacted hydrocarbon solution of C<sub>9</sub> fractions. The peracetic acid prepared *in situ* was used as an oxidant, the amount of that was measured by the weight ratio of hydrogen peroxide to the initial resin. The introduction of oxidant was dosed under stirring for one hour at 50-55°C, after that the tempera-

ture was raised to 75°C, and the process was carried out during 180 minutes with sampling. After synthesis, the reaction mixture was washed with water to the neutral pH, and the polymer was isolated by removing the solvent or unreacted hydrocarbons at reduced pressure.

## 2.2. Methods of research

The initial and modified resin samples were investigated by standard methods [18]. NMR  $^1\text{H}$  spectra of resin were recorded using an NMR Fourier spectrometer (AVANCE AV-300 «Bruker») in  $\text{CDCl}_3$ . IR spectra of resin were recorded using an IR Fourier spectrometer (FT-801 «Simex») using KBr glass.

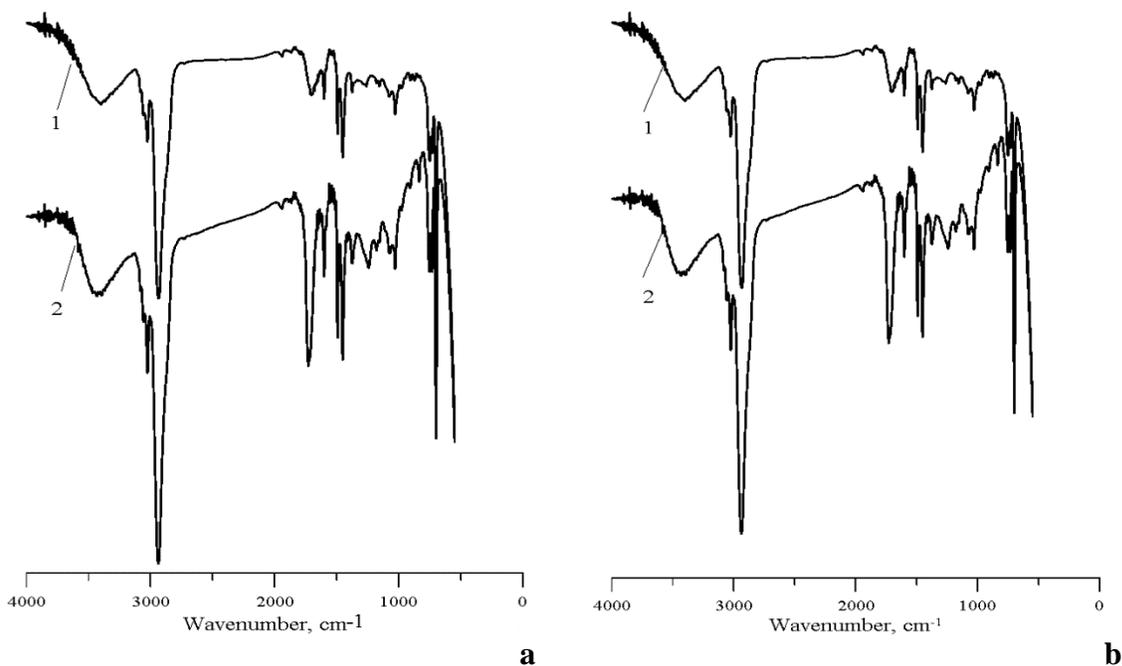
## 3. Results and discussion

Polymerization of liquid pyrolysis products fractions, containing diene hydrocarbons, leads to obtaining an unsaturated resin which is capable of being oxidized spontaneously when storing. Purposeful modification of resin allows avoiding this disadvantage and obtaining a resin with polar functional groups and, therefore, with a new complex of properties.

Epoxidation of unsaturated polymers is carried out by using organic lowest aliphatic peracids advantageously. Polymers, synthesized by different methods of initiation such as thermal, free-radical, ion ones, are applied for epoxidation.

In this work modification of petroleum resin ( $\text{PR}_{\text{C}_9}$ ) was carried out by using hydrogen peroxide and acetic acid, taken in an equimolar ratio, in the presence of a strong acid catalyst ( $\text{H}_2\text{SO}_4$ ), thereby obtaining the equilibrium solution of peracetic acid in the reaction medium. The amount of hydrogen peroxide was varied within the range from 0.01 to 0.75 mass parts per 1 part of resin.

It is known that epoxidation of unsaturated polymers results in the product which contains functional groups (hydroxyl, aldehyde, ketone, carboxyl), formed as a result of the secondary reactions, along with basic functional groups (epoxy groups) [11-12]. It is confirmed by the results of the spectral analysis which are presented in Fig. 1.



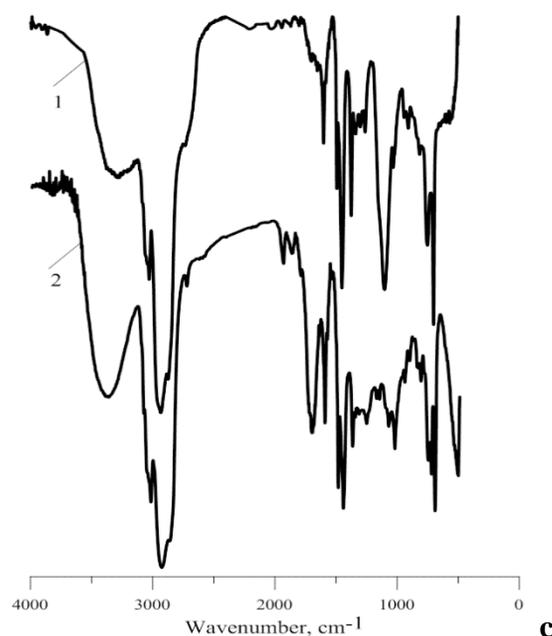


Fig. 1. The IR spectra of the initial resin (1) obtained by thermal (a), initiated (b), ionic polymerization (c); the modified resin (2) based on them (a, b, c) at the 0.5:1 «oxidative system:PR<sub>C9</sub> resin» component ratio

PR prepared both by thermal (PR<sub>C9\_T</sub>) and initiated (PR<sub>C9\_IN</sub>) polymerization is oxidized during the storage. The absorption bands corresponding to valent vibrations of the carbonyl group in the range of 1713-1730 cm<sup>-1</sup> and of the hydroxyl group in the range of 3440-3449 cm<sup>-1</sup> (Fig. 1a-1b, spectrum 1) in the IR spectra testify it. Besides, the absorption bands in the range of 1100-1105 cm<sup>-1</sup>, corresponding to vibrations of titanium and aluminum alkoxide groups of the deactivation products of the catalyst system by propylene oxide (Fig. 1c, spectrum 1), should be noted in the IR spectra of the resin (PR<sub>C9\_ION</sub>) obtained by ionic polymerization with TiCl<sub>4</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl.

As a result of the modification process, the absorption bands of the symmetric and asymmetric vibrations of the epoxide ring in the range of 1240-1244 cm<sup>-1</sup>, 1175-1180 cm<sup>-1</sup>, 834-836 cm<sup>-1</sup> appear in the IR spectra of the products. At the same time, the intensity of the absorption bands in the range of 1713-1730 cm<sup>-1</sup>, 3440-3449 cm<sup>-1</sup>, which indicates a parallel process of further resin oxidation, increases. Double bonds of the initial resin in the epoxidation reaction leads to the decrease of the absorption bands intensity of valence and deformation vibrations of the =C-H group (3024-3025 cm<sup>-1</sup>, 976-979 cm<sup>-1</sup>, respectively).

The intensities correlation of absorption bands of carbonyl (1713-1730 cm<sup>-1</sup>) and epoxy groups (1240-1244 cm<sup>-1</sup>, 1175-1180 cm<sup>-1</sup>, 834-836 cm<sup>-1</sup>) in the IR spectra of the modified products with the absorption band of the aromatic ring (1600 cm<sup>-1</sup>) indicates an advantageous epoxidation process of the resin obtained by ionic polymerization. Along with epoxidation, the process of oxidation by the Prilezhaev method plays a significant part when obtaining resin by a radical mechanism.

The results of chemical analysis of the modified resin: bromine number (BN, g/100 g), acid number (AN, mg/g), epoxy number (EN, %) are shown in Tab. 1-3, respectively. The research of the modified resin properties (MPR<sub>C9\_T</sub>, MPR<sub>C9\_IN</sub>, MPR<sub>C9\_ION</sub>) is carried out at the different oxidant amount and process duration.

Increasing of the oxidant amount from 0.01 to 0.75 mass parts per 1 part of resin and of the process duration leads to significant decrease of the bromine number within 30-60 minutes modification reaction for the resin obtained by radical polymerization or to BN smooth decrease using the resin synthesized by an ionic mechanism.

Table 1. Bromine number (g/100 g) of the modified resin

Resin	Ratio of components «oxidative system:PR <sub>C9</sub> resin»	Process duration, h				
		0.5	1.0	1.5	2.0	3.0
MPR <sub>C9_T</sub>	0.00 : 1	14.8	14.8	14.8	14.8	14.8
	0.01 : 1	5.1	4.3	3.6	3.5	3.4
	0.25 : 1	4.9	3.9	3.4	3.2	3.2
	0.50 : 1	2.1	1.8	1.5	1.5	1.2
	0,75 : 1	2.0	1.7	1.5	1.4	1.2
MPR <sub>C9_IN</sub>	0.00 : 1	19.9	19.9	19.9	19.9	19.9
	0.01 : 1	5.3	4.2	3.6	3.4	3.2
	0.25 : 1	4.9	3.9	3.4	3.2	3.2
	0.50 : 1	2.1	1.8	1.5	1.5	1.2
	0,75 : 1	2.1	1.7	1.5	1.4	1.2
MPR <sub>C9_ION</sub>	0.00 : 1	33.2	33.2	33.2	33.2	33.2
	0.01 : 1	32.6	31.4	28.3	26.1	15.3
	0.25 : 1	32.2	31.0	26.6	24.2	14.2
	0.50 : 1	27.2	22.3	18.2	15.2	8.3
	0.75 : 1	27.0	17.2	12.4	8.6	8.2

Table 2. Epoxy number (%) of the modified resin

Resin	Ratio of components «oxidative system : PR <sub>C9</sub> resin»	Process duration, h				
		0.5	1.0	1.5	2.0	3.0
MPR <sub>C9_T</sub>	0.00 : 1	0.2	0.2	0.2	0.2	0.2
	0.01 : 1	0.5	0.6	0.7	0.8	1.0
	0.25 : 1	1.2	1.5	1.6	1.8	2.2
	0.50 : 1	1.3	1.7	2.0	2.3	2.8
	0,75 : 1	1.2	1.5	1.6	1.7	1.8
MPR <sub>C9_IN</sub>	0.00 : 1	0.1	0.1	0.1	0.1	0.1
	0.01 : 1	1.1	1.4	1.5	1.8	1.8
	0.25 : 1	1.1	1.7	1.9	2.2	2.3
	0.50 : 1	1.0	1.1	1.3	1.5	1.7
	0,75 : 1	0.9	1.0	1.1	1.3	1.4
MPR <sub>C9_ION</sub>	0.00 : 1	0.0	0.0	0.0	0.0	0.0
	0.01 : 1	5.4	5.8	6.5	7.2	7.7
	0.25 : 1	6.1	6.4	7.1	7.8	8.2
	0.50 : 1	9.3	10.2	10.5	11.8	12.9
	0.75 : 1	7.2	7.9	8.3	9.1	9.4

Table 3. Acid number (mg/g) of the modified resin

Resin	Ratio of components «oxidative system : PR <sub>C9</sub> resin»	Process duration, h				
		0.5	1.0	1.5	2.0	3.0
MPR <sub>C9_T</sub>	0.00 : 1	3.0	3.0	3.0	3.0	3.0
	0.01 : 1	5.5	6.8	8.3	9.6	9.8
	0.25 : 1	9.5	10.6	10.9	12.9	16.8
	0.50 : 1	10.2	12.5	17.0	19.0	24.1
	0,75 : 1	15.4	19.3	22.9	26.0	34.4
MPR <sub>C9_IN</sub>	0.00 : 1	5.1	5.1	5.1	5.1	5.1
	0.01 : 1	6.2	7.4	9.1	11.0	14.0
	0.25 : 1	8.9	14.0	15.1	16.2	16.8
	0.50 : 1	16.5	22.6	27.1	29.1	30.2
	0,75 : 1	17.9	23.5	26.9	31.9	34.7
MPR <sub>C9_ION</sub>	0.00 : 1	0.0	0.0	0.0	0.0	0.0
	0.01 : 1	2.4	3.2	3.9	4.7	5.6
	0.25 : 1	4.5	5.6	7.2	8.5	10.1
	0.50 : 1	5.1	6.8	8.4	9.6	12.3
	0.75 : 1	7.2	9.5	10.6	13.4	17.2

The presence of large amounts of aliphatic acids or acid catalysts, high temperature or high process duration reduces the epoxy group stability. Therefore, based on the obtained values of the epoxy number, the increase of the «oxidative system: PR<sub>C9</sub> resin» component ratio is more than 0.5 : 1.0 and of the process duration above 120 minutes is inexpedient.

The oxidation process contribution (acid number increasing) grows with the increase of oxidant amount or process duration; it is especially evident for resin obtained by radical polymerization.

When studying PR by NMR <sup>1</sup>H-spectroscopy, 6 proton types are isolated in the spectra [14]. This is aromatic (A), olefin (B), methyl and methylene in  $\alpha$ -position to the benzene ring or oxygen atom (C), methine of paraffin or naphthenes (D), methylene of paraffin or naphthenes (E), methyl (F) protons. The values of the normalized integrated intensity (I, %, the percentage of protons of various types) are given in Tab. 4.

Table 4. Values of the normalized integrated intensity (I, %) of MPR<sub>C9</sub> protons

Proton type (ppm)	«Oxidative system : PR <sub>C9</sub> resin» component ratio				
	0:1	0.1:1	0.25:1	0.5:1	0.75:1
MPR <sub>C9_T</sub>					
A (6.3-8.3)	23.7	27.3	26.7	27.9	27.1
B (3.8-6.3)	4.3	3.3	2.1	1.6	1.7
C (3.1-3.8)	2.7	4.4	5.3	5.8	7.0
D (2.1-3.1)	26.7	22.3	22.5	22.5	20.4
E (1.4-2.1)	29.4	29.2	29.2	31.8	32.4
F (0.1-1.4)	13.0	13.5	14.2	10.5	11.4
MPR <sub>C9_IN</sub>					
A (6.3-8.2)	26.1	29.6	29.9	30.1	30.8
B (4.4-6.3)	5.9	3.4	3.3	0.0	0.0
C (2.9-4.4)	3.1	4.4	4.3	6.8	6.6
D (2.1-2.9)	24.2	21.4	20.2	23.0	22.2
E (1.4-2.1)	28.1	27.9	28.4	28.0	29.2
F (0.1-1.4)	12.7	13.4	13.8	12.0	11.2
MPR <sub>C9_ION</sub>					
A (6.4-8.2)	19.9	19.9	20.5	20.7	20.3
B (4.4-6.4)	6.4	6.3	6.1	5.9	5.6
C (3.3-4.4)	3.4	3.5	4.5	4.6	5.2
D (2.5-3.3)	11.6	11.6	11.2	13.2	11.3
E (1.4-2.5)	39.4	39.4	39.5	38.1	39.2
F (0.1-1.4)	19.4	19.4	18.1	17.4	18.4

Double bonds of the initial resin in the epoxidation reaction confirm the decrease of normalized integrated intensity of B-type protons and simultaneous increase of normalized integrated intensity of C-type protons.

#### 4. Conclusions

1. Modification of petroleum resins synthesized by thermal, initiated and ionic polymerization with peracetic acid, prepared *in situ*, allows introducing polar groups (epoxy, carbonyl, hydroxyl) into the resin composition.
2. When increasing the oxidant amount and process duration, oxidation of petroleum resin is parallel to the epoxidation process. The maximum values for «oxidative system : PR<sub>C9</sub> resin» component ratio are (0,25-0,50) : 1 for the 120 min. process duration.
3. Under these conditions, the most typical reaction is oxidation for a saturated resin obtained by radical polymerization or epoxidation for more unsaturated resin obtained by ionic polymerization.

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\*Corresponding author, address: 30, Lenin Avenue, Tomsk, 634050, Russia; tel.: (+7-3822) 606-121; fax: (+7-3822) 564-320; e-mail: [bondli@tpu.ru](mailto:bondli@tpu.ru)