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## DETERMINING STRUCTURE OF PETROLIUM POLYMER RESINS OBTAINED ON THE BASIS OF HIGH-BOILING FRACTIONS OF PYROLYSIS LIQUID PRODUCTS

L.I. Bondaletova, V.G. Bondaletov, O.V. Verevkina, A.A. Manankova

Tomsk Polytechnic University  
E-mail: bondaletov@mail.tomsknet.ru

*On the basis of experimental spectra and spectra calculated with the help of ACDLabs (HNMR) NMR <sup>1</sup>H program the structure of petroleum polymer resins obtained by polymerization of high-boiling fractions of pyrolysis liquid products has been specified. Close fit between calculated and experimental results is obtained.*

Using by-products and wastes of petroleum chemical manufactures decreases significantly the environmental load and may serve as a source of extra income at correct organization of technological process. At the present multipurpose utilization of raw material in petroleum refining industry is especially actual for saving unrenewable oil resources. Obtaining ethylene from virgin oil the quantity of the formed by-products – pyrolysis liquid products (PLP) – is comparable with end product output. The most valued products obtained from PLP are petroleum polymer resins (PPR) which can substitute more scarce and expensive materials on the basis of vegetable raw materials in manufacturing lacquers and paints.

Significant attention is given to the problems of PPR synthesis in scientific literature [1–4]. One of the main tasks of investigation is studying macromolecule structure that is connected with the necessity of synthesis of resins with specified property complex.

Studying high-molecular compounds determination of composition and structure of macromolecule, molecular weight of polymer chain and end group nature is of great importance. It is possible to obtain objective notion about the structure of high-molecular compound only by means of comparing data collected as a result of chemical and physical investigations; it is also possible to use efficiently computer programs for modeling compound structure and calculation of their NMR <sup>1</sup>H spectra.

The aim of the given paper is studying the structure of PPR synthesized by polymerization of various unlimited fractions of pyrolysis liquid products. Composition and properties of pyrolysis liquid products is determined to a considerable degree by raw material and conditions of pyrolysis which can often change in practice.

Two types of resins which were obtained by catalytic polymerization of high-boiling fractions of PLP: styrene fraction (SF) (PPR<sub>SF</sub>) and dicyclopentadiene fraction (DCPDF) with boiling limits 130...190 °C (PPR<sub>DCPDF</sub>) were chosen as the objects of investigation.

### Experimental part

Resinous components formed as a result of oxidation and polymerization of unstable unlimited and diene hydrocarbons at PLP storage in plant conditions in the amount of 10,9 % for the first sample and 8,3 % for the second sample were separated from original fractions by atmospheric distillation up to 200 °C.

Quantitative identification of boiled away components of products of PLP processing was carried out by the method of gas-liquid chromatography at chromatographer LHM-80 with flame-ionization detector in steel capillary column of 15 m length, inner diameter 0,25 mm, stationary phase – apiezon L. Carrier gas is nitrogen, velocity is 80 ml/min, sample volume is 1 microliter.

The results of analysis of fraction volatile components are given in Table 1.

**Table 1.** Fraction sample composition

Mixture components	Content of hydrocarbons, %	
	Sample 1	Sample 2
Cyclopentadiene	1,7	1,4
Benzene	1,8	1,8
Toluene	7,9	1,7
Ethylbenzene	2,9	0,6
Xylene ( <i>m</i> - + <i>p</i> -)	9,3	1,2
Styrene mixture + <i>o</i> -xylene	20,6	1,4
$\alpha$ -Methyl styrene	3,2	0,8
Dicyclopentadiene	26,8	50,3
Indene	3,5	9,6
Unidentified hydrocarbons	22,3	31,2

It follows from Table 1 that the given samples of PLP contain 45...60 % of unlimited hydrocarbons and the first sample is enriched with styrene and benzene alkyl substituted and the second sample by dicyclopentadiene. Therefore, the first sample takes the title of styrene fraction and the second sample of dicyclopentadiene one.

The original fractions were polymerized under the influence of metal-complex catalyst on the basis of titanium tetrachloride and triethylaluminum taken in molar ratio 1 : 0,33 at temperature 80 °C during 3 h. Concentration of titanium tetrachloride amounted to 2 % of original fraction mass. Catalyst complex was deactivated with propylene oxide.

Resins were extracted from reaction solution by separation of unreacted hydrocarbons by distillation at pressure 13300 Pa in nitrogen atmosphere or resin sedimentation from solution in unreacted hydrocarbons into ethanol, the ratio solvent : precipitant was kept equal to 1 : 5. Molecular weight of PPR samples was determined cryoscopically in benzene. Unsaturation of resins was estimated by bromine value magnitude which was determined by standard method [5]. ЯМР  $^1\text{H}$  spectra were recorded at spectrometer *BS-467 «Tesla»* at operation frequency 100 MHz, inner standard.

### Results discussion

After polymerization the unreacted hydrocarbons were separated by distillation at low pressure and analyzed. Resin output amounted to 40 and 45 % respectively for SF and DCPDF. The results of analysis are presented in Table 2.

The results indicate the fact that petroleum polymer resin obtained on the basis of SF is enriched with styrene and resin on the basis of DCPDF contains considerable quantity of dicyclopentadiene. However, considerable quantity of unidentified components the most part of which is unlimited compounds present in composition of dicyclopentadiene fraction.

Molecular weight and bromine value of PPR samples extracted by removal of unreacted hydrocarbons (the 1<sup>st</sup> method) or sedimentation from reaction solution (the 2<sup>d</sup> method) are given in Table 3.

**Table 2.** Content of hydrocarbons before and after polymerization

Components	SF		DCPDF	
	Unreacted hydrocarbons, %	Monomers entered into polymer composition, %	Unreacted hydrocarbons, %	Monomers entered into polymer composition, %
Cyclopentadiene	0,4	1,3	0,3	1,1
Benzene	1,8	–	1,8	–
Toluene	7,9	–	1,7	–
Ethylbenzene	2,9	–	0,6	–
Xylene ( <i>m</i> - + <i>p</i> -)	9,3	–	1,2	–
Styrene mixture + <i>o</i> -xylene	8,9	11,7	1,3	0,1
$\alpha$ -Methyl styrene	1,3	1,9	0,3	0,5
Dicyclopentadiene	16,3	10,5	36,5	13,8
Indene	3,4	0,1	3,0	6,6
Unidentified hydrocarbons	7,8	14,5	8,3	22,9

**Table 3.** PPR properties

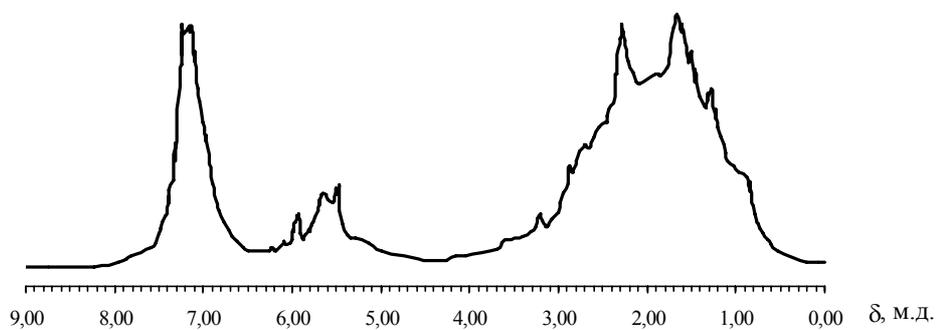
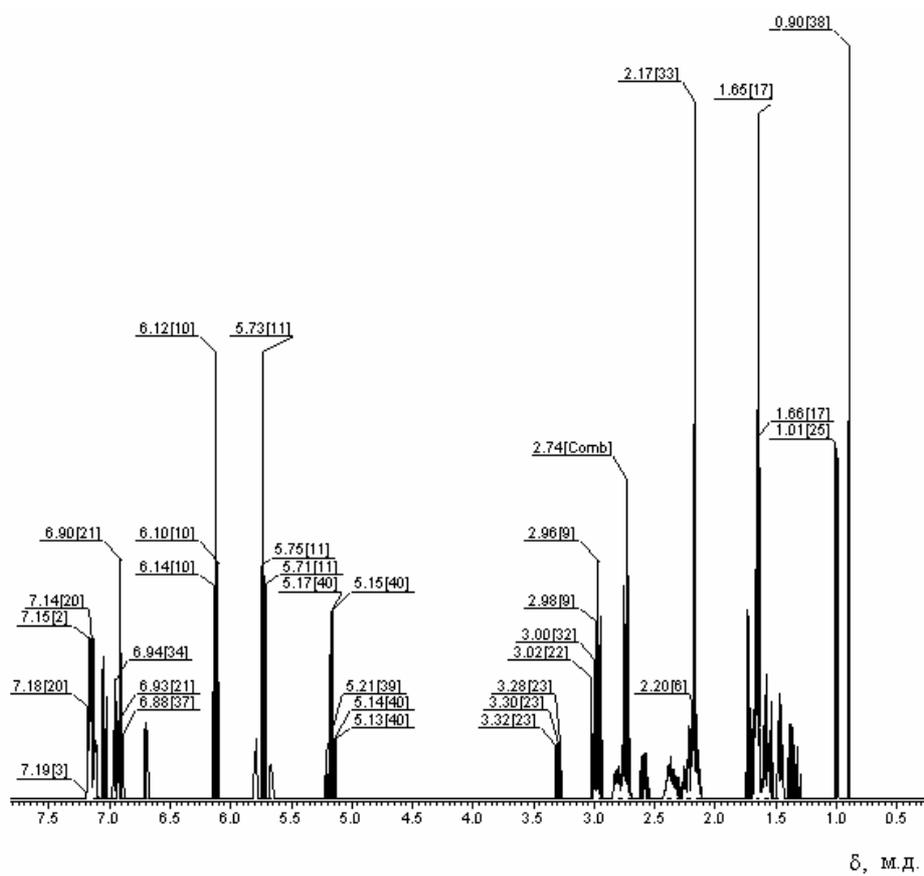
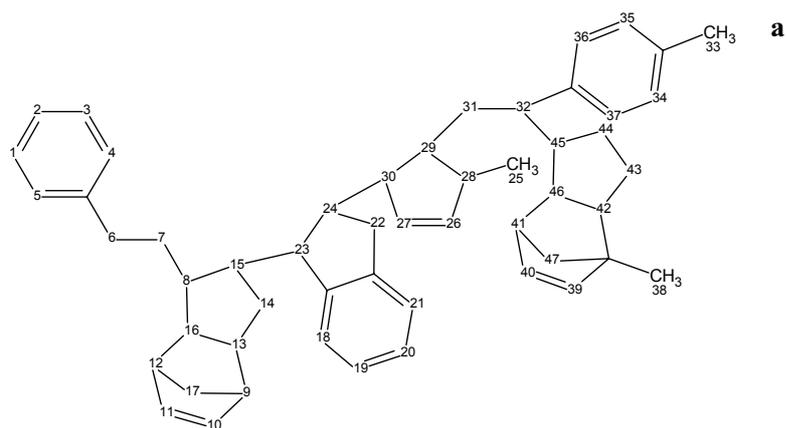
Sample	Molecular weight, g/mole		Bromine value, g Br <sub>2</sub> /100 g	
	1 <sup>st</sup> method	2 <sup>d</sup> method	1 <sup>st</sup> method	2 <sup>d</sup> method
PPR <sub>SF</sub>	500	540	57,9	69,6
PPR <sub>DCPDF</sub>	450	560	108,6	96,4

Constancy or a certain increase of molecular weight and increase of bromine value for samples of PPR<sub>SF</sub> resins extracted in different ways indicate more rapid removal of unreacted high-boiling hydrocarbons by the second method. For the sample PPR<sub>DCPDF</sub> at resin sedimentation the unlimited oligomeric products are probably also removed that results in increasing molecular weight of overprecipitated sample and decreasing bromine value. Comparing magnitudes of molecular weight and bromine value it is possible to estimate the amount of double bonds in molecule. The obtained results indicate the fact that there are at the average 3–4 double bonds in composition of synthesized PPR molecule.

Studying PPR and petroleum hydrocarbons resins in NMR  $^1\text{H}$  spectra the protons of six types are singled out; they are characterized by certain values of chemical shift (м. д.): aromatic – 6,2...8,0; olefinic – 4,0...6,2; methylic and methylen in  $\alpha$ -position to benzene ring or double bond – 2,0...3,6; methine paraffins and naphthene – 1,5...2,0; methylene paraffins and naphthene-1,05...1,5; methylic – 0,5...1,05 [1]. Values of integral intensities of singled out types of protons are given in Table 4.

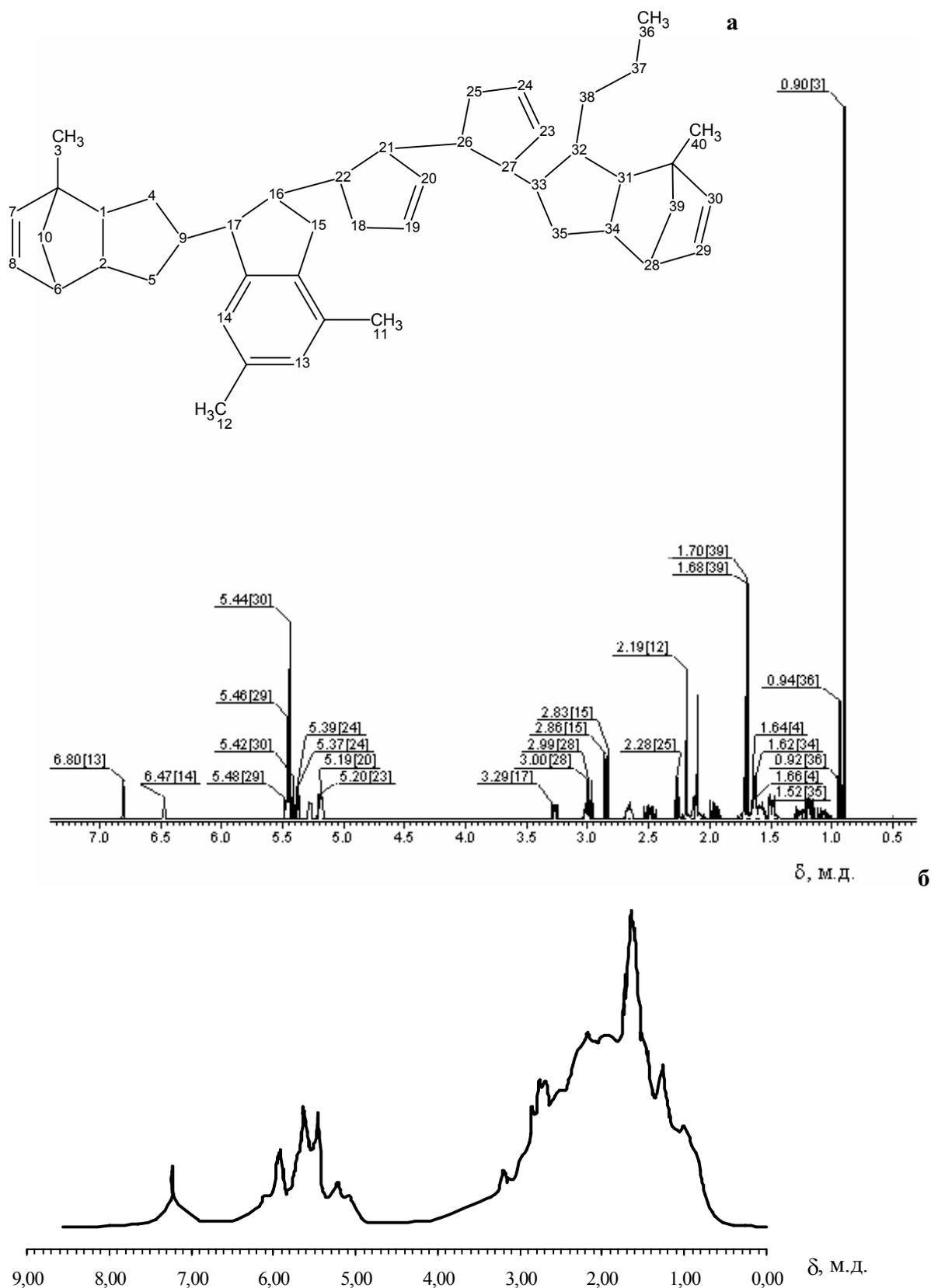
By the results of Table 4 it is possible to judge that the resin on the basis of SF is the aromatic linear resin that is confirmed by content of olefinic protons and bromine value magnitudes (Table 3). PPR<sub>DCPDF</sub> is the aliphatic linear resin with high unsaturation due to a high content of dicyclopentadiene links in copolymer.

Taking into account all obtained data the conjectural structures of PPR molecules were simulated and their ЯМР  $^1\text{H}$  spectra were computed with the help of *ACDLabs (HNMR) 2.0* program. Correspondence of spectra computed with the program to the real spectra



**Fig. 1.** Structural formula (a), computed (b) and experimental (c) NMR  $^1\text{H}$  spectra of  $\text{PPR}_{5f}$

**B**



**Fig. 2.** Structural formula (a), computed (b) and experimental (c) NMR  $^1\text{H}$  spectra of  $\text{PPR}_{\text{DCPDF}}$

was checked up by comparing model and real NMR  $^1\text{H}$  spectra of monomers: indene, dicyclopentadiene,  $\alpha$ -methyl styrene. The result of comparison showed the possibility of using this program for obtaining NMR  $^1\text{H}$  spectra as the position of the main peaks and their intensity corresponded to the real spectra.

**Table 4.** Normalized integral intensities of PPR protons, %

Original fraction	Method of resin extraction	Magnitudes of proton chemical shift, ppm					
		6,2...8,0	4,0...6,2	2,0...3,6	1,5...2,0	1,05...1,5	0,5...1,5
Experimental samples							
SF	1	19,7	9,6	32,6	18,0	13,5	6,7
SF	2	21,8	8,8	29,4	22,4	10,9	6,7
SF	2*	17,2	6,3	37,4	16,4	13,9	8,8
DCPDF	1	2,6	14,4	38,7	24,9	13,1	6,2
DCPDF	2	2,4	9,8	26,3	44,4	11,2	5,9
DCPDF	2*	2,8	11,0	33,5	24,5	19,1	9,1
Model samples							
SF		21,0	9,5	34,0	19,0	10,8	5,4
DCPDF		2,7	14,2	39,2	20,9	12,8	10,1

\* – low-molecular part separated at PPR overprecipitation

NMR  $^1\text{H}$ -spectra of experimental resin samples and computed NMR  $^1\text{H}$  spectra of the model structures are

given in Fig. 1, 2. Analyzing spectra it is necessary to understand that the computed spectrum is the spectrum of a model molecule with constant magnitude of molecular weight while spectra of experimental samples are influenced by polydispersity of the obtained resins. In computed spectra the possibility of deformation is also excluded owing to the absence of low-molecular impurities.

Correspondence or similarity of experimental and computed NMR  $^1\text{H}$  spectra was determined by correlation analysis of characteristic proton content (Table 4). The satisfactory coincidence of computed and experimental sample spectra was obtained. The correlation coefficient amounts to 0,98 for PPR<sub>SF</sub>; and it is 0,96 for PPR<sub>DCPDF</sub>.

Thus, by the example of PPR obtained from high-boiling fractions of PLP of virgin petroleum the possibility of identification of their structure with the help of combination of model and computed NMR  $^1\text{H}$  spectra was determined. The results of the given researches have practical meaning as they allow predicting more precisely chemical properties of PPR and possibilities of their further modification.

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