

## Mechanism of Interaction Between Hydrolytic Lignin and Poly(acrylonitrile)

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### Abstract

Interaction between polyacrylonitrile (PAN) and hydrolytic lignin (THL) in mixed binary solution dimethyl sulfoxide/water (70:30) allowed us to obtain homogeneous forming solution of the THL/PAN composite. This forming solution was used for preparation of fibers and films which served as precursors for carbon materials. In the present work, we considered and substantiated the proposed mechanism of the formation of the THL/PAN composite based on the structure of the initial polymers. We believe that interaction between reactive groups present in PAN and THL leads to the formation of graft copolymer. Fundamentally, this reaction is possible and may proceed according to the well-known Ritter mechanism. It was demonstrated that the process of grafting nitrile groups to THL macromolecules is controlled by duration and temperature of interaction between the initial compounds in solution; this process is completed in 10 h at a temperature of 120 °C. Tentative calculation shows that for each statistically averaged PAN macromolecule there are five THL molecules with activated hydroxyl groups. These forming solutions are suitable for moulding fibers which serve as precursors for carbon fibrous materials.

## 1. Introduction

Along with cellulose, lignin is one of the main constituents of organic natural materials. They are the most widespread natural compounds. Depending on a number of factors, lignin content in wood ranges from 20 to 30%. Lignin is an irregular strongly branched heteropolymer of complex architecture; synthesis of this compound is controlled by unregulated natural factors. Although lignin possesses many useful properties, it is still considered a waste product. The main portion of lignin-containing compounds (technical hydrolytic lignin) goes to waste and presents a certain environmental threat. Examples of successful use of THL in industry are described in a number of publications. However, less than 2–3% of total amount of lignin produced after processing wood pulp is used. One of important aspects of practical application of THL is extracting certain organic com-

pounds from this product. These organic materials are used in chemical industry as raw materials for synthesis of different useful compounds. In a number of cases, lignin is used for modifying chemical products used in metallurgy, construction, rubber industry, in production of synthetic resins, adhesives, plastics etc.

Generally, the studies concerning interaction between lignin and synthetic polymers are application-oriented and aimed at solving problems of materials science. Interactions between lignin and other macromolecular compounds include intermolecular polymerization and polycondensation. Possibility of the formation of a given composite is determined by kinetics of interaction between reactive groups and by a number of external and internal factors (structure of reactants, conditions of intermolecular reaction).

There are two types of lignin-polymer reactions. The first type includes polymer-analogous

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transformations leading to the formation of various copolymers. The second type involves reactions of macromolecules with oligomers; these reactions result in changes in functionality of one of components or in formation of sparse crosslinks. Therefore, properties of the initial components change significantly.

The process studied in the present work (formation of THL/polyacrylonitrile copolymer) can be assigned to the first type of reactions. The formation of a new composite which is described in detail in [2] is of practical importance. The obtained THL/PAN composite is a promising material for preparation of carbon fibers with high sorption capacity. In the present study, we consider possible reactions leading to the formation of this composite and suggest the mechanism of interaction between lignin and PAN. This reaction allows using THL as a source for obtaining pore-forming composites.

## 2. Experimental

### 2.1. Materials

Non-treated lignin (product of softwood conversion) was manufactured at Kirov Biochemical Plant, LLC according to the Russian State Standard GOST 18300. The product possessing an initial humidity of 65–70% was spread in thin layers (2 cm) onto closed platforms and dried at ambient temperature for 7 days until the humidity lowered down to 4–5%. After sieve fractionation, the product (in the form of grains with dimensions of 1–0.25 mm) was dispergated using an Omicron fine grinding instrument. In the following experiments, the fractions with grain dimensions of less than 5  $\mu\text{m}$  were used.

Polyacrylonitrile used in our experiments is a technical copolymer of acrylonitrile with methacrylic (6%) and itaconic acids (1%) manufactured by Scientific-production association “Nitron”. Its molecular weight is 20–40  $\cdot 10^3$  Da, MWD is 4–6. The commercial solvent (reagent grade dimethyl sulfoxide (DMSO) (specifications 600-3818-89)) was obtained from “Vekton” JSC.

#### 2.1.1. Preparation of samples for analysis

A series of experiments aimed at revealing the role of binary solutions in the formation of composites was conducted using the samples in the form of solutions, films and fibers.

#### 2.1.2. Preparation of solutions

Polyacrylonitrile was dissolved in DMSO (mass ratio of components was 1:9).

After exposure for 1 day at ambient temperature, THL was added to the formed solution at mixing; the mixture was homogenized for 2 days. The THL: PAN mass ratio was 80:20, the total amount of polymeric components in DMSO solution was 3–5%.

#### 2.1.3. Preparation of films and fibers

The obtained forming solutions were used for preparing films and fibers. Films were obtained by spill casting onto glass surface, and fibers were molded using a SV-1000 syringe pump at a rate of 150 mL  $\times$  h<sup>-1</sup>. Fiber molding was carried out in precipitating bath at 80 °C for 15 min. The molded fibers were preoxidized at temperatures from 20 to 230 °C at a heating rate of 7 grad  $\times$  min<sup>-1</sup>; the product was exposed at 230 °C for 30 min. Then the fibers were carbonized in argon atmosphere; the temperature was increased up to 800 °C at a similar rate.

When carbonization was complete, the fibers were tested. Dispersion parameters and specific surface area were determined. It was revealed that polydispersity varies in a wide interval (from micropores to macropores with radii ranging from 2 to 300 nm). Depending on carbonization conditions, specific surface area of fibrous carbon adsorbents varies from 20 to 800 m<sup>2</sup>  $\cdot$  g<sup>-1</sup>. Yield of adsorbent prepared from the composite precursor is 35–42%.

#### 2.2. Pyrolysis-gas chromatography/mass spectrometry

The selective pyrolysis of THL samples treated with the DMSO/H<sub>2</sub>O solvent mixture (at various DMSO/H<sub>2</sub>O ratios) was performed. An EGA/PY-3030 pyrolysis reactor (Frontier Lab) equipped with a cryotrap (cooled to –197 °C) was used; helium was used as a carrier gas. The heating rate was 30 grad  $\times$  min<sup>-1</sup>; the final temperature was 800 °C. Samples were taken in the following four temperature ranges (corresponding to the boundaries of peaks of releasing volatile thermodestruction products): 40–100, 100–250, 250–450, and 450–800 °C. Chromatographic studies of pyrolysis products were performed using an Ultra-Alloy 5MC capillary column (0.25 mm in diameter, 30 m in length, with helium as a carrier gas and gas flow rate of 1 mL  $\times$  min<sup>-1</sup>). The heating rate was

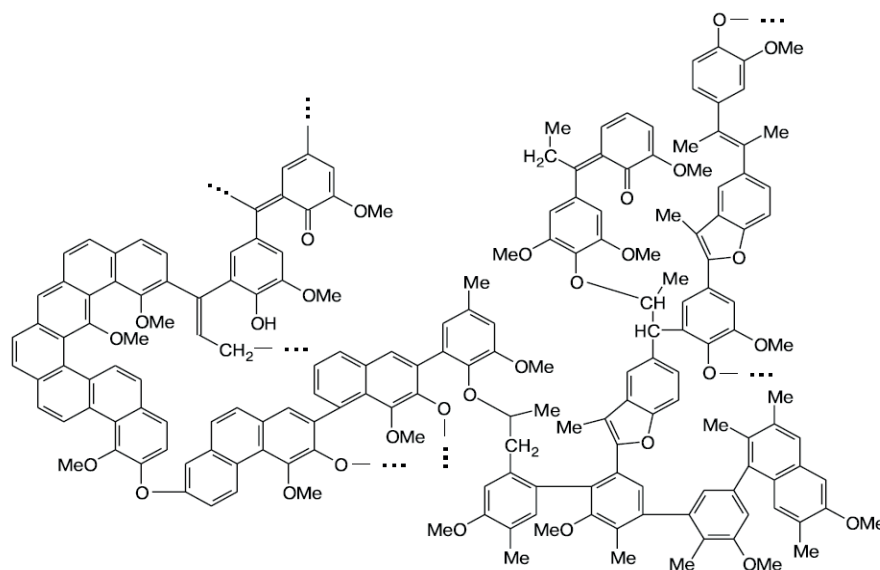


Fig. 1. Conventional structure of hydrolytic lignin fragment (M.I. Chudakov) [5].

10 grad  $\times$  min<sup>-1</sup>; the final temperature was 280 °C. The mass (m/e) scanning range was 15–600.

### 3. Results and discussion

As was stated above, interaction between PAN and THL is hypothetically based on the Ritter reaction, which suggests the presence of the corresponding oxygen-containing functional groups in THL.

Judging from the literature data [3], the potential “partners” for nitrile groups in this reaction are hydroxyl groups. The amount of hydroxyl groups in the initial THL was established from the data given in [4] (Table 1).

**Table 1**  
Chemical and functional<sup>a</sup> compositions of THL

Parameter	Content, %	Content, per 100 phenyl propane units (PPU)
Moisture	24.27	-
Ash	2.32	-
Acidity (in sulfuric acid equivalent)	1.68	-
Hydroxyl groups (total)	8.57	65-70
Phenolic hydroxyl groups	1.96	25-30
Methoxy groups	12.16	90-92
Carbonyl groups	1.25	20
Carboxyl groups	1.63	31

<sup>a</sup> The values of functional parameters are given for absolutely dry THL free from resins and water-soluble contaminants.

Reactivity of OH-groups in THL depends not only on their amount in the initial sample but also on spatial organization of the THL macromolecule. Thus far, unambiguous definition of hydrolytic lignin has not been given in scientific literature. The clearest characteristic of this product is formulated in the monograph by M.I. Chudakov [5], who made a significant contribution into the studies of hydrolytic lignin. THL is “a complex and unpredictable mixture of products of hydrolytic decomposition of wood waste including lignin proper, some portion of sparingly soluble polysaccharides, reducing compounds, resins, cellulose, ash, residual sulfuric and organic acids, and moisture”.

Other sources [6–8] consider THL as an amorphous compound based on dimeric structural units (diaryl propanediol); the terms “technical sulfate lignin” or “hydrolytic lignin” are used as synonyms for “technical lignin”. In the review [8] all products of commercial production of lignin are termed “technical lignins”.

In the present work, we use the definition given by Chudakov [5], which reflects fundamental structure of THL enriched in condensed aromatic compounds (Fig. 1).

At the same time, analysis of experimental data on chemical composition of THL (Table 1) reveals discrepancy between these quantitative parameters and the structure suggested by M.I. Chudakov.

As seen from the given experimental data, THL contains sufficient amount of reactive OH-groups capable of interaction with nitrile groups of PAN.

In addition to the “core” of THL with high molecular mass, the studied samples may include low molecular mass products of partial THL destruction; the presence of these compounds was noted in our previous works [10–13]. Comparison between the supposed structure of hydrolytic lignin presented in [5] and the data from Table 1 allowed us to estimate the maximum number of contacts between hydroxyl groups of HL and CN groups of PAN. This value is approximately 10% from THL molecular mass (provided that reactivity and availability of OH-groups are similar to those of PAN nitrile groups). Calculation of possible gross formula of THL-PAN composite can be presented in the following form:

$$MM_{\text{THL}} \times 10 \text{ } MM_{\text{CN-units}}$$

where  $MM_{\text{THL}}$  is the molecular mass of HL according to the formula given in Fig. 2;  $MM_{\text{CN-units}}$  is the molecular mass of a CN unit reacting with OH-group of THL.

$$C_{185}H_{148}O_{26} \times 10 \cdot 26 = 2764 \times 260$$

Gross formula of the composite

Theoretical formula yields the amount of nitrile groups per one THL macromolecule (approximately 10%, to a certain accuracy), and this value is in agreement with the data of functional analysis (i.e., amount of carboxyl groups). However, in calculation of THL gross formula, total amount of oxygen atoms suggested in Fig. 1 was taken into account. It should also be considered that about 60% of this amount is included in methoxy groups, which cannot participate in the reaction with nitrile groups. Thus, we obtained that in the case of favorable arrangement of hydroxyl groups, only

4–5% of total amount of oxygen atoms in THL can react with PAN nitrile groups. Since the THL-PAN composites [2] were prepared from the PAN sample with a molecular mass of about 50 KDa, the corresponding amount of nitrile groups (potential reactants in the Ritter reaction) can interact with a significant amount of THL. Under ideal circumstances, the scheme of this interaction may be presented as follows.

The possibility of a given mutual arrangement of interacting macromolecules is related to the structures of THL and PAN. THL is the condensed structure which includes a central “core” with substituents containing functional (OH) groups located at the periphery. PAN is a linear polymer with a backbone in the form of zigzag or spiral and asymmetrically located CN substituents. Depending on MM and MWD, PAN chains can be arranged chaotically. For the same reason, interaction between PAN and hydroxyl groups of THL can be realized in space according to the laws of indeterminate chaos. Degree of conversion depends on mobility of macromolecules, which is controlled by temperature and duration of reaction between two polymers. Figure 3 shows dependences of conversion degree on time and temperature. It can be clearly seen that with increasing time of contact and temperature of the reaction mixture, the end product becomes enriched in nitrogen; when the reaction proceeds for 10 h at 120 °C, almost all PAN molecules become attached to THL.

Infrared (IR) spectra of the end product of this reaction (Fig. 4) indicate the presence of amide bonds (the bands at 1550 and 1620  $\text{cm}^{-1}$ ). Thus, the Ritter reaction proceeds according to the following scheme:

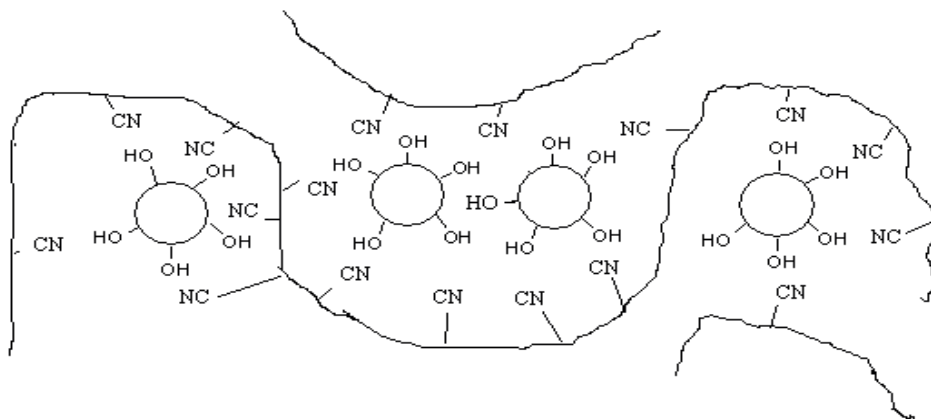
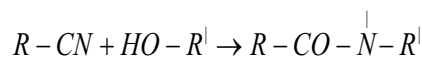


Fig. 2. Mutual arrangement of PAN and THL macromolecules (schematic representation).

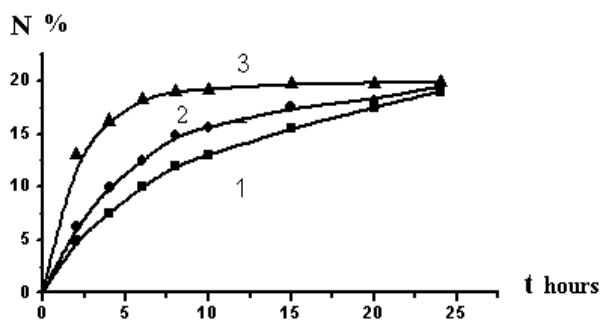


Fig. 3. Dependence of conversion of PAN nitrile groups into amide bonds (N, %) on the duration of interaction between THL and PAN; 1 – at ambient temperature; 2 – at 50 °C; 3 – at 120 °C.

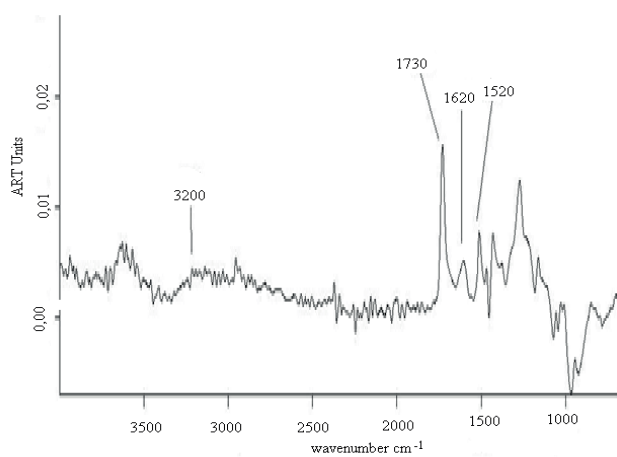


Fig. 4. IR spectrum of the product of interaction between THL and PAN (50 °C, 20 h).

Besides, the data presented in [14] give us grounds to assume that sharp decrease in intensity

of the peaks attributed to phenolic hydroxyl groups (in the 3600–3000 cm<sup>-1</sup> region) as compared to those in the spectra of lignin indicates significant decrease in the amount of these groups (resulting from their reaction with nitrile groups). These changes in spectra correlate with decrease in intensities of the peaks attributed to aliphatic hydroxyl groups in the 1085–1030 cm<sup>-1</sup> range. The predominant participation of phenolic or aliphatic hydroxyl groups in the Ritter reaction is possibly determined by steric factors (availability of these groups bound to condensed THL core). It was noted in several communications [15] that peaks related to valence vibrations of ether bonds may also lie in the 1085–1030 cm<sup>-1</sup> range. Therefore, we can assume that attack of nitrile groups result in breaking these bonds and formation of the corresponding amide bonds.

Thus, the data presented in Fig. 3 and changes in spectral characteristics of products of reaction between THL and PAN indicate that the presence of hydrogen-containing functional groups in THL is the necessary condition for obtaining this composite. The above scheme demonstrates the trend in mutual spatial arrangement of functional groups in the reaction mixture. Based on concentration ratio, we can assume that at least for each statistically averaged PAN macromolecule there are five THL macromolecules; hydroxyl groups of THL participate in the reaction as the most reactive sites in this polymer. In this case, the structure of complex can be presented as follows (Fig. 5).

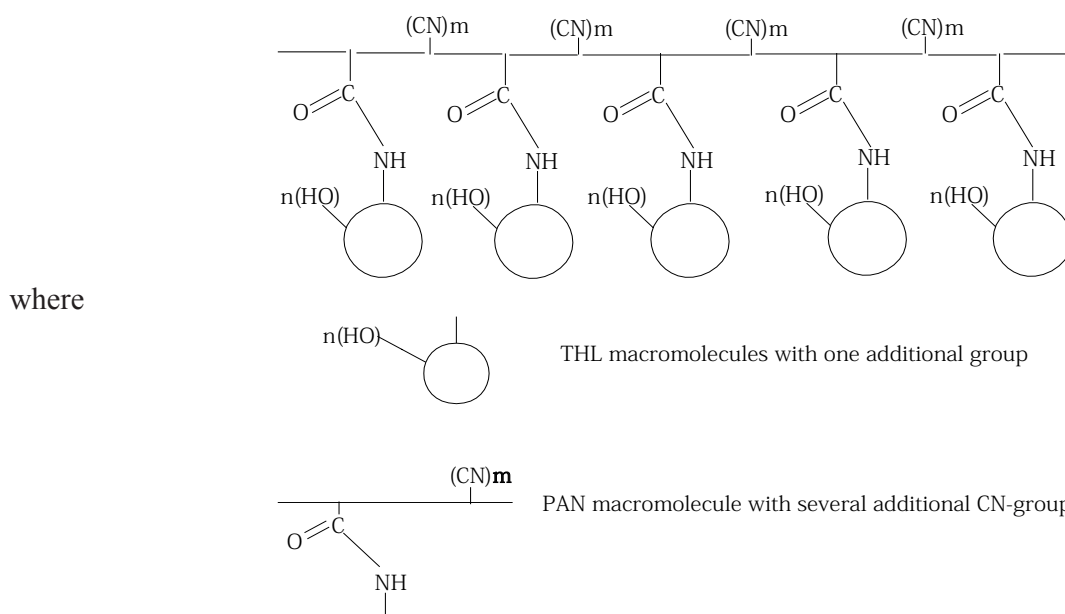
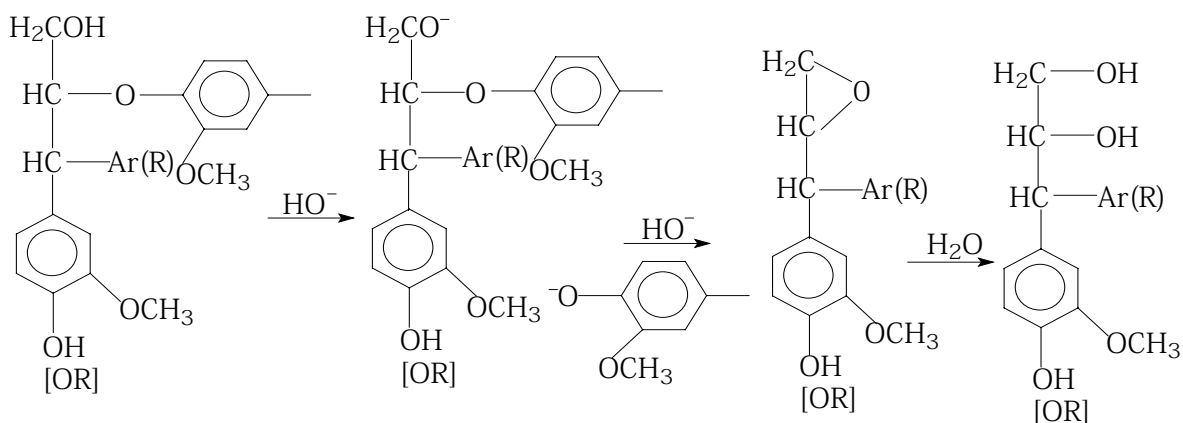


Fig. 5. Schematic representation of the formation of amide bonds between PAN and THL (the PAN content in the mixture is 20%).

Fig. 6. Cleavage of  $\beta$ -ether bonds in hydrolytic lignin.

**Table 2**  
Content of carbon atoms of benzene rings per one phenyl propane unit

Chemical shift, ppm.	162-136	136-125	125-106
Signal assignment	$C_{Ar-O}$	$C_{Ar-C}$	$C_{Ar-H}$
Björkman lignin (I)	2.3	1.2	2.5
Technical hydrolytic lignin (Kirov biochemical plant)	2.2	1.4	2.4
Technical hydrolytic lignin (Lobva biochemical plant)	2.3	1.4	2.3

Conventional character of this scheme is related to the fact that PAN molecule can interact with two or more OH-groups of one THL macromolecule, since PAN backbone is sufficiently flexible. Besides, MWD of PAN may exert certain influence on the process; broadening MWD should result in increasing reactivity of low molecular weight fractions. Some spatial hindrances can also affect reactivity of nitrile groups. Their activity in the Ritter reaction decreases due to possible participation in the formation of various hydrogen bonds.

It should be noted that efficiency of interaction between hydrolytic lignin and poly(acrylonitrile) is also determined by nature of solvents which in a way affects reactivity of functional groups in polymers. It is known [16] that DMSO is the unique solvent used in experiments with poorly soluble polymers. In the present work, we used its good dissolving ability, unlimited miscibility with water (leading to the formation of binary mixtures), good solubility of PAN in DMSO and excellent ability of this solvent to penetrate into porous materials for destruction of supramolecular structure of THL. Use of binary mixtures DMSO:H<sub>2</sub>O with 70:30 ratio between components led to maximum dissolving (swelling) of THL and obtaining polydisperse set of fractions with enhanced solubility.

In a number of cases, gradual loosening of THL structure results in breaking weak ether bonds between alkyl and aryl substituents at  $\beta$ -carbon atoms of propane chain in lignin according to the scheme presented in [13].

In addition to reactive phenoxy groups in THL, intermediate compounds presented in the scheme contain a large number of oxygen-containing bonds. At elevated temperatures, in the process of polymer-analogous reactions, these bonds may be transformed into other covalent bonds.

It is necessary to note that degree of condensation of aromatic structures in THL may vary depending on production conditions of a given chemical plant. For example, let us consider semi-quantitative analysis of <sup>13</sup>C NMR spectra of one phenyl propane unit (PPU) of lignin. We compare peaks in the main regions attributed to aromatic carbon rings (162–136, 136–125 and 125–106 ppm). These spectra were registered for lignin samples produced by three hydrolysis plants. The calculations have demonstrated that the Björkman lignin (which is almost similar to the natural product) contains one carbon-carbon bond between carbon atom of benzene ring ( $C_{Ar-1}$ ) and carbon atom of aliphatic chain ( $C_{Al-1}$ ) per 5 PPU. These bonds ( $C_{Ar-C}$ ) are typical of condensed lignin

structures of the 5-5 type; their number depends on the technology used in lignin treatment. Table 2 gives the contents of benzene carbon atoms per one PPU calculated for three lignin samples.

It can be seen that the highest amount of  $C_{Ar-C}$  (1,6) bonds was detected in the hydrolytic lignin produced by Kirov plant; we can assume that in this sample, three C-C bonds per five PPU are contained. These differences demonstrate another possibility of changing density of crosslinks between THL and PAN macromolecules during their interaction.

#### 4. Conclusions

1) It is established that interaction between THL and PAN (the Ritter reaction) in dimethyl sulfoxide or binary mixture DMSO-H<sub>2</sub>O leads to the formation of intermolecular amide bonds and yields irregular graft copolymer.

2) Completeness of reaction between nitrile groups of PAN and oxygen-containing functional groups of THL is determined by concentration of these groups, duration and temperature of interaction between the initial polymers. Amount of contacts between THL and PAN depends on properties of these compounds.

3) The principal features of THL are the amount of hydroxyl groups in one PPU of the initial lignin, degree of THL condensation, conditions of preliminary treatment of THL. The important factors for PAN are its molecular mass and MWD, stereoregularity of structure, and quality of a solvent.

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