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The Modification of Polyurethanes by Highly Ordered Coordination Compounds of Transition Metals

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1. Introduction

One of the ways to influence the chemical structure of polyurethanes is to use metal complex systems based on transition metal chlorides for their synthesis. The significance of this trend is conditioned by the ability of metal complexes to order the macromolecular chains, as well as affect the electrical properties of polyurethanes (Davletbaeva et al., 1996, 2001).

The synthesis of metal coordination polymers is a way of affecting the processes of crosslinking of macrochains; interchain and intraionic interactions; and, thereby, preparing polymer materials with special properties (Dirk et al., 1986; Kingsborough & Swager, 1999; Reynolds et al., 1985; Thuchide & Nishide, 1977; Wang & Reynolds, 1988). From the standpoint of designing materials with electric and magnetic properties, it is promising to form in a polymer matrix chains of transition metal ions bound by exchange interaction.

Conventional methods for the creation of interactions of this type in a polymer are primarily based on the presence of certain units in a macromolecule, e.g., those including the phthalocyanine and azomethine moieties. For example, metal atoms in metal phthalocyanine liquid crystalline complexes are bound to one another by chloride bridges and play the role of a spacer between phthalocyanine units, thus promoting overlap of electronic orbitals of parallel molecules (Shirai et al., 1977, 1979).

As a result, the electric conductivity of metal-coordination polymers obtained on the basis of these complexes is increased by a few orders of magnitude relative to undoped systems. The coordination bonding of comb-like liquid crystalline polymers can also give rise to stacked structures. Interaction between metal ions is revealed in such polymers, which is realized owing to the association of metal ions in an indirect manner, through ester oxygen bridges.

However, this approach is seriously limited and cannot be used for the creation of stacked metal-coordinated fragments in a disordered polymer matrix (Brostow, 1990; Carrher, 1981; Serrano & Oriol, 1995).

Metal complex structuring is promising in terms of the influence on properties of polyurethanes. The significance of this trend is conditioned by the ability of metal complexes to order the macromolecular chains, as well as affect the electrical properties of polyurethanes.

2. Coordination compounds based on the aromatic isocyanates and copper (II) chloride for the synthesis of polyurethanes

In the early studies (Davletbaeva et al., 1998) devoted to imparting special properties to polyurethanes by their coordination bonding, it was shown that the interaction of aromatic isocyanates with copper chloride (CuCl_2) in the acetone medium in the presence of trace amounts of water proceeded as a sequence of chemical transformations including simple addition and decomposition reactions, redox processes, and subsequent complexation (Fig. 1).

The ultimate products are polynuclear complexes of azoaromatic compounds, in which copper ions occurring in two variable oxidation states are connected by chloride bridges (Fig. 1). As it is seen from the structural formulas, some copper ions are stabilized at the initial degree of oxidation due to the formation of heterovalent pairs connected by chloride bridges. Free isocyanate groups present in these compounds are able to react with oligodiols of different nature. Polyurethanes obtained in such manner form polymer network by coordination bonding of urethane groups and azogroups which are the part of a macrochain.

It is shown that the chloride bridges are replaced by heteroatoms that are present in polymer chains while metal ions are coordinatively bound to macromolecules to crosslink them and, occurring in two interacting variable oxidation states, to form local centers of exchange interactions. As a result of electron transfer from one local coordinated unit to another, which is mediated by electron-donating groups, such as an ester group, the conductivity of polyurethane increases by several orders of magnitude.

3. Reactions of aromatic isocyanates and urethane prepolymers with coordination compounds of iron (III)

Further studies established that similar structural units could be formed even in the polyurethane matrix itself as a result of its modification with metal complexes synthesized for this purpose. A characteristic feature of these coordination compounds is the presence of chloride-bridged metal ions in their structure. One of such crosslinking metal complex system was prepared by the reaction of iron chloride (FeCl_3) with ethanolamine (EA). It was found that reactions involving aromatic isocyanates and EA in the coordination sphere of the iron ion (III) led to the formation of azoaromatic compounds shown in figure 2.

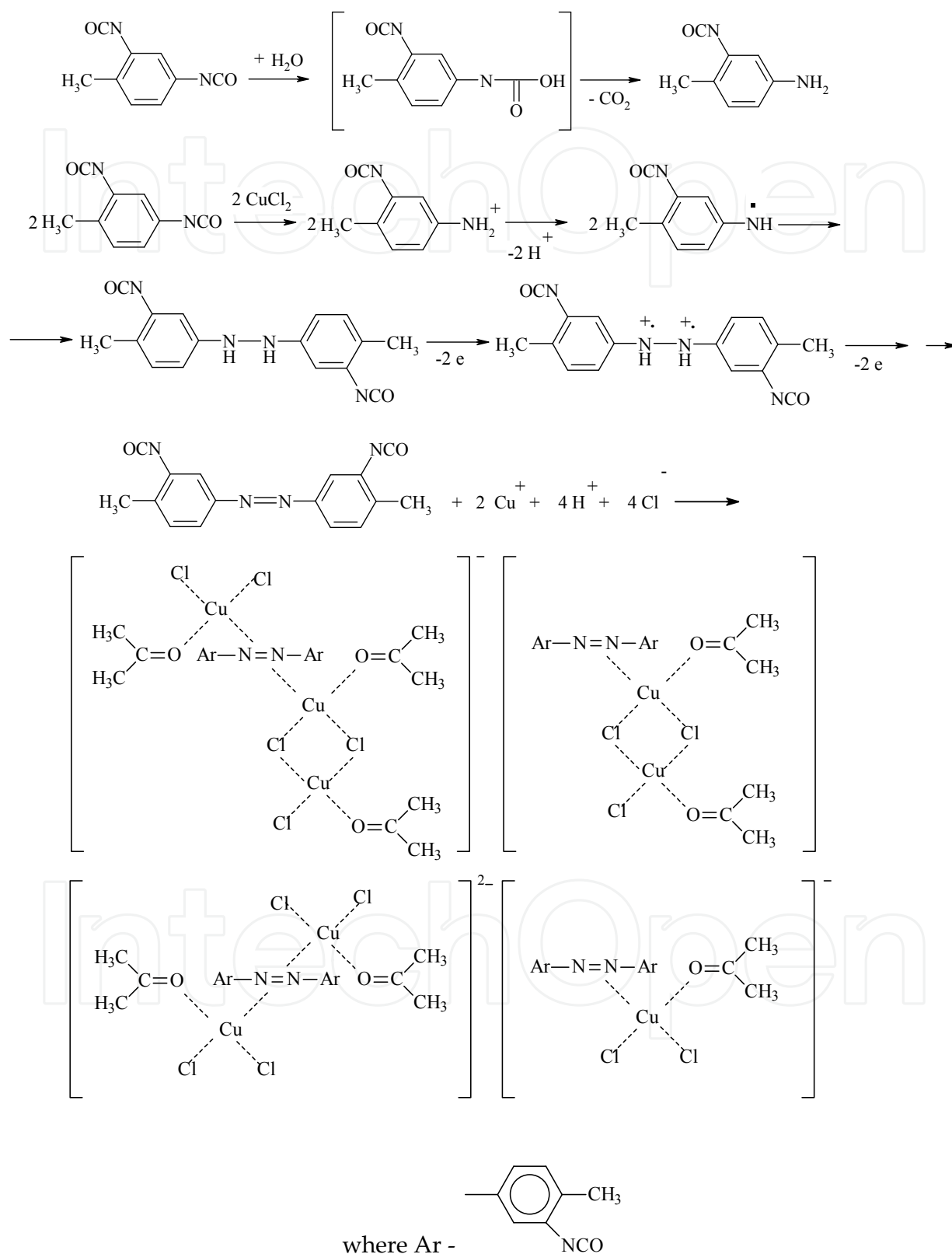


Figure 1. Formation of polynuclear complexes of azoaromatic compounds.

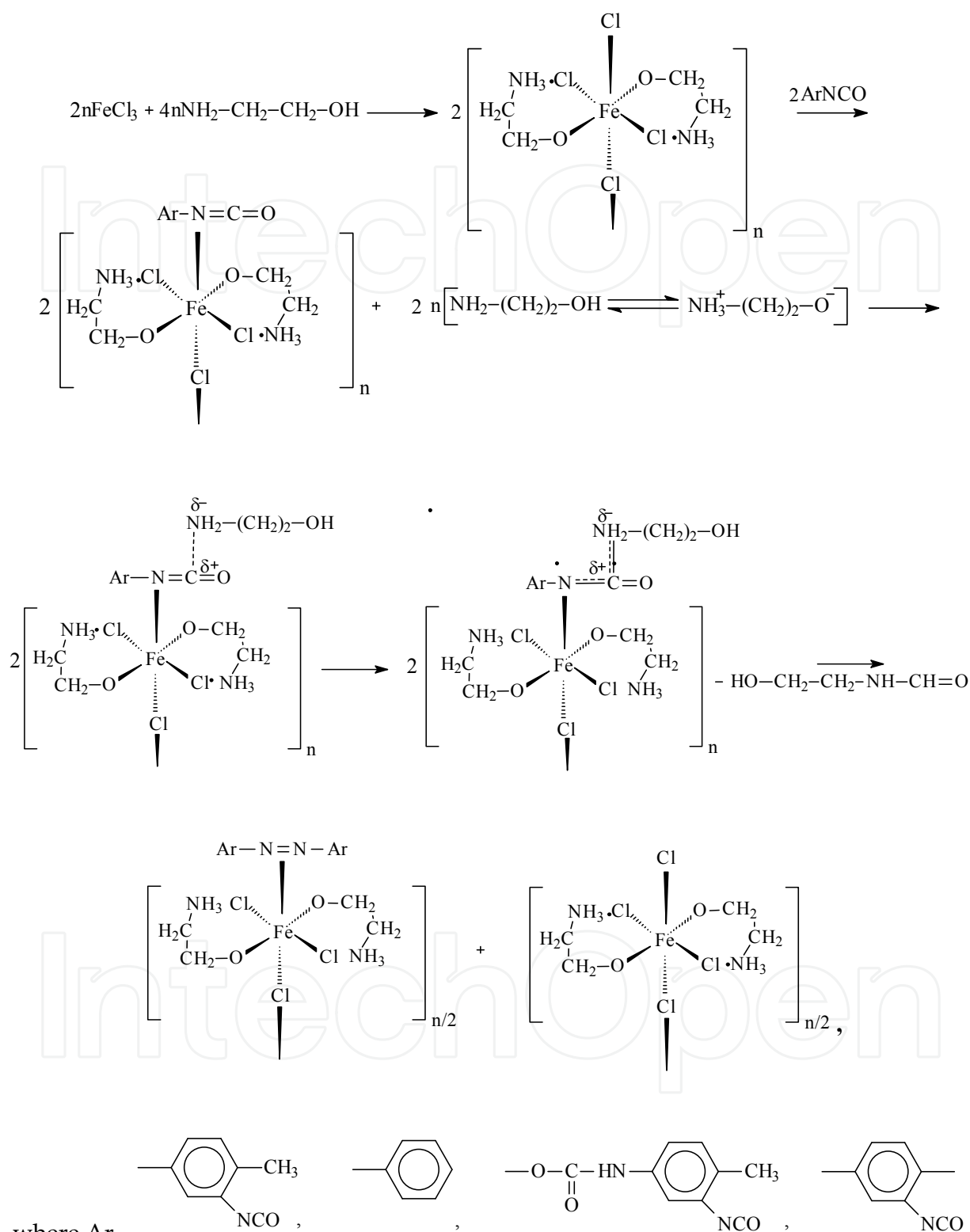


Figure 2. Scheme of formation of azoaromatic compounds.

The continuation of this reaction is the formation of stack coordination compounds in which metal ions form coordination bonds with azogroups (Fig. 3).

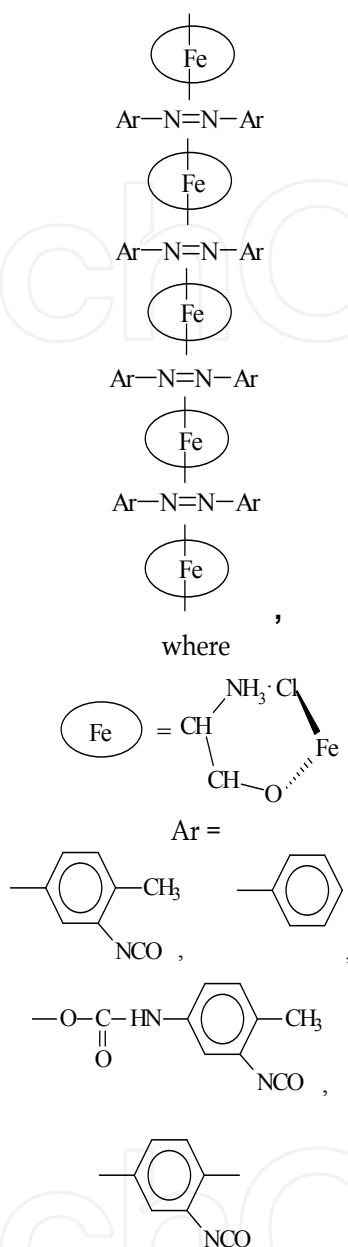


Figure 3. Formation of stack coordination compounds.

Mössbauer studies of iron coordinated compounds reveal that the magnetic ordering is observed at relatively high temperature (80 K). Mössbauer spectrum obtained in transmission geometry at the temperature of the sample being equal to 80 K consists of two components, namely, a doublet in the middle of the spectrum corresponding to the residues of the initial FeCl_3 , dissolved in the matrix (less than 10% of the total area under the spectrum) and the magnetically ordered component with a hyperfine field average value of about 430 kE and the isomer shift, indicating a high-spin state of the Fe (III) ion. The absence of partial component in the middle of the spectrum is caused by the long average size of supramolecular structures chains (Fig. 4).

The Mössbauer study confirms the columnar structure of the obtained metal complexes, the possibility of their fixation in a flexible-chain polymer matrix containing electron-donating groups, and the existence of magnetic ordering at temperatures below 70 K. Sizes of very thin magnetic fields correspond to high-spin state of iron(III) ions ($S=5/2$).

It is known that to achieve the effect of magnetic ordering it is necessary that the chain of interacting ions of iron (III) should be long enough and combine up to a few thousand ions. The criterion for judging the length of the chain of magnetic ordered iron ions is relatively high blocking temperature of supermagnetism and the barrier value of effective anisotropy field. In our view, due to significant anisotropy in the structure of the complex the most likely assumption is the increasing of the potential barrier with the increase of chain length. The longer the chain, the higher its strength and the ability to build columns in a polymer matrix, and the specific properties of the structured polymer matrix are more pronounced as well.

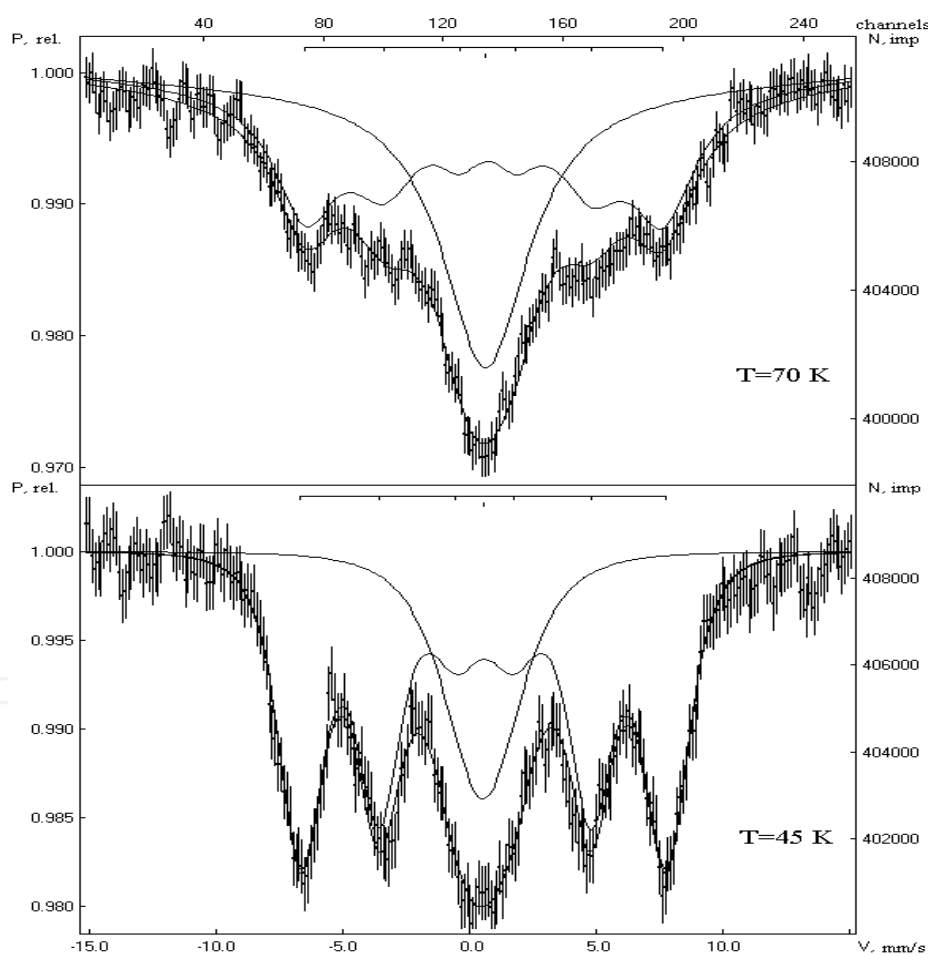


Figure 4. The Mössbauer spectrum of metal complex system based on FeCl_3 and EA.

The metal complex system is used for structuring urethane prepolymer containing terminal isocyanate groups. Considering the high flexibility of the urethane prepolymer chain, it can be assumed that the urethane groups will be coordinately bound with iron ions. The result of this interaction should be the formation of columnar structures directly in the polymer

matrix. Mössbauer studies of urethane prepolymer confirm these assumptions. The resulting spectra are also of superparamagnetic nature at temperatures below 47K (Davletbaeva et al., 2006).

When polyurethanes are modified by coordination compounds synthesized on the basis of FeCl_3 and EA, the minimum values of specific volume electrical resistance (about $10^8 \text{ Ohm}\cdot\text{cm}$) are recorded in the concentration area of 0,1% in terms of iron chloride. It should be noted that the ions of iron (III) in the above reactions do not change the oxidation level.

4. Modification of urethane prepolymer by coordination compounds of copper (I, II)

In one of the worked out highly ordered coordination compounds of transition metals for modification of polyurethanes N,N' -Diethylhydroxylamine (DEHA) is used as a ligand exhibiting the properties of a reducing agent. The most appropriate transition metal compound is copper (II) chloride. Some of the Cu (II) ions interacting with DEHA reduce the oxidation level and turn into Cu (I) (see Fig. 5).

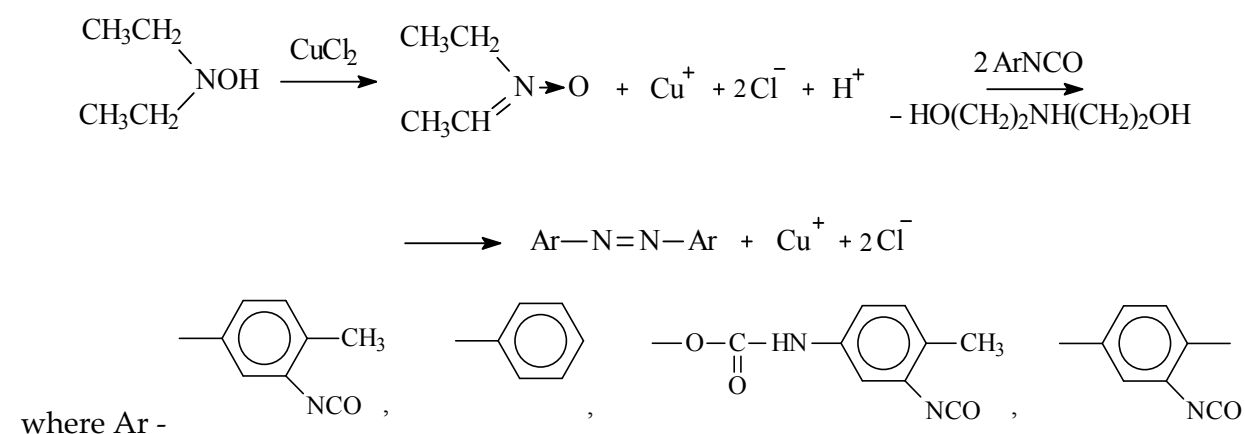


Figure 5. The mechanism of interaction of copper (II) chloride with DEHA.

It was ascertained that the metal complex system showed the ability to interact with aromatic isocyanates to form azoaromatic compounds. The result was the formation of columnar coordination compounds (Fig. 6).

It was established, that metal-complex modification of polyurethanes results in the change of their physicommechanical properties and spasmodic reduction (by 3-4 orders) of volumetric and superficial electric resistance. The reduction of the specific bulk electrical resistance by 3-4 orders is the most significant effect accompanying the metal-complex binding of polyurethanes. In this case the electrical resistance falls spasmodically depending on the nature of flexible chains of polyurethanes, the range of transition -metal ions concentrations. If the content of metal-complex modifying agent is increased further, the electrical resistance increases to some extent. The main role in the mechanism of charge transmission in metal-coordinated polyurethanes is assigned to electron-donating groups which are included in the structure of flexible chains of polyurethane matrix and the presence of transition metal ions having two degrees of oxidation in it.

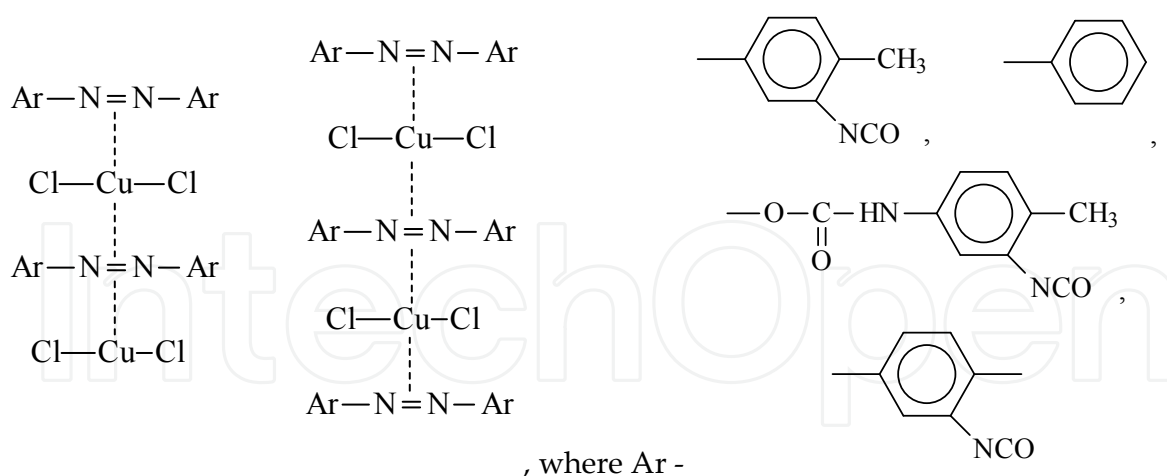


Figure 6. Formation of columnar coordination compounds.

5. Modification of polyurethanes by heteronuclear complexes based on molybdenum (V) and copper (II) chlorides

To study the effect of the coordination compounds structure on the electrophysical properties of the modified polyurethanes the heteronuclear metal complexes based on transition metals of IV and V periods were synthesized. CuCl_2 was used as the chloride of 3d-metal, and MoCl_5 was used as the chloride of the 4d-metal. DEHA was used as a ligand. Cu (II) has 3d-orbitals that are involved in coordinating binding, in the case of Mo (V) this role is performed by 4d-orbitals. Therefore, it is assumed that when heteronuclear complexes of the columnar structure are formed, where the CuCl_2 is in excess, the ions of molybdenum could cause the interruption of chains of exchange interactions between 3d-ions (Fig. 7). It is found that the metal complex system, obtained on the basis of $[\text{CuCl}_2]:[\text{DEHA}] = 1:0,7$ has $\rho_v = 2600 \text{ Ohm}\cdot\text{sm}$ at room temperature, while the system based on $[\text{MoCl}_5]:[\text{DEHA}] = 1:0,7$ has $\rho_v = 1300 \text{ Ohm}\cdot\text{sm}$. The heteronuclear complex obtained at the ratio of $[\text{CuCl}_2]:[\text{MoCl}_5]:[\text{DEHA}] = 0,9:0,1:0,7$ at room temperature exhibits $\rho_v = 5250 \text{ Ohm}\cdot\text{sm}$, while the complex obtained at ratio of $[\text{CuCl}_2]:[\text{MoCl}_5]:[\text{DEHA}] = 0,8:0,2:0,7$ has already $\rho_v = 73800 \text{ Ohm}\cdot\text{sm}$.

Homonuclear and heteronuclear metal complexes were used for polyurethane modification. It was found that both modifying systems were able to react with the urethane prepolymer. When the metal complex structuring of polyurethanes by heteronuclear complexes based on 3d- and 4d-ions took place q_v values remained similar to the unmodified sample. With the increase of the concentration of heteronuclear complex the specific volume electrical resistance of polyurethanes actually increased slightly (Fig. 8). Another situation is observed in the case of polyurethanes modification by homonuclear coordination compounds. In this case the introduction of metal complexes based on copper led to the decrease of q_v by three orders. However, when polyurethanes were modified by homonuclear metal complex compounds based on Mo (V) q_v decreased by 5 orders.

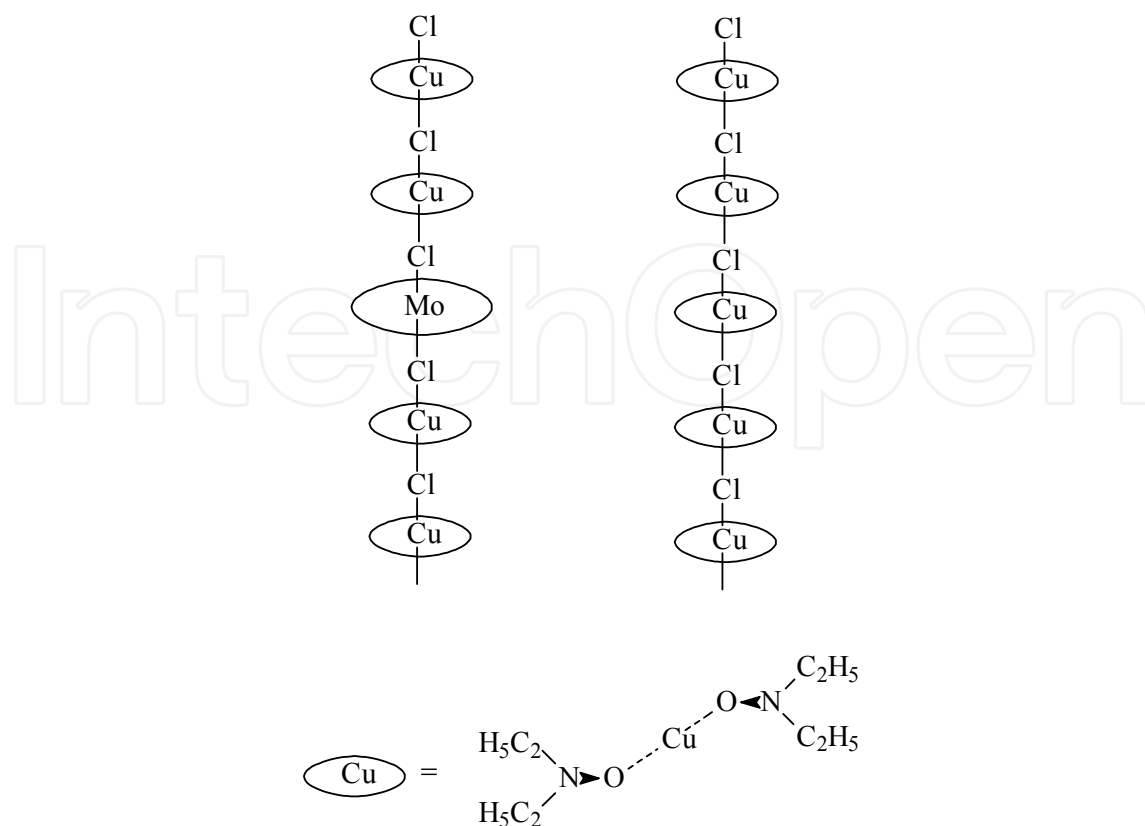


Figure 7. Scheme of the formation of columnar homonuclear and heteronuclear coordination compounds of transition metal.

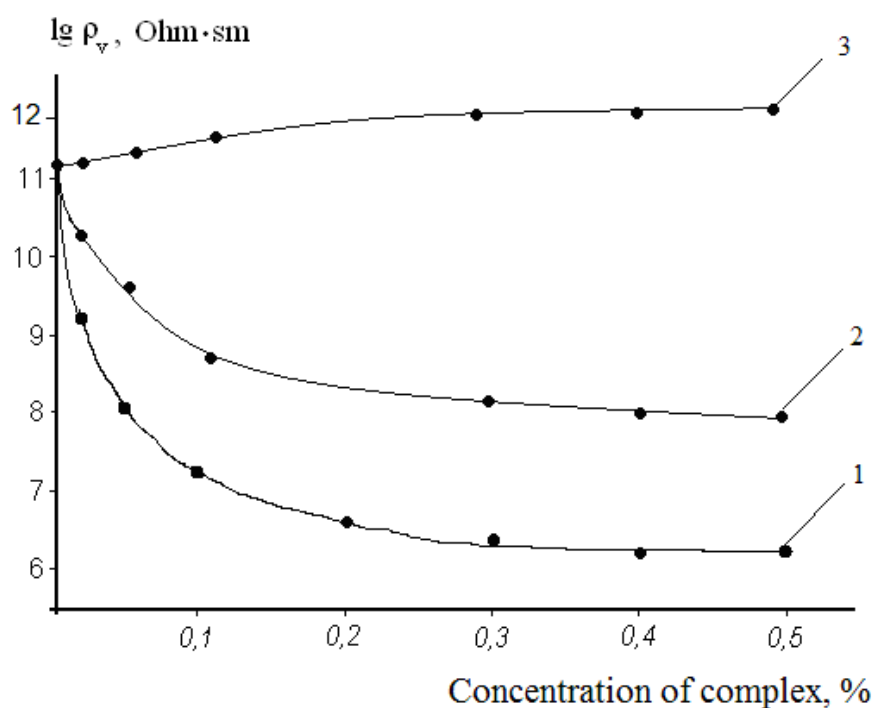


Figure 8. Dependence of ρ_v (Ohm·sm) of polyurethanes on the concentration (%) of metal complexes based on: 1-MoCl₅-DEHA; 2-CuCl₂-DEHA; 3-CuCl₂-MoCl₅-DEHA.

6. Catalytic properties of coordination compounds of copper in the reaction with isocyanate and urethane groups

The next step was to change the ligand composition of metal complex modifying system based on CuCl_2 and DEHA. The aminopropyltriethoxysilane (AGM) was used as a part of modifying system. The use of the AGM as an additional component to the DEHA was caused by some reasons. The first reason is that the AGM is able to take part in the reactions of sol-gel synthesis, resulting in the hydrolysis of ethoxy-component and subsequent polycondensation of the forming silanol groups. The second reason is the presence of electron-donor amine groups in the AGM which are able to form complexes. Besides, amines can lead to reduction of copper (II) to copper (I). Thereby this substance is interesting in terms of the influence on the reactivity of isocyanate groups and the supramolecular structure of polyurethane, which has domain nature.

Titrimetric determination of concentration of isocyanate groups in UPTI during its interaction with metal complex system based on CuCl_2 , DEHA and AGM at 100°C , was carried out. UPTI is industrial prepolymer synthesized on the base of 1 mol polyoxitetramethyleneglicol and 2 mols 2,4-toluene diisocyanate.

It was found that at relatively low concentrations of metal complex (0.01 and 0.05% in terms of CuCl_2) in the first ten minutes from the start of the reaction process, the concentration of isocyanate groups started to rise, and only after that it fell. When the content of metal complex was 0.1, 0.5 and 0.75% in terms of CuCl_2 the concentration of isocyanate groups began to fall significantly (see fig. 9).

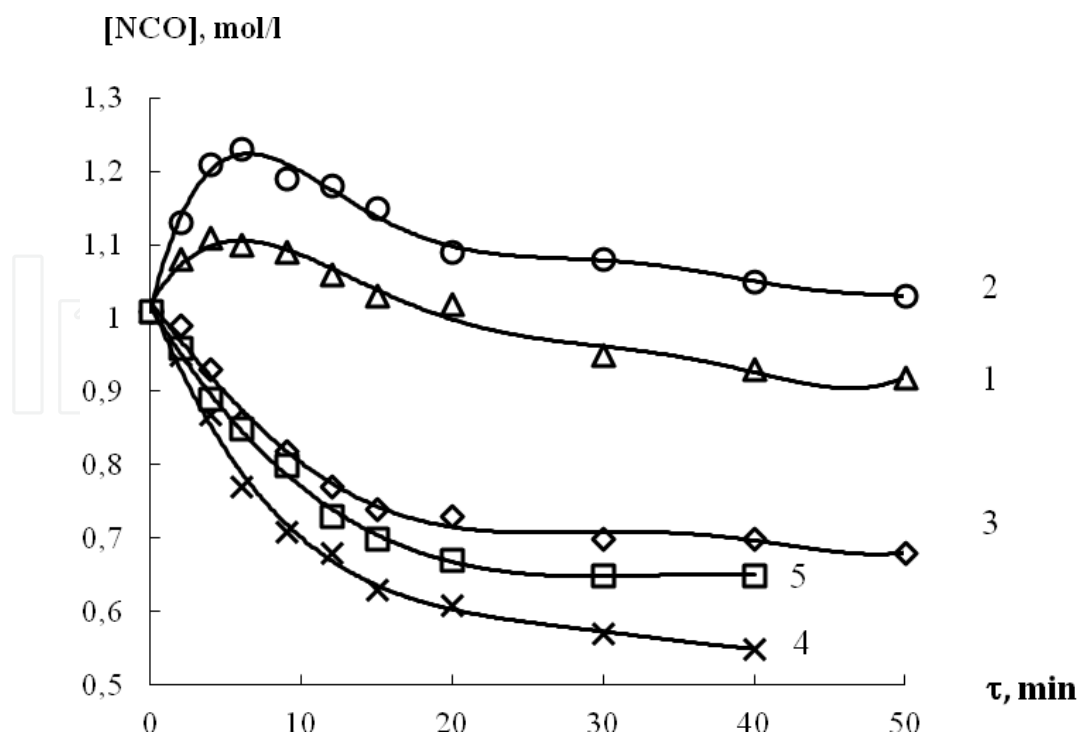


Figure 9. Isocyanate groups consumption curves in system UPTI – CuCl_2 -DEHA-AGM, $T=100^\circ\text{C}$, at a content of CuCl_2 : 1 - 0,05%; 2 - 0,1%; 3 - 0,25%; 4 - 0,5%; 5 - 0,75% (wt.).

The titration data confirm the results of IR-spectroscopic studies. It is established that the absorption band at 1731 cm^{-1} due to the stretching vibrations of carbonyl component of urethane group decreases at low concentrations of metal complex in the first ten minutes from the start of the reaction process. At the same time the intensity of the absorption band at 2273 cm^{-1} due to the stretching vibrations of isocyanate group grows. Later the growth of the intensity of the absorption band at 1731 cm^{-1} and the decrease at 2273 cm^{-1} are observed. Besides in the first ten minutes from the start of the reaction the IR-spectroscopy shows the reduction of the intensity of the absorption band at 3293 cm^{-1} due to the stretching vibrations of N-H-bond that is a part of urethane group. At relatively high concentrations of metal complex ($\geq 0.25\%$) the interaction is accompanied by the growth of the intensity of the absorption band at 2120 cm^{-1} due to the formation of carbodiimide group.

The research suggested that at relatively low concentration of metal complex the urethane group dissociates to isocyanate and hydroxyl groups, while at high concentrations of metal complex the isocyanate groups consume to the formation of carbodiimide groups. The part of isocyanate groups is hypothetically consumed on the formation of the azoaromatic groups. It is known that it is impossible to analyze azoaromatic groups using infrared spectroscopy. In this regard, studies were carried out using electron spectroscopy.

Electronic spectrum (Fig. 10) showed absorption at 350 nm, typical for trans-azoaromatic compounds. The absorption in the area 480 nm characterizes the coordination compounds of copper (II).

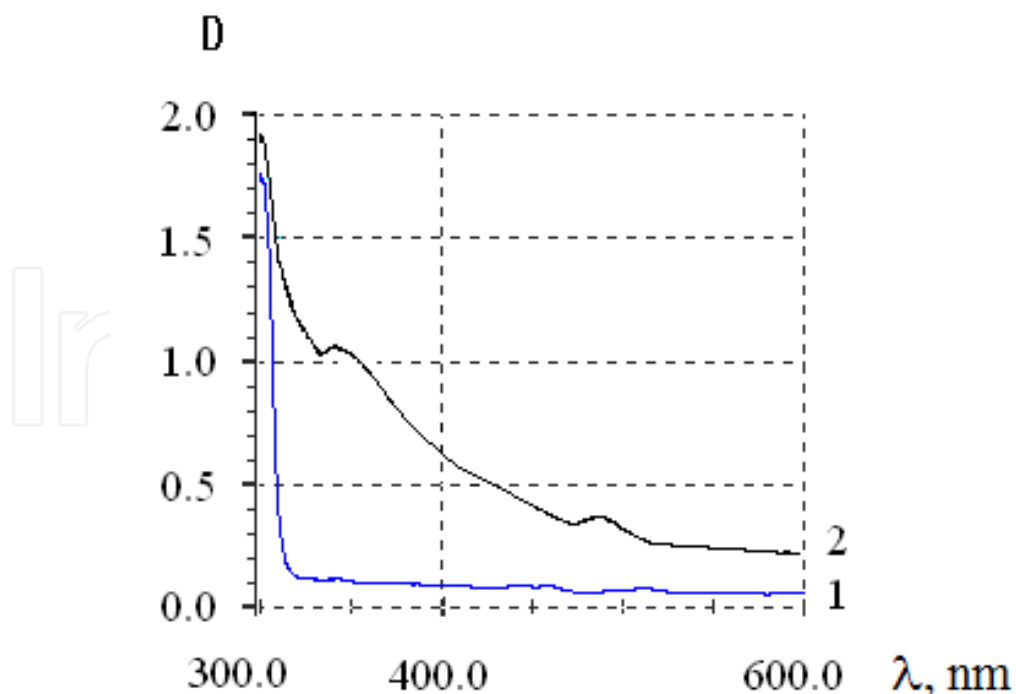


Figure 10. Electron spectrum of urethane prepolymer (1) and prepolymer (2) modified by 0.5% (wt.) metal complex system based on CuCl_2 - DEHA - AGM.

Metal complex system, derived on the basis of CuCl_2 , DEHA and AGM was further used to modify polyurethanes. We measured the dependence of the volume resistivity (ρ_v) of polyurethanes on the concentration of metal complex modifier (Fig. 11).

It turned out that the use of the worked out metal complex system caused the leap of ρ_v by 4 orders (10 000 times) observed at low concentrations of metal complex 0.01%. Here we should note that while using metal complex system based on CuCl_2 and DEHA (no AGM) a stepwise drop of ρ_v was observed at much higher concentration of the complex - 0.1%.

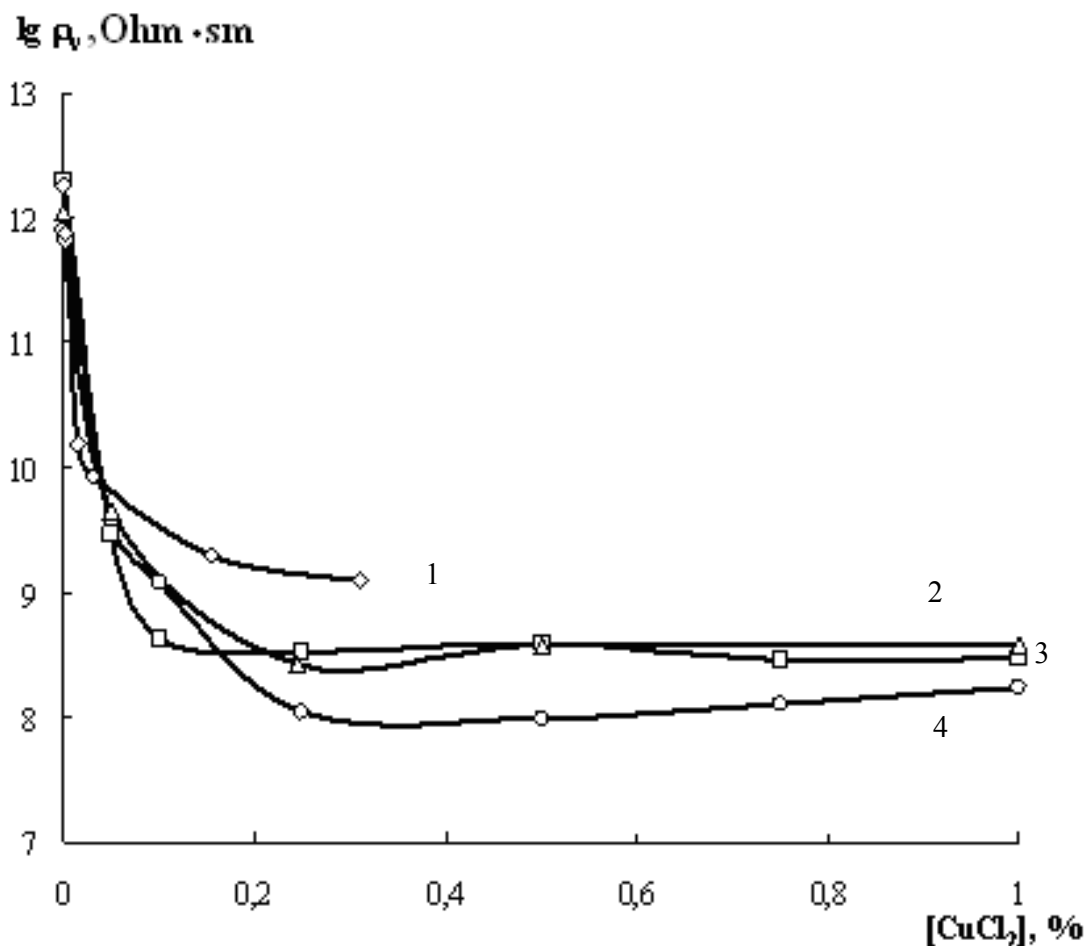


Figure 11. Volume resistivity-concentration diagram of modified polyurethanes under molar ratio of [UPTI]: [Diamed-X] = 1:Y:

1. $[\text{CuCl}_2]:[\text{AGM}]=1:4$ ($Y=0.9$);
2. $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:0,25$ ($Y = 0.9$);
3. $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:0,25$ ($Y = 0.7$);
4. $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:0,25$ ($Y = 0.5$).

It was found that the use of metal complex systems based on CuCl_2 , DEHA and AGM could significantly reduce the dosage of curing agent 4,4-methylene-bis-o-chloroaniline (Diamed-X) for urethane forming system based on UPTI.

7. The use of highly ordered coordination compounds of copper for receiving the rigid polyurethane foam

Metal complexes derived from CuCl_2 , DEHA and AGM were also tested as modifiers of the polyol component used in the manufacturing of rigid polyurethane foam. It was found that metal complex system based on CuCl_2 , DEHA and AGM had a significant impact on the rise and curing time of foam, reducing it (Fig. 12).

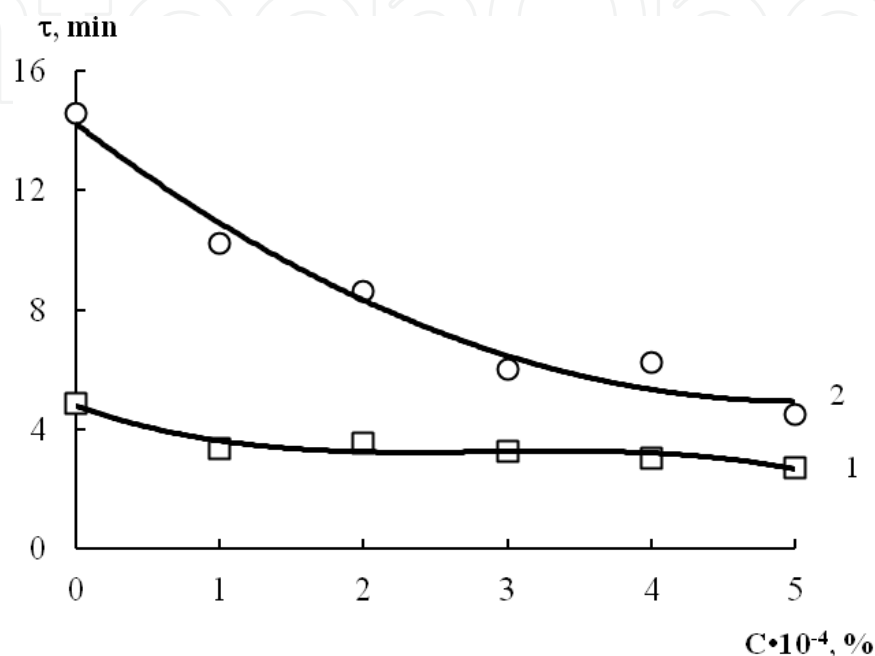


Figure 12. Rise (1) and curing (2) time of foam as a function of metal complex concentration based on $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:0,25$ in terms of CuCl_2 (%)

It was also established that the increasing of the molar ratio of the AGM in metal complex system led to even greater decrease in rise and curing time of foam (Fig. 13).

In order to establish the role of the AGM in the foaming process it was loaded alone in polyol component (Figure 14). It was found that the AGM also reduces the rise and curing time of the foam. However, these parameters were more than two times higher than the parameters that caused the addition of metal complex system.

We also used metal complex system based on CuCl_2 and DEHA as the control modifying system. In this case, in the wide range of concentrations of modifier the foam "collapsed". That is, the foam rose and the subsequently settled out. It should be also mentioned that the density of foam produced using metal complex system CuCl_2 - DEHA - AGM did not change in comparison with polyurethane foam obtained by the unmodified polyol component.

Thus, these studies show a significant catalytic effect of the metal complex modifier on foaming. In this connection it should be noted that the polyol component is a complicated balanced system that contains catalysts of amine nature and organotin compounds already. Our results suggest that the metal complex systems act as a cocatalyst.

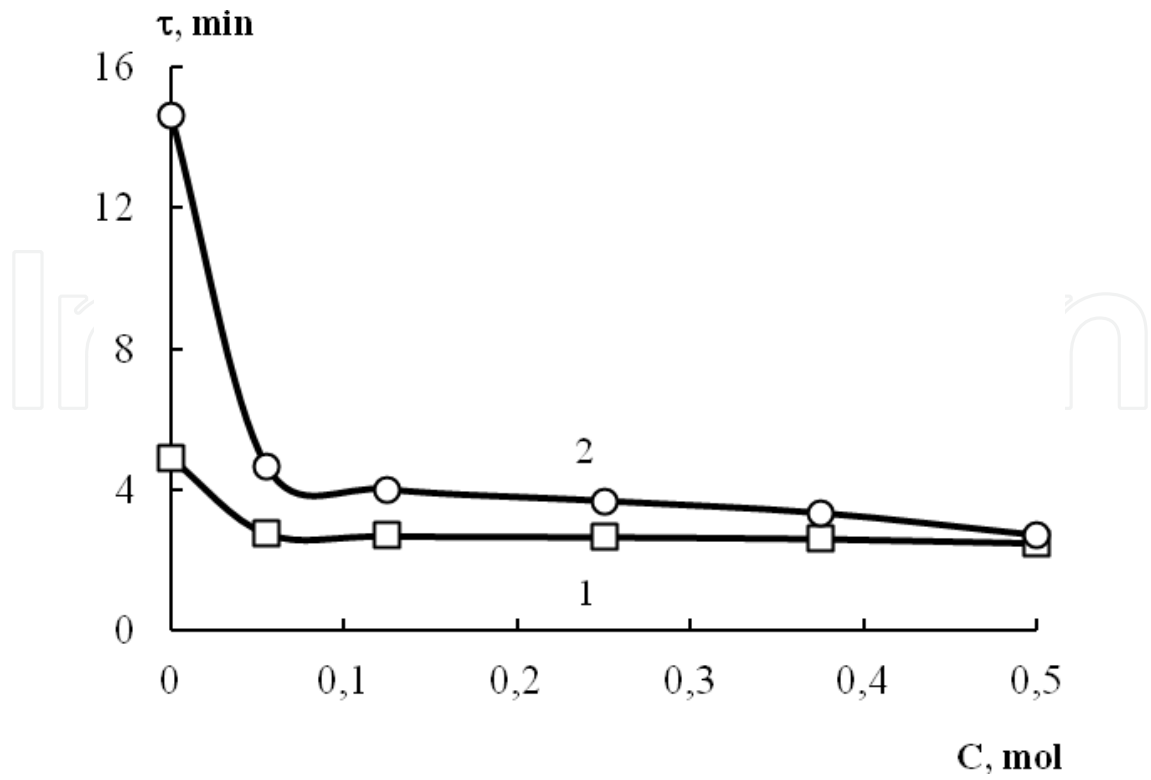


Figure 13. Rise (1) and curing (2) time of foam as a function of modifier concentration based on $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:X$, where X is a mole fraction of AGM in the metal complex overall concentration (mol)

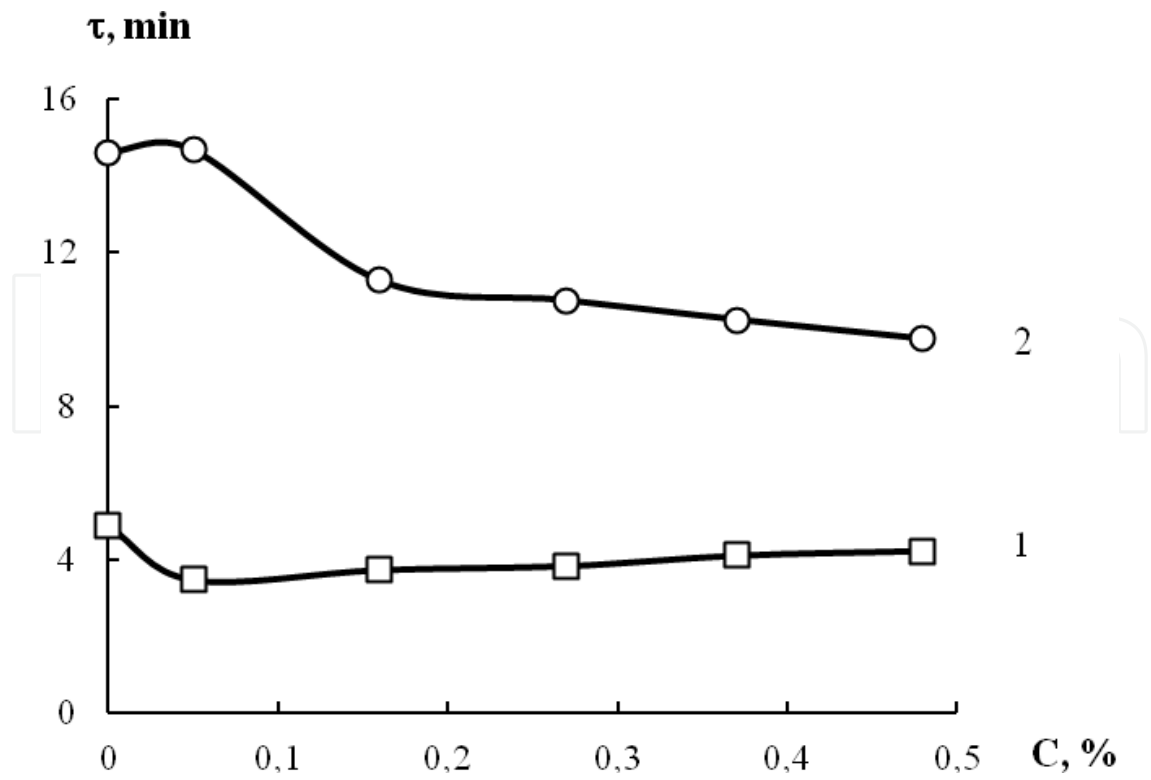


Figure 14. Rise (1) and curing (2) time of foam as a function of AGM concentration.

The next step was the research of such polyurethane foam key indicators as moisture absorption (Fig. 15) and water absorption (Fig. 16-17). It was found that the modified foam had enhanced characteristics as compared with unmodified polyurethane foam.

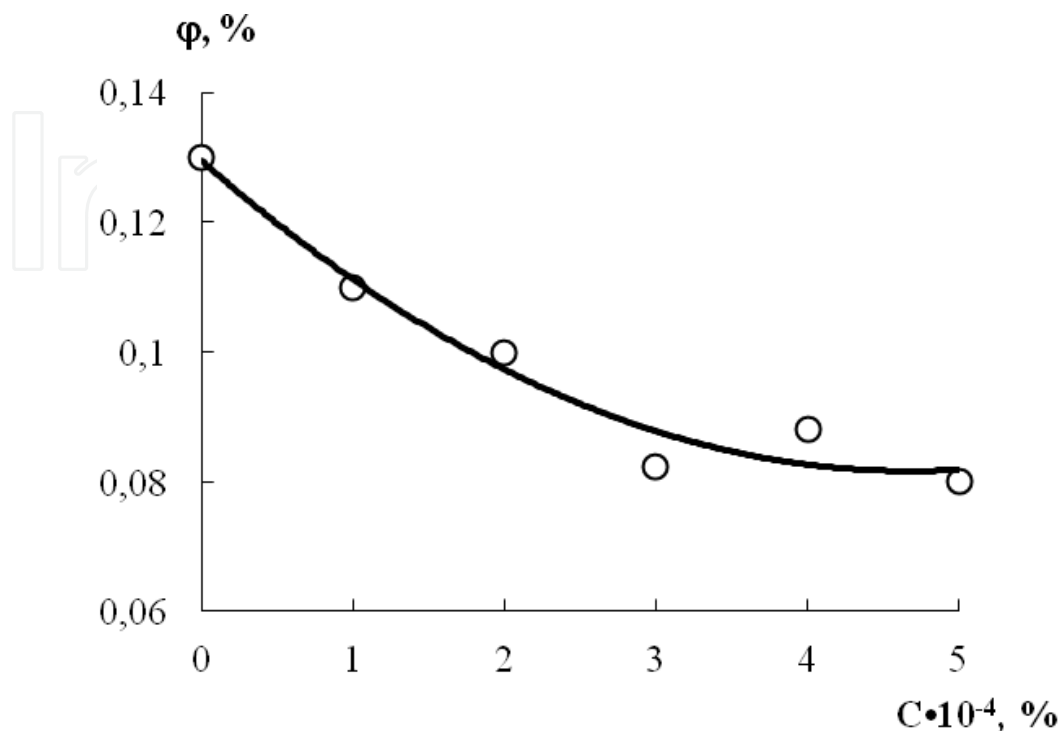


Figure 15. Moisture absorption of rigid foam as a function of metal complex concentration based on $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:0,25$ in terms of $\text{CuCl}_2 (\%)$

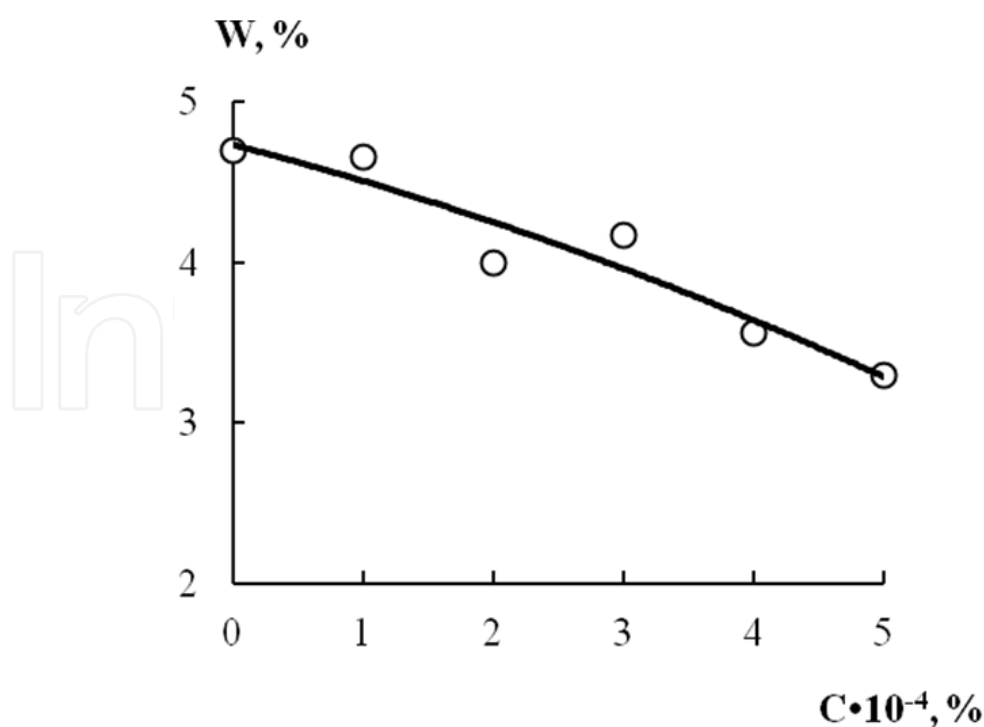


Figure 16. Water absorption of rigid foam as a function of metal complex concentration based on $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:0,25$, where in terms of $\text{CuCl}_2 (\%)$

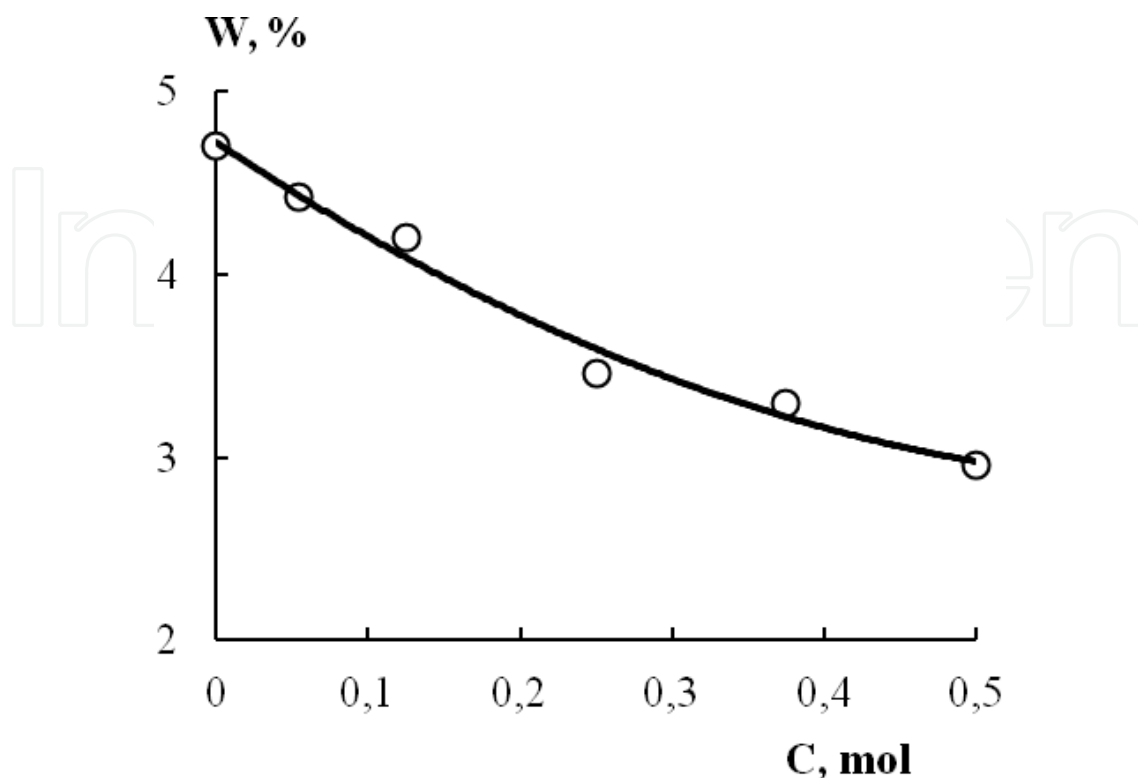


Figure 17. Water absorption of rigid foam as a function of modifier concentration based on $[\text{CuCl}_2]:[\text{DEHA}]:[\text{AGM}]=1:1,48:X$, where X is a mole fraction of AGM in the metal complex overall concentration (mol)

In conclusion, it should be noted that in order to achieve a positive result very small amounts of modifiers are required.

8. Conclusion

We considered the methods of obtaining transition metal coordination compounds that were active in reactions with isocyanate and urethane groups.

The feature of these metal complexes is that the metal ions are arranged in a chain of atoms linked together by chloride bridges. It is established that the chain of exchange-coupled transition metal ions remains in the polyurethanes structured by metal complex compounds. This circumstance is the cause of stepwise decrease in the specific volume resistivity of the modified polyurethanes.

It seems to be interesting for further research in this field to study the effect of metal complex binding on the physical and mechanical properties of polyurethanes. The most promising materials in terms of improving strength properties and heat resistance are thermoplastic urethanes.

Author details

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