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# Formation of Polyurethane Modifying Agents on the Basis of Chlorides of Transition Elements and 2,4-Toluene Diisocyanate

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## Abstract

Results of electrochemical research of the formation mechanism of metal-containing modifying agent for polyurethanes in the systems like $CuCl_2$–2,4-toluene diisocyanate (2,4-TDI), $FeCl_3$–N, N'-diethyl hydroxylamine (DEHA)–2,4-TDI, and $CoCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$, $NiCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ are summarized. It was found that the presence of water provides a necessary condition for the reactions proceeding in the systems of the first type; in the case of system with $FeCl_3$, the availability of a reducer (DEHA) has the same effect; and the additional introduction of an oxidizer ($H_2O_2$) does in the systems like $CoCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ and $NiCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$. It has been demonstrated that as a result of redox processes that run in these systems, polynuclear heterovalent complexes of transition elements with 4,4′-dimethyl-3,3′-diisocyanatoazobenzene are formed, and those with nitron are formed upon DEHA addition. Important function of chloride ions has been observed during formation of heterovalent pairs in modifying agents for polyurethanes.

## INTRODUCTION

Metal-containing polymers are one of the major elements of modern-day technologies. Embedding the transition elements in an organic polymeric matrix leads not only to enhancement of many physico-mechanical properties of polymer (for example, heat and wear resistance), but also to the new properties, for example, to magnetic susceptibility, higher indexes of thermal and electric conductivities, biological and catalytic activity.

At present, several methods of producing the metal-containing polymers have been developed, which are based on the incorporation of metals or their salts in a polymer melt [1]. However, these methods do not allow the attainment of uniform distribution of metal particles over the bulk of polymer. This worsens physico-mecha-nical characteristics of the material.

The most promising are the methods of adding complexes of metals immediately during the synthesis of a polymer [2–4]. These methods lead to modification of polymer chemical structure, which allows obtaining the structurally homogeneous tailor-made products. The optimum way for chemical modification of a polymer is an introduction of the metal-containing dopant in a polymer-forming system, the dopant representing the product of interaction of some of monomers, which form a given polymer, with complexes of transition elements.

Based on oligoetherdiols and on the products of the reaction between 2,4-toluene diisocyanate

(2,4-TDI) and chlorides of transition elements (modifying dopants), metal-containing polyurethanes (MCPU) have been synthesized [5–7]. The produced materials possess the enhanced physico-mechanical characteristics and elevated (by 5–6 orders of magnitude) electrical conductivity as compared to unmodified polyurethanes [5–7].

Authors of work [5] have made the assumption that higher than usual conductivity of MCPU may be determined by heterovalent pairs of transition elements that are formed as a result of the redox reactions proceeding during synthesis of polymer.

Electrochemical methods represent the most informative methods that make it possible to recognize the mechanism of redox processes that run during synthesising the admixture for modification of polyurethane and a polymer around it.

This work summarizes the results of our research into the mechanism of formation of agents for polyurethane modification in $CuCl_2$–2,4-toluene diisocyanate (2,4-TDI), $FeCl_3$–N,N′-diethyl hydroxylamine (DEHA)–2,4-TDI, $CoCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$, $NiCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ systems by electrochemical methods.

## RESULTS AND DISCUSSION

Electrochemical study of the above-mentioned systems was conducted by the voltamperometry method with a steady-state platinum electrode in the acetonitrile medium with addition of 0.1 M $Et_4NBF_4$ with respect to Ag/0.1 M $AgNO_3$ in MeCN as a supporting electrolyte. The experimental procedure is described in works [8, 9].

### *$CuCl_2$–2,4-TDI system*

In consequence of electrochemical research of $CuCl_2$–2,4-TDI system in acetonitrile we performed earlier [8], it has been found that presence of small (~4 %) amount of water in solvent is needed for the redox reactions to proceed in this system. The beginning of the process is caused by $CuCl_2$-catalyzed interaction of isocyanate group of 2,4-TDI with water to form arylamine. Only one NCO group at *para*-position reacts with water [10]. The second group remains free and retains the capability for the subsequent polyreaction.

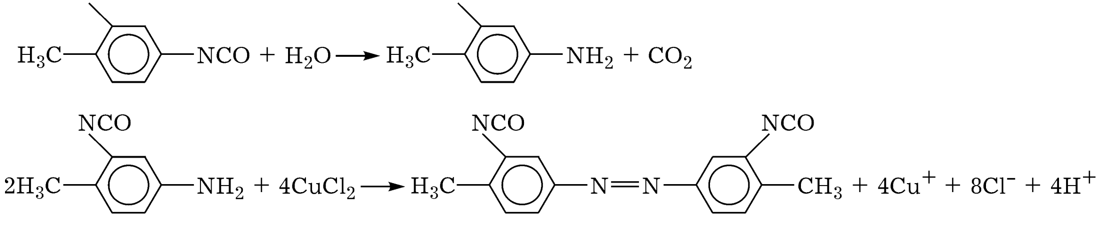
Arylamine being formed in hydrolysis of 2,4-TDI reacts with $CuCl_2$. The latter is partially reduced into CuCl, and arylamine is oxidized to 4,4′-dimethyl-3,3′-diisocyanatoazobenzene as it was found by voltamperometry [8], EPR, IR and UV spectroscopy methods [11]. Diisocyanatoazobenzene has an azogroup, which forms coordination bond with Cu(I) ions, and has two isocyanate groups that are capable to be involved in polyreaction later on.

The processes that run in $CuCl_2$–2,4-TDI–$H_2O$ system can be described by the Scheme 1.

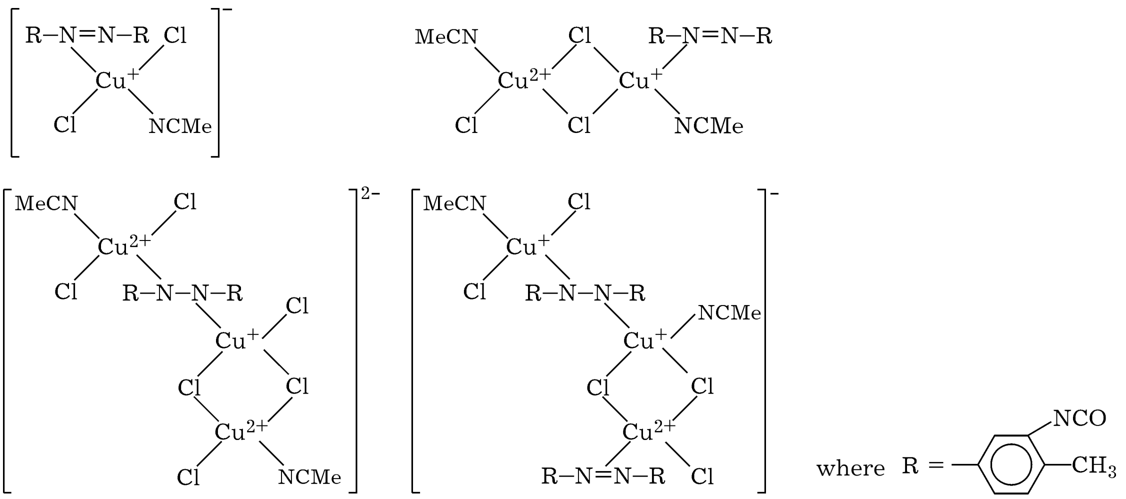
Redox reaction in this system becomes possible owing to the coincident potentials of $CuCl_2$ reduction and arylamine oxidation ($E_{1/2} = +0.50$ V). 2,4-TDI does not undergo any oxidation-reduction transformations over the wide range of variation of the potential from +2.00 to −2.00 V.

Reduction of $CuCl_2$ into CuCl runs incompletely owing to chloride-ions that appear as a result of the reduction process:
$CuCl_2 + e \rightarrow CuCl + Cl^-$.
These ions, when interacting with $CuCl_2$ molecules, form stable $[CuCl_4]^{2-}$ complexes, which stabilize ions of metal (~10 %) in the initial oxidation state [12] following the scheme: $CuCl_2 + 2Cl^- \rightarrow [CuCl_4]^{2-}$.

The existence of planar square $[CuCl_4]^{2-}$ complexes is confirmed by deep UV



Scheme 1.



Scheme 2.

spectroscopy and visible spectroscopy methods [11, 13]. Stability of $[CuCl_4]^{2-}$ complexes that are formed in $CuCl_2$–2,4-TDI–$H_2O$ system is so great that the additional chloride ions introduced in this system stop the redox reaction at any stage of conversion.

Capability of chloride-ions to stabilise Cu(II) ions results in the fact that copper in $CuCl_2$–2,4-TDI–$H_2O$ system exists in different oxidation states ($Cu^{2+}$ and $Cu^{+}$), in consequence of which heterovalent pairs Cu(II)–Cu(I) are present in the modifying admixture.

Thus, resulting from the redox reactions, which run in the $CuCl_2$–2,4-TDI–$H_2O$ system, is formation of mono-, di-, and trinuclear heterovalent complexes of copper with 4,4′-dimethyl-3,3′-diisocyanatoazobenzene. Scheme 2 presents some of the possible structures.

Presence of these polynuclear speciations in the studied system has been recognized by methods of gel permeation chromatography, mass spectrometry, and electronic spectroscopy [11] and this is in agreement with evidence of works [12, 14], which demonstrate that copper chlorides in the non-aqueous media exist in the form of polynuclear speciations. Chloride ions act as the bridges between copper cations.

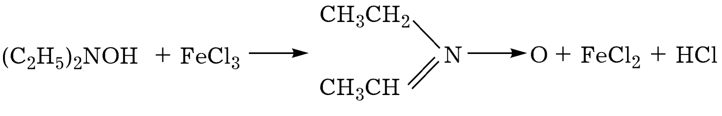
The use of alternative anions, like $[NO_3]^-$ and $[SO_4]^{2-}$, instead of $Cl^-$ ions leads to the complete reduction of Cu(II) to Cu(I) by arylamine; therefore, no formation of heterovalent pairs in $Cu(NO_3)_2$–2,4-TDI–$H_2O$ and $CuSO_4$–2,4-TDI–$H_2O$ systems occurs.

### *$FeCl_3$—DEHA—2,4-TDI system*

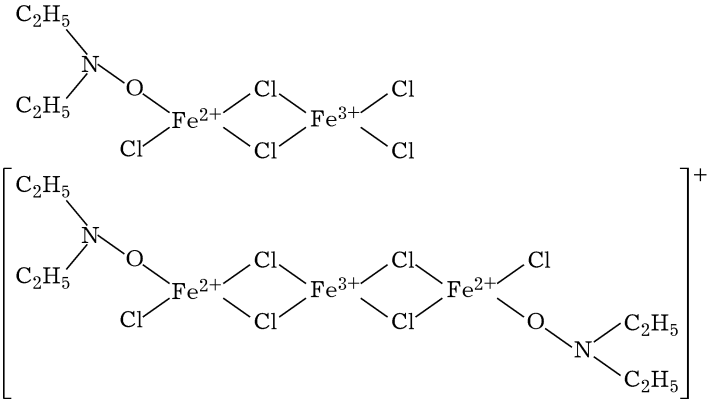
In view of more negative value of $FeCl_3$ reduction potential ($E_{1/2} = -0.30$ V) relative to arylamine oxidation potential ($E_{1/2} = +0.50$ V), a reducer that is stronger than arylamine must be added besides water in $FeCl_3$–2,4-TDI–$N_2O$ system for the redox processes to run. We used DEHA as such reducer, which, as shown in [15], is easily oxidizable to nitron when $E_{1/2} = -0.30$ V and is applicable as solvent for chlorides of transition elements when obtaining the modifying agent for polyurethanes [16].

DEHA partially reduces $FeCl_3$ into $FeCl_2$ thus being oxidized into nitron (Scheme 3).

Partial reduction of Fe(III) to Fe(II) is caused by chloride ions that result from redox reaction. These ions stabilise ions of metal (~10 %) in the initial oxidation state by forming the stable $[FeCl_4]^-$ and $[FeCl_6]^{3-}$ complexes with $FeCl_3$ [17]. Therefore, $FeCl_3$–DEHA–2,4-TDI system (in



Scheme 3.



Scheme 4.

much the same way as $CuCl_2$–2,4-TDI–$H_2O$ system) always contains Fe(III)–Fe(II) heterovalent pairs. Iron ions in 2+ and 3+ oxidation states are linked to each other by chloride bridges. This fact confirms once again the important part played by chloride ions in formation of heterovalent complexes.

The reactions listed above yield polynuclear heterovalent iron (II) and iron (III) complexes with nitron. Some of the conjectured structures of these complexes are presented in the Scheme 4.

The data we obtained are in agreement with the results of work [18].

### *$CoCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ and $NiCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ systems*

The modifying agent can be obtained on the basis of chlorides of other metals, for example $CoCl_2$ and $NiCl_2$. However, as opposed to $CuCl_2$ and $FeCl_3$ (which can be easily reduced and which form the redox pairs conjugated with arylamine and DEHA that yield heterovalent complexes), cobalt and nickel chlorides cannot be reduced by arylamine and DEHA since they show the smaller values of reduction potentials (−1.80 and −1.78 V, respectively). Therefore, when synthesising Co- or Ni-containing modifying agents, cations of different metals with different oxidation states have been used: $CoCl_2$–$FeCl_3$ and $NiCl_2$–$FeCl_3$. However, the organic chelating agent that fixes these heterovalent pairs is necessary in these cases too. We applied the complex obtained through interaction of 2,4-TDI with $H_2O_2$ as such a compound.

Study of electrochemical behaviour of $CoCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ and $NiCl_2$–$FeCl_3$–2,4-TDI–$H_2O_2$ systems has demonstrated that oxidation state of metals in complexes that formed in these systems is preserved, and only their organic part is modified.

2,4-TDI is oxidized by hydrogen peroxide into 4,4′-dimethyl-3,3′-diisocyanatoazobenzene, which forms subsequently polynuclear heterovalent complexes with chlorides of metals of different valence. The structures of these chlorides are similar to the structures of complexes given above that form in $CuCl_2$–2,4-TDI–$H_2O$ and $FeCl_3$–DEHA–2,4-TDI systems.

Thus, this work considers two variants for synthesising the polyurethane modifying agent: in the first case, heterovalent pairs arise due to redox reactions that proceed during synthesis of the agent; in the second case, heterovalent pairs of different metals are already present in the initial mixture while it is produced and their stabilization occurs by addition to oxidates of 2,4-TDI.

In all cases, heterovalent ions of metals are linked by chloride bridges and are involved in polynuclear complexes with oxidates of arylamine, DEHA, and 2,4-TDI. Besides chloride bridges, these complexes contain labile terminal chlorine atoms, which can be readily replaced by alternative electron-donating groups during polymerisation.

Adding of the produced agents at the stage of polymer formation leads to modification of the polyurethanes by metallocomplexes. The polyurethanes possess the elevated (by 5-6 orders of magnitude) electrical conductivity, which is related to Cu(II)–Cu(I), Fe(III)–Fe(II), Fe(III)–Co(II), and Fe(III)–Ni(II) heterovalent pairs [5–7].

Results we acquired are confirmed by evidence of the research on polyurethanes modified by the products of interaction of copper (II) and iron (III) chlorides with DEHA and 2,4-TDI. It is had been found [7] that the structures of these polymers include polynuclear complexes of copper and iron of different oxidation state.

## CONCLUSIONS

Chemical modification by metal-containing dopants added at various stages of synthesis can be applied to alternative polymers too.

When obtaining the modifying agent, it is required that the organic co-reagent is, at least, bifunctional: one functional group must be capable to react with complexes of transition elements, while another must be capable of further polymerization transformations. Meanwhile, the co-reagent must exhibit the properties of strong ionizing solvent, for example, it must enter into redox reaction with ions of a transition element (like arylamine or DEHA), whereas the oxidation products of an applied reagent must possess the capability for the subsequent complex formation.

The finished complexes of transition elements, for example cluster compounds of transition elements with the organic ligands capable to enter into polyreactions, can be applied as a modifying dopant for polymer.

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