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**INVESTIGATION BY ROTATIONAL VISCOMETRY METHODS,  
NMR <sup>119</sup>Sn SPECTROSCOPY AND QUANTUM CHEMISTRY OF THE  
EFFECT OF A CATALYTIC SYSTEM BASED ON  
TIN DI-*n*-BUTYLDILAUROATE AND POLYFLUORINATED  
TETRAAMINE ON THE CURING PROCESS OF ELASTIC  
POLYURETHANES**

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**Abstract:** The modifying effect of the bisalkylation product tris-(2-aminoethylamine) 1H,1H,9H-trihydroperfluorononan-1-ol – polyfluorinated tetraamine on the curing process of polyurethane elastomers has been studied. Based on experimentally determined rate constants of the reaction mass viscosity, a synergistic catalytic effect of tin di-*n*-butyldilaurate and polyfluorinated tetraamine on the urethane formation reaction was revealed. Multicenter mechanisms of catalytic participation have been studied using NMR <sup>119</sup>Sn spectroscopy and quantum chemical analysis.

**Keywords:** polyurethane elastomers, fluoropolymers, polyfluorinated amines, catalysis, organo-tin compounds, structure formation, modification, NMR spectroscopy, quantum chemical calculations, coordination bonds.

**Introduction**

Elastic polyurethanes are widely used as monolithic sports, roofing and waterproofing coatings [1-3]. The structure formation process of polyurethane elastomers is rather complicated and includes multiple chemical and physical-chemical processes combined to form a cross-linked polymer [3]. As catalysts of urethane-, biureo- and allophanate formation there can be used salts of metals (tin, cobalt, lead, zinc, copper, manganese, iron, cadmium, vanadium, bismuth, potassium, aluminum, cerium), tertiary amines and heterocyclic compounds (triethylamine, triethylenediamine,

*N,N*-diethylcyclohexylamine, *N,N,N',N'*-tetramethylbutane diamine, *N*-ethylmorpholine, pyridine), as well as their mixtures [4].

The unique structural feature of *N*-polyfluoroalkylation products of tris-(2-aminoethylamine) with polyfluorinated alcohols  $H(CF_2CF_2)_nCH_2OH$  is the varying substitution degrees presence of amino groups in the molecule and fluorinated fragment [5], which are collectively able to influence the physical and chemical assemblies ratio in the polyurethane mesh and the final material properties. Therefore, the study of curing polyurethane elastomers process in the presence of polyfluorinated tetraamines requires separate research.

The aim of the invention is to study the effect of a catalytic system based on tin di-*n*-butyldilaurate and a polyfluorinated amine synthesized by the bisalkylation of tris-(2-aminoethylamine) with a polyfluorinated alcohol ( $n=4$ ), to a process for the curing of elastic polyurethanes by rotational viscosimetry, NMR  $^{119}Sn$  spectroscopy and quantum-chemical analysis (*ab initio*, DFT).

## Experimental part

### ***The elastomeric composition preparation.***

Polymer compositions are obtained using a laboratory mixer by mixing (stirring speed 250 rpm<sup>-1</sup>) for 10 min 100 pts.wt oligoetherpolyol, 1 pts.wt chain branching agent, 1.5 pts.wt plasticiser, 1.5 pts.wt surfactant, 0.1 pts.wt urethane-formation catalyst and 1 pts.wt polyfluorinated tetraamine. Further, 100 pts.wt isocyanate was added to the reaction mass and stirred again for 7 minutes. The resulting mixture was poured into molds and kept at room temperature (cold curing method) until the Sh A hardness yield of the elastomer on the plateau.

Oligoetherpolyol Laprol 5003-2-B10 (TU 2226-023-10488057-95, PAO Nizhnekamskneftekhim) is a polymerization product of propylene oxide with glycerin, followed by block copolymerization with ethylene oxide with the following characteristics: hydroxyl number of 35 mg KOH/g, water mass fraction not more than 0.1%. The compositions curing was carried out with toluylene diisocyanate (the content of the 2,4-isomer was 80.5%) Desmodur T80 (Wanhua, China).

Grade grade glycerin (GOST 6259-75) was used as a chain branching agent. The urethane formation catalyst was tin di-*n*-butyldilaurate (in the form of a 2.5% solution in white spirit). DOA dioctyl adipate (GOST 8728-88) was used as the plasticizer. Oxyethylated monoalkylphenol Neonol AF 9-12 (TU 2483-077-05766801-98, PAO Nizhnekamskneftekhim) was used as the non-ionogenic surface-active substance.

Catalytic *N*-polyfluoroalkylation of tris-(2-aminoethylamine) 1H,1H,9H-trihydroperfluorononane-1-ol was carried out according to the procedure [5]. The bis-alkylation

product (polyfluorinated tetraamine) is a yellow oil-like substance with boiling point 133-136°C (15 mm Hg. Ct).

### **Research Methods**

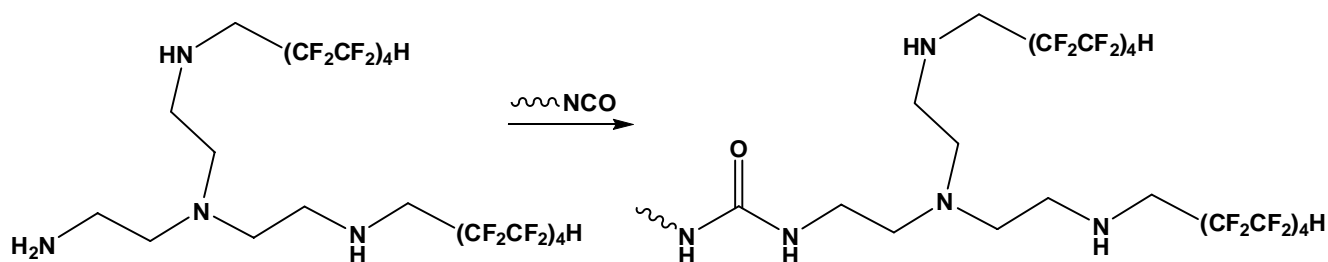
Rheological properties were studied at  $25 \pm 1^\circ\text{C}$  (shear rate  $1 \text{ s}^{-1}$ ) on Brookfield DV-II+Pro and RPE polymer-1 with cylinder-cylinder working unit viscosimeters. The arithmetic mean of three parallel determinations is taken as a result of the test. Viscosity growth rate constants are calculated for two sections of re-kinetic curves anorphosis obtained by taking log on the axis of dynamic viscosity values  $\eta$  (Pa·s) for viscosity dependence on curing time (min)  $\eta$ - $\tau$  [6,7]. For all dependencies  $\eta$ - $\tau$  is typical the presence of different duration initial section (induction period), within which value  $\eta$  varies insignificantly, and then intensively increases according to law close to exponential. In coordinates  $\ln\eta$ - $\tau$ , experimental dependencies have the form of two rectilinear sections with different angular coefficients and corresponding constants of the reaction mass  $K_{\eta 1}$  and  $K_{\eta 2}$  viscosity growth rate.

NMR spectra of  $^{119}\text{Sn}$  (149.22 MHz) in the form of the first derivative of the absorption signal are recorded at  $-5 \pm 0.2^\circ\text{C}$  (to exclude chemical interaction between components) on a Bruker AVANCE 400 NMR spectrometer. Chemical shifts are indicated relative to  $\text{Sn}(\text{CH}_3)_4$ . The number of accumulations is not less than 6144 to obtain a good signal-to-noise ratio. Solutions in carbon tetrachloride with the following concentrations: toluylene diisocyanate – 0.05 mol/l, oligoetherpolyol – 0.10 mol/l, tin di-*n*-butyldilaurate – 0.03 mol/l, polyfluorinated tetraamine – 0.04 mol/l were prepared for spectral analysis.

The activation barriers of interactions, as well as the electron geometric structure of the molecules, were calculated in Gamess (*ab initio*, STO-3G\*\*) and Priroda software products (DFT method using a non-empirical gradient approach and PBE functional in the TZ2P basis).

### **Results and discussion**

The structural feature of the used modifier is the presence of a reactive primary amino group which, under conditions of migration polymerisation of diisocyanate and polyol, interacts with NCO groups of 2,4- and 2,6-toluylene diisocyanate to form disubstituted ureas (Scheme 1).



**Scheme 1.**

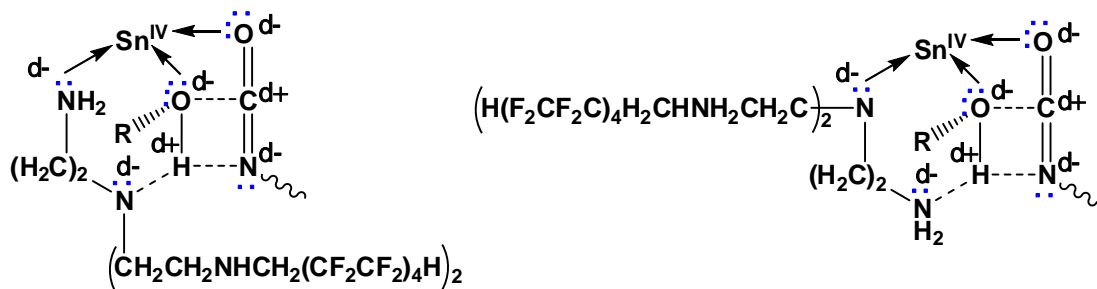
The study of the kinetics of curing of the polyurethane compositions made it possible to identify that the introduction of the modifier contributes to an increase in the reaction mass viscosity when measured under isothermal conditions (Table 1). The growth in values of the rate constants of the reaction mass viscosity increase in the case of injection of the polyfluorinated tetramine is due to the main catalysis of the urethane formation process involving a tertiary nitrogen atom.

**Table 1.** Values of reaction mass viscosity increase rate constants during polyurethane elastomers formation.

| Catalytic system   | Rate constant $K_{\eta}$ (25 °C)            |   |
|--|---|---|
|  | $K_{\eta 1} \cdot 10^{-2}, \text{min}^{-1}$ | $K_{\eta 2} \cdot 10^{-2}, \text{min}^{-1}$ |
| tin di- <i>n</i> -butyldilaurate                             | 0,80  | 3,10  |
| polyfluorinated tetramine                                    | 0.43  | 1,95  |
| tin di- <i>n</i> -butyldilaurate – polyfluorinated tetramine | 1,80  | 5,30  |

Possible mechanisms of catalytic participation of tin di-*n*-butyldilaurate and polyfluorinated tetramine (separately, together) in the reaction of diisocyanate and polyol leading to urethane formation have been investigated by methods of quantum-chemical analysis and molecular modeling. The analysis is carried out under conditions in which the reaction coordinate was fixed according to the O-H bond of the oligoetherpolyol. According to the data of the DFT density functional method, the formation of associates, as well as the coordination bond  $\text{C}=\text{O} \rightarrow \text{Sn}^{\text{IV}}$  and  $\text{O} \rightarrow \text{Sn}^{\text{IV}}$  in the “tin-organic catalyst – toluylene diisocyanate – polyol” system, contributes to an energy gain of 310.5 kJ/mol. For a “polyfluorinated amine – toluylene diisocyanate – polyol” system (taking into account the interactions of  $\text{N} \rightarrow \text{Sn}^{\text{IV}}$ ,  $\text{HN} \rightarrow \text{Sn}^{\text{IV}}$  and  $\text{H}_2\text{N} \rightarrow \text{Sn}^{\text{IV}}$ ), this value is significantly lower and is 157.2 kJ/mol, which is consistent with the data on the determination of the rate constants  $K_{\eta}$ , according to which the polyfluorinated tetramine occurs on the catalytic activity of tin di-*n*-butyldilaurate.

The use of a catalyst system based on an organotin catalyst and a polyfluorinated tetramine provides maximum energy gain of 394.7 kJ/mol. Donor-acceptor complexes formation due to vacancy 5d-orbitals of Sn<sup>IV</sup> tin di-*n*-butyldilaurate and non-divided oxygen and nitrogen electron pairs of isocyanate groups and polyfluorinated tetraamine collectively will contribute to the most effective elongation ("activation") of polyol (denoted as R-OH) OH-bond and facilitating the urethane formation (Scheme 2).

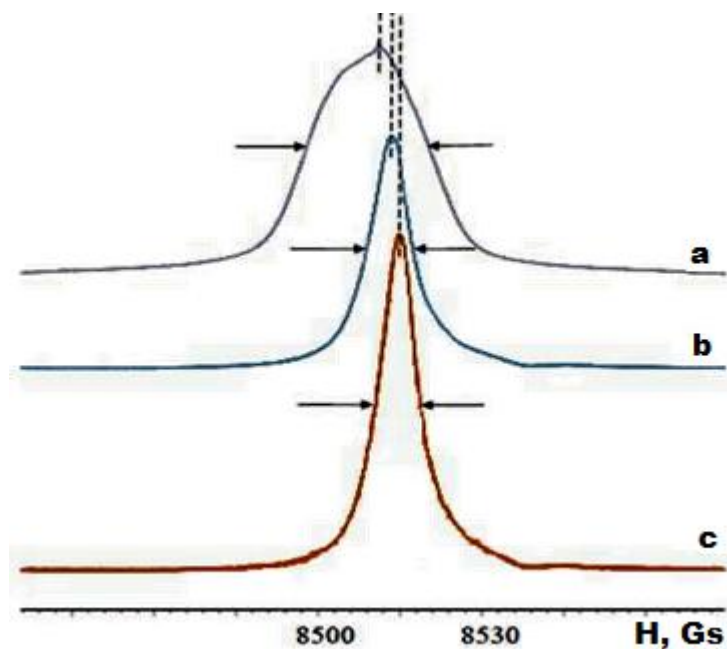


**Scheme 2.**

According to the results of calculations performed by the *ab initio* method, a change in the dipole moment of the interacting particles with 5.18 D (in the absence of a polyfluorinated tetraamine) to 7.60 D is observed for a system including simultaneously tin di-*n*-butyldilaurate and a polyfluorinated tetraamine, as well as a decrease in the charge on the diisocyanate NCO group nitrogen atom from  $-0.269$  to  $-0.377$ . Positive charge on oxygen atom of polyol OH-group increases from 0.233 to 0.279. Furthermore, the H-O bond elongation occurs (the bond length H-O of the oligoetherpolyol increases from 0.956 Å in the presence of an organotin catalyst to 2.218 Å using a bicomponent catalyst system). Such increase of distance between atoms indicates communication break and proton transition to nitrogen atom with urethane group formation. The energy barrier of the urethane formation reaction with the participation of tin di-*n*-butyldilaurate is 208.5 kJ/mol, and with the additional introduction of the polyfluorinated tetraamine the energy barrier is already 153.1 kJ/mol.

The effect on the position, width and shape of the tin di-*n*-butyldilaurate resonant lines spectrum with the addition of the polyurethane formulation (Figure 1) corresponding components studied by NMR <sup>119</sup>Sn experimental spectroscopy methods. The spectrum of the initial tin di-*n*-butyldilaurate is represented by a wide line with an extremum at  $H \sim 8512$  G and a chemical shift in the region  $\delta_1 = -590,2 - 665,2$  ppm, and a narrow central line with  $\delta_2 = -653,5$  ppm. Decomposition of this resonance line into components shows that these lines are close to a Gaussian shape, but have different amplitudes (the relative intensity of the narrow line is 1.3 times greater than the intensity of the wide line). The resonant line asymmetric broadening is due to intramolecular polynuclear

interactions ( $C=O \rightarrow Sn^{IV}$ ,  $O \rightarrow Sn^{IV}$ ), and the narrow line corresponds primarily to the contribution of intermolecular polynuclear interactions ("peripheral" effect).



**Figure 1.** Experimental spectra of NMR  $^{119}Sn$ : *a* – tin di-*n*-butyldilaurate; *b* – tin di-*n*-butyldilaurate + toluylene diisocyanate + oligoether polyol; *c* – tin di-*n*-butyldilaurate + polyfluorinated tetraamine + toluylene diisocyanate + oligoether polyol. *H* – magnetic field.

Introduction of toluylene diisocyanate, oligoetherpolyol and, finally, polyfluorinated tetraamine results in form, width and position transformation of observed line. The only one dominant narrow resonant line with a tendency for its narrowing and preservation of asymmetry in the NMR spectrum is observed along with the shift of the maximum. Such changes are related to the reorganization of the coordination environment  $Sn^{IV}$  by involving different structural fragments (amino groups with the different degree of tetraamine substitution and NCO groups with a linear structure) into multi-center donor-acceptor interactions resulting in a single signal with a maximum relative intensity. The presence of a weakly expressed arm in the area  $H \sim 8539$  G corresponds to the contribution of products formed during partial absorption of water vapor by toluene diisocyanate to form another type of coordination with  $Sn^{IV}$ .

Thus, the effect of a catalytic system based on tin di-*n*-butyldilaurate and a polyfluorinated tetraamine on the curing elastic polyurethanes process has been investigated and shows that there is a synergistic effect of accelerating the urethane formation reaction associated with the formation of multi-site polyassociative interactions arising between an organotin catalyst, tetraamine, toluylene

diisocyanate and oligoetherpolyol, which collectively contribute to facilitating the formation of urethane.

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