

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Bottom-Up Nanostructured Segmented Polyurethanes with Immobilized *in situ* Transition and Rare-Earth Metal Chelate Compounds – Polymer Topology – Structure and Properties Relationship

---

Nataly Kozak and Eugenia Lobko

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/48002>

---

## 1. Introduction

The formation of the polyurethanes (PU) with immobilized *in situ* co-ordinating metal compounds allows obtain structurally homogeneous systems with uniform dispersed nanosize metal containing sites. Aggregation of these metal chelate compounds is prevented due to complexing with polar groups of the polymer matrix.

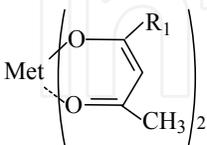
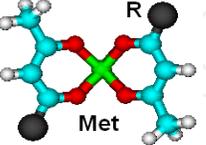
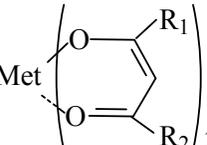
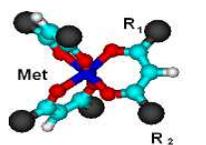
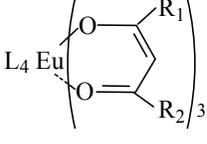
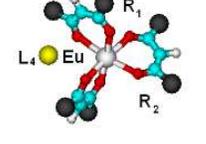
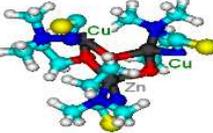
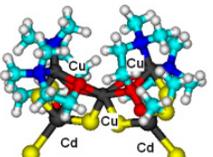
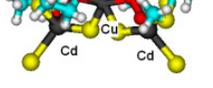
At the same time due to complex formation between the metal compound and polymer functional groups, the structuring of the forming matrix occurs on a nanoscale level. As a result, in the presence of small amounts of metal chelate compound (0,5-5%wt) both change of the polyurethane structure and properties can be observed. To understand the nature of above phenomena the influence of the weak interactions «macromolecule - metal» were analyzed on the metal-containing PUs structure, molecular dynamics and properties.

The present study investigates the formation of nanostructured linear and cross-linked polyurethanes (LPUs and CPUs, respectively) with immobilized *in situ* mono- and poly-heteronuclear chelate compounds of rare-earth and transition metals. Influence of PU topology on self organization processes in polymer matrix and its properties is also subject of analysis.

### 1.1. Materials, methods and instrumentations

Polypropylene glycol (PPG, MW 1000) was dried under vacuum at 120 °C for 2 h. Tolylene diisocyanate (mixture 80/20 of 2,4- and 2,6- isomers) (TDI) was distilled under vacuum.

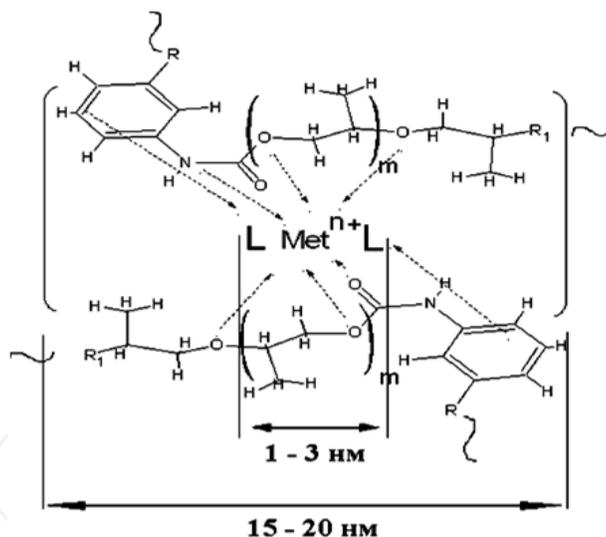
Diethylene glycol (DEG) was distilled under vacuum at 105 °C. Trimethylol propane (98%) (TMP) was dried under vacuum at 40-45 °C for 2-4 h. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), 1,4-dioxane and N,N'- dimethylformamide (DMF) were distilled at 40 °C, 101 °C, 153 °C, respectively. The following chelate compounds of transition and rare-earth metals as PU modifier were used:

		<p>(R=CH<sub>3</sub>) Cu(acac)<sub>2</sub> - Copper(2+) acetylacetonate Ni(acac)<sub>2</sub> - Nickel(2+) acetylacetonate (R = -OC<sub>2</sub>H<sub>5</sub>) Cu(eaac)<sub>2</sub> - Copper (2+) ethyl acetoacetate (R = -CF<sub>3</sub>). Cu(tfacac)<sub>2</sub> - Copper (2+)trifluoro acetylacetonate</p>
		<p>(R<sub>1</sub>=R<sub>2</sub>=-CH<sub>3</sub>) Co(acac)<sub>3</sub> - Cobalt (3+) acetylacetonate Cr(acac)<sub>3</sub> - Chromium (3+) acetylacetonate Gd(acac)<sub>3</sub> - Gadolinium (3+) acetylacetonate Nd(acac)<sub>3</sub> - Neodymium (3+) acetylacetonate Er(acac)<sub>3</sub> - Erbium (3+) acetylacetonate (R<sub>1</sub> = -C(CH<sub>3</sub>)<sub>3</sub>, R<sub>2</sub> = -(CF<sub>2</sub>)<sub>2</sub>-CF<sub>3</sub>) Eu(fod)<sub>3</sub> - Europium (3+) tris(6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) (R<sub>1</sub> = thiophene, R<sub>2</sub> = CF<sub>3</sub>) Eu(TTA)<sub>3</sub> - Europium (3+) thenoyltrifluoroacetate</p>
		<p>(R<sub>1</sub> = thiophene, R<sub>2</sub> = -CF<sub>3</sub>; L<sub>4</sub> = phen) Eu(TTA)<sub>3</sub> phen - Europium (3+) tris(thenoyltrifluoroacetate) phenanthroline (R<sub>1</sub> = thiophene, R<sub>2</sub> = -CF<sub>3</sub>; L<sub>4</sub> = triphenylphosphine oxide) Eu(TTA)<sub>3</sub> TPPO -Europium (3+) tris (thenoyltrifluoroacetate) (triphenylphosphine oxide)</p>
<p><math>[Met_k^1 Met_m^2 Met_n^3 R_p^1 R_q^2 R_r^3] \cdot Sol_t</math> <math>p, q, k, m = 1, 2, 3, 4;</math> <math>n, r, t = 0, 1;</math> where Me<sub>2</sub>Ea = deprotonated residue of dimethyl aminoethanol Dea = doubly deprotonated residue of diethanolamine</p>		<p><math>k=2, m=1, n=0, p=3, q=3, r=0, t=1,</math> R<sup>1</sup>=NCS, R<sup>2</sup>=Me<sub>2</sub>Ea, Sol= CH<sub>3</sub>CN [Cu<sub>2</sub>Zn(NCS)<sub>3</sub>(Me<sub>2</sub>Ea)<sub>3</sub>].CH<sub>3</sub>CN</p>
		<p><math>k=2, m=3, n=0, p=6, q=4, r=0, t=2,</math> R<sup>1</sup>=Br, R<sup>2</sup>=Me<sub>2</sub>Ea, Sol= dmsol [Cd<sub>2</sub>Cu<sub>3</sub>Br<sub>6</sub>(Me<sub>2</sub>Ea)<sub>4</sub>(dmsol)<sub>2</sub>]</p>
		<p><math>k=1, m=2, n=2, p=3, q=4, r=4, t=0,</math> R<sup>1</sup>= H<sub>2</sub>Dea, R<sup>2</sup>= NCS, R<sup>3</sup>= Dea [Ni(H<sub>2</sub>Dea)<sup>2</sup>][CoCu(Dea)<sup>2</sup>(H<sub>2</sub>Dea)(NCS)]<sup>2</sup>(NCS)<sup>2</sup></p>

**Table 1.** The PU modified chelate compounds of transition and rare-earth metals.

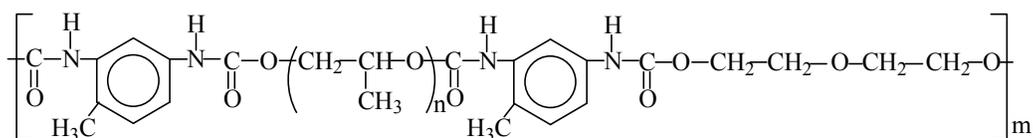
In metal chelate compounds used as PU modifier metal ions are already surrounded with organic ligands. This facilitates solvation of modifier in polymer. The listed above transition and rare-earth metal chelate compounds are commercial products (Aldrich). The heteroligand rare-earth metal compounds were synthesized by Professor Svetlana B. Meshkova's group (A. V. Bogatsky Physic-Chemical Institute of National Academy of Sciences of Ukraine, Odessa). Polyheteronuclear metal complexes of Cu (2+), Cd (2+), Zn (2+), Ni (2+) and Co (3+), described in (Skopenko et al., 1997; Vinogradova et al., 2002), were provided by Prof. V. Kozozay's group (Kiev Taras Shevchenko University). Polyheteronuclear metal chelate compounds can realize unexpected coordination states of transition metal ions. That, in turn, can give new properties to a polymer formed in their presence.

PUs were synthesized in two stages according to standard procedure described in detail elsewhere (Saunders&Frish,1968; Wirspza,1993) using PPG-1000 and TDI based prepolymer. DEG was used as chain extender to obtain LPU (Scheme 2). TMP was used as cross-linking agent to obtain CPU (Scheme 3). Metal chelate compounds were added into reaction mixture as solution in CH<sub>2</sub>Cl<sub>2</sub>, 1,4-dioxane or DMF to obtain the metal containing PUs with homogeneous distribution of modifier (from 0,5 to 5 %wt.) in polymer matrix. High ability of metal chelate compound to complex formation leads to enrichment of PU matrix with heteroligand macro complexes of 3d- and 4f-metal with prevalence of outer-sphere coordination of macro chains. Such macro complexes act like coordination linkages between polymer chains and form "coordination nodes" in PU (Scheme 1).



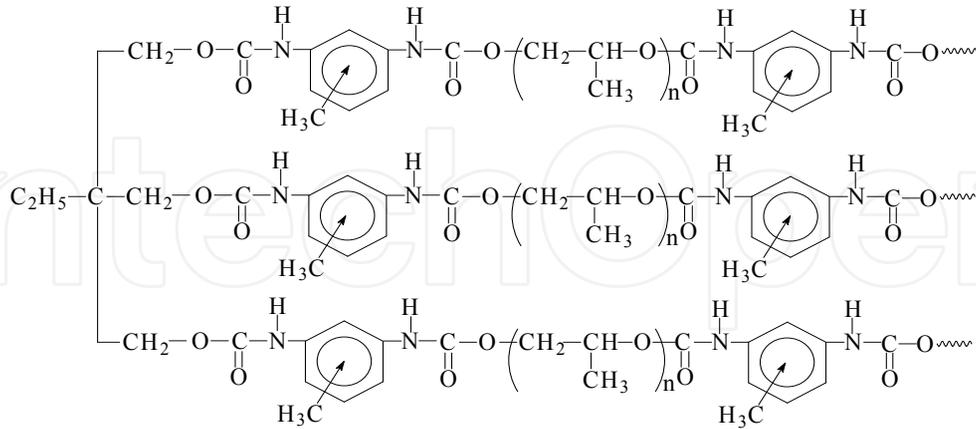
**Scheme 1.** The coordination junction of PUs networks.

Thus, in the LPU (Scheme 2) in the presence of chelate metal compounds the "coordination nodes" can form.



**Scheme 2.** The general formula of LPU.

In the metal containing CPU both the chemical linkages (Scheme 3) and the “coordination nodes” can form (Scheme 1).



**Scheme 3.** The fragment of PU network with cross-linkage.

Wide-angle X-ray scattering (WAXS) profiles of studied samples were recorded on a Dron-4-07 diffractometer with Ni-filtered Cu-K $\alpha$  radiation and Debay-Sherer optical schema. Distance between PU atomic layers ( $d$ ) was estimated using the Bragg equation:

$$\lambda = 2d \sin \theta \quad (1)$$

where  $\lambda$  – the X-ray wave length ( $\lambda = 0,154$  nm);  $\theta$  – the diffraction maximum angular position, degrees.

Small-angle X-ray scattering (SAXS) profiles were recorded using KPM-1 X-ray camera (Kratky et al., 1966). The Schmidt's method (Schmidt & Hight, 1960) was used to smooth out the SAXS-profiles to point collimation. X-ray measurements are carried out using monochromatic Ni-filter of Cu-K $\alpha$  radiation at temperature  $22 \pm 2$  °C. The Bragg's period of uniform electronic density scattering elements was estimated through the equation:

$$D = 2\pi / q \quad (2)$$

The X-band EPR-spectra were recorded at temperature 20°C using radio spectrometer PE-1306 equipped with frequency meter ChZ-54. The magnetic field was calibrated using 2, 2-diphenil-1-picrylhydrazyl (DPPH) ( $g=2,0036$ ) and ions of Mn(2+) in MgO matrix ( $g=2,0015$ ).

Stable nitroxide radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) was used as paramagnetic spin probe (SP). Nitroxide SP was introduced into PU films via diffusion of its saturated vapor at 30°C for 2 hours with subsequent keeping at 20°C for 24 hours.

Correlation time ( $\tau$ ) of SP rotational diffusion in the range of its fast motion ( $10^{-11} < \tau < 10^{-9}$ s) was calculated according (Vasserman & Kovarskii, 1986) as follows:

$$\tau = 6,65 \Delta H_{(+1)} (\sqrt{I_{+1} / I_{-1}} - 1) \times 10^{-10} c, \quad (3)$$

where  $\Delta H_{(+1)}$  – is width of the low-field- component of TEMPO EPR-spectrum,  $I_{+1}$  and  $I_{-1}$  – are intensities of low-field and high-field components of the spectrum, respectively.

The differential scanning calorimetry in temperature interval from 223 to 750 K was performed using Perkin Elmer DSC 2 instrument with the IFA GmbH's software. The heating rate was 0,05-2 grad/min.

Micro images in light transmission were obtained using an optical microscope XY-B2 (NS Instr. Co.) equipped with digital video ocular ICM 532 and AMCAM/VIDCAP (Microsoft) image processing system.

The surface tension of PUs ( $\gamma_{sg}$ ) was determined according to Elton's equation (Tavana et al., 2004) using measurement of contact wetting angle with ethyleneglycol (EG) as wetting liquid at 20°C:

$$\gamma_{sg} = 0,5\gamma_{lg}(1 + \cos\theta) \quad (4)$$

where  $\gamma_{sg}$  and  $\gamma_{lg}$  are the surface tension on solid-gas and liquid-gas boundaries, respectively;  $\theta$  is the boundary wetting angle; solid is PU; liquid is EG.

The mean value of  $\gamma_{sg}$  was calculated as average of 5 different measurements and error of measurements did not exceed the value of 0,5 mN/m.

The spectra of luminescence were obtained using the luminescent spectrometer SDL-1 (LOMO) in an excitation by the mercury lamp. The emission of the most intensive line with the maximum on 365 nm was selected with light filter UFS-2.

Two-electrode method measurements of conductivity at a direct current (dc) were conducted using a Hiresta UP high resistivity meter (Mitsubishi Chemicals, Japan). A dc voltage of 10 V was applied across the sample thickness. The samples were dried over night in an oven at 40°C under vacuum and then kept in dried environment, for the elimination of any moisture effects.

Dielectric relaxation analysis was performed using dielectric spectrometer on the base on alternating current bridge R5083. Complex dielectric permittivity,  $\epsilon^* = \epsilon' - i\epsilon''$ , of disc-like specimens (diameter: 20 mm) sandwiched between gold-coated brass electrodes was measured over the frequency window from 102 to 105 Hz in the temperature interval from –40 to 120 °C. They have been analyzed from the traditional point of view (Pathmanatham & Johari, 1990; Pissis & Kanapitsas, 1996). Additional formalisms such as: complex admittance  $\sigma^*$ , electrical modules  $M^*$  and impedances  $Z'$ ,  $Z''$  were used according to formulas.

$$\epsilon' = C_1 / C_0, \text{tg}\delta = \omega RC_1 \text{ and } \epsilon'' = \epsilon' \cdot \text{tg}\delta \quad (5)$$

$$\sigma^* = \sigma' + \sigma'', \sigma' = \omega\epsilon'', \sigma'' = \omega\epsilon' \quad (6)$$

$$M^* = M' + M'', M' = \epsilon'' / (\epsilon'^2 + \epsilon''^2), M'' = \epsilon' / (\epsilon'^2 + \epsilon''^2) \quad (7)$$

$$Z' = M'' / (\omega C_0), Z'' = M' / (\omega C_0) \quad (8)$$

$C_0$  and  $C_1$  – are instrument and standard capacitor capacities,  $\omega$  – cyclic frequency.

The electron spectra of the copper (2+) containing PU films and of copper (2+) chelate compounds solutions in dichloromethane ( $c = 10^{-2}M$ ) in the ultra-violet and visible region were recorded using the spectrometer Specord UV-VIS.

The quasi-elastic neutron scattering (QENS) was recorded using the multi detector spectrometer "NURMEN" on the atomic reactor BBP-M (The institute of the nuclear research of the NAS of Ukraine). The self-diffusion of chloroform used as low molecular probe liquid in swelled PU films was analyzed.

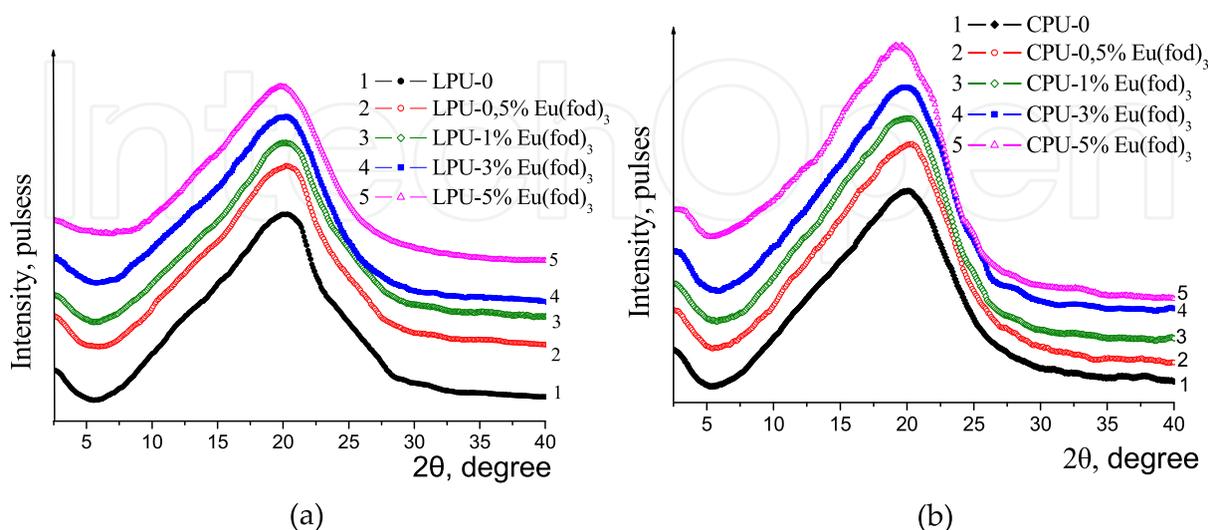
## 2. Heterogeneity of metal containing polyurethanes

### 2.1. Structural heterogeneity of PU according to X-ray data

Formation of a polymer matrix in the presence of metal chelate compounds favours creation of a new hierarchy in structural organization of the polymer as compared with metal free system. This effect is caused by complex formation between metal chelate compound and functional groups of the forming polymer (Ying, 2002; Kozak et al., 2000).

Figure 1 represents the WAXS and Figure 2 presents SAXS intensity profiles of metal-free PU and PU modified with metal  $\beta$ -diketonate. The asymmetric diffuse diffraction maxima (Figure 1) point on the amorphous structure of the metal-free and metal containing CPU and LPU. For the LPU the short-range order parameter  $d$  (equation 1) is equal to 0.44 nm and don't depend on the metal chelate compound amount (table 1). For the CPU the Bragg's period ( $d$ ) changes from 0.44 to 0.46 nm with increasing of the modifier amount from 0,5 to 5% wt.

The PU's SAXS profiles are characterized by the presence of one amorphous maximum with  $q_m$  positions varying from 1,7 to 2,0  $nm^{-1}$  (Figure 2). Such maximum points on the existence of changeover period of uniform electron density scattering elements and areas of uniform distribution of hard and flexible blocks in PU. The Bragg's period ( $D$ ) falls from 3,7 to 3,1 nm with increasing of the modifiers amount from 0,5 to 5% wt. (table 1).



**Figure 1.** The WAXS intensity profiles of CPU (a) and LPU (b): metal-free (1), modified with 0,5% (2), 1% (3), 3% (4) и 5% (5)  $Eu(fod)_3$ .

System	$2\theta$ , degree	$d$ , nm	$q_m$ , $\text{nm}^{-1}$	$D$ , nm
CPU-0	20	0.44	1.7	3.7
CPU-0,5% $\text{Eu}(\text{fod})_3$	20	0.44	1.7	3.7
CPU-1% $\text{Eu}(\text{fod})_3$	19.9	0.45	1.76	3.6
CPU-3% $\text{Eu}(\text{fod})_3$	19.9	0.45	1.76	3.6
CPU-5% $\text{Eu}(\text{fod})_3$	19.4	0.46	2.0	3.1
LPU-0	20	0.44	1.7	3.7
LPU-0,5% $\text{Eu}(\text{fod})_3$	20	0.44	1.7	3.7
LPU-1% $\text{Eu}(\text{fod})_3$	20	0.44	1.9	3.3
LPU-3% $\text{Eu}(\text{fod})_3$	20	0.44	1.8	3.5
LPU-5% $\text{Eu}(\text{fod})_3$	20	0.44	1.9	3.4

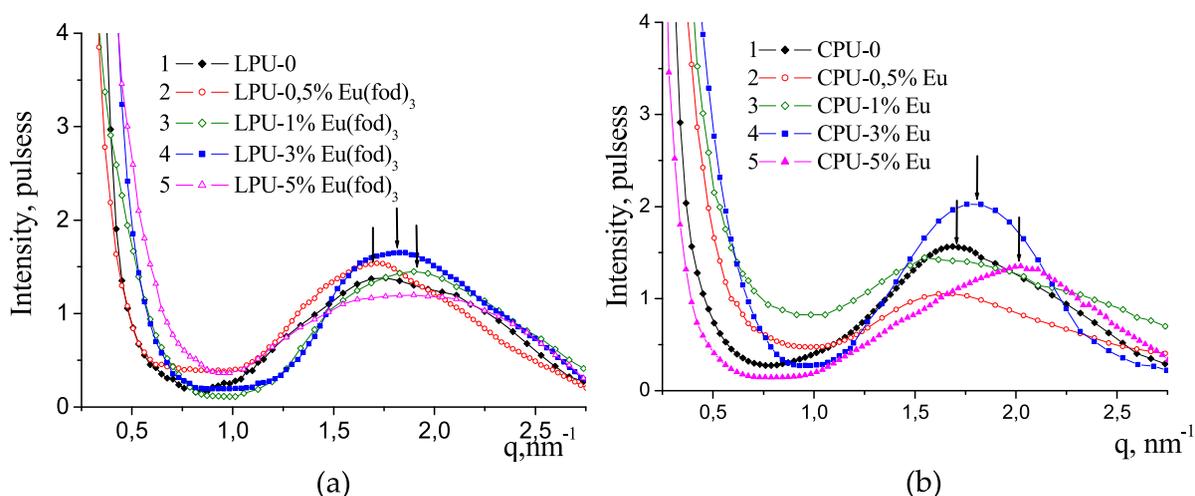
$2\theta$  - the diffraction maximum angular position, degrees;

$d$  - distance between PU atomic layers from WAXS, nm;

$q_m$  - value at maximum intensity of  $I(q)$  relationship,  $\text{nm}^{-1}$ ;

$D$  - changeover period of uniform electronic density scattering elements from SAXS, nm.

**Table 2.** X-ray structural characteristic of LPU and CPU



**Figure 2.** The SAXS intensity profiles of CPU (a) and LPU (b): metal-free (1), modified with 0,5% (2), 1% (3), 3% (4) and 5% (5)  $\text{Eu}(\text{fod})_3$ .

Analysis according (Porod, 1982) of heterogeneity range ( $l_p$ ) and average diameter ( $l_1$ ,  $l_2$ ) of different scattering elements in CPU-0, CPU-Cr and CPU-Co indicate existence of two types of nanosize heterogeneities in the bulk of PU. The first one (with  $l_1 < D$ ) is inherent to segmented PU. The second one (with  $l_2 > D$ ) is generated in the presence of transition metal chelate compound. We can define the latter structures as “metal chelate compound – polyurethane” complexes with polymer chains as macro ligands (Kozak et al., 2006; Nizelskii & Kozak, 2006) (Scheme 1).

Thus, the immobilization *in situ* of metal chelate compounds in polyurethane is accompanied with enrichment of polymer matrix with the nanosize heteroligand macro complexes of metal formed simultaneously with organic nanosize structures typical for metal-free polymer.

## 2.2. Dynamic heterogeneity of PU according to EPR data

The structural heterogeneity of PU influences the local segmental mobility of macro chains, resulting in “dynamic heterogeneity” of the systems. The analysis of mobility of SP introduced into the polymer gives information concerning such heterogeneity.

Calculated values of  $\tau$  are listed in the table 2. They characterize the hindered rotation of SP in PUs of different topology. The greater value of  $\tau$  is, the harder rotation of the probe occurs in polymer matrix.

System	$\tau \cdot 10^{-10}$ , c	System	$\tau \cdot 10^{-10}$ , c
CPU-0	45	LPU-0	48
CPU-1%Cu(eacac) <sub>2</sub>	43	LPU-1%Cu(eacac) <sub>2</sub>	69
CPU-1%Ni(acac) <sub>2</sub>	42	CPU-1%CuCd	45
CPU-1%Cr(acac) <sub>3</sub>	50	CPU-1%CuZn	32
CPU-1%Co(acac) <sub>3</sub>	49	CPU-1%CuNiCo	51

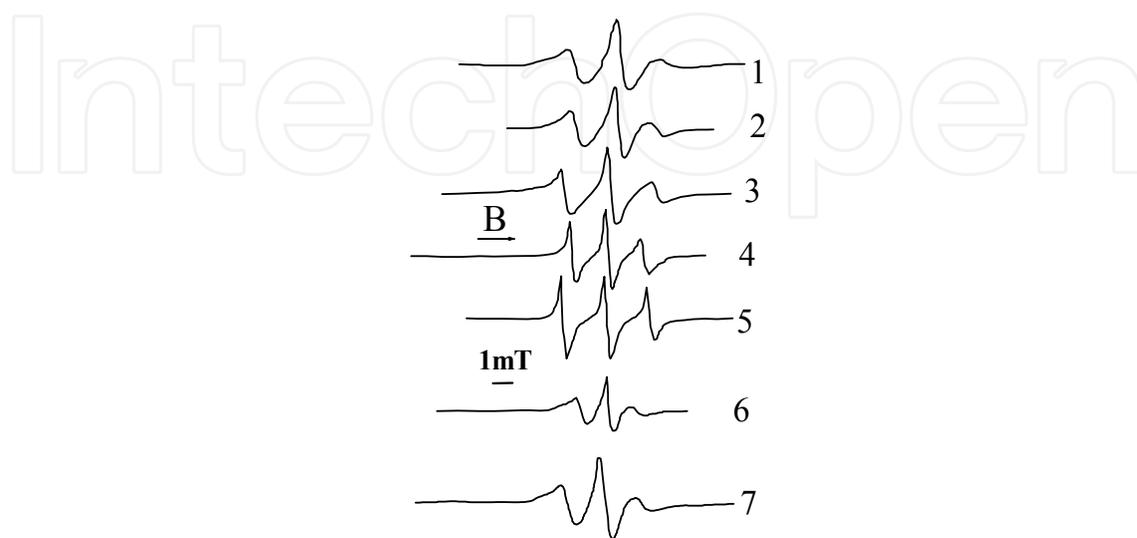
**Table 3.** The correlation time of TEMPO in CPUs and LPUs, modified with 1% of metal chelate compounds.

As it can be seen from the table 2, in CPU modified with 1%wt. Co(3+) and Cr(3+) chelate compounds the values of  $\tau$  increase indicating reduction of SP mobility as compared with metal-free CPU. In the contrary, for CPUs modified with 1%wt. Cu(2+), Ni(2+) values of  $\tau$  decrease as compared with metal-free CPU. This means that Co(3+) and Cr(3+) containing CPUs have more dense macro chain packing as compared with metal free CPU. Whereas Cu(2+) and Ni(2+) containing CPUs possess looser macro chain packing. Similarly to (Lipatov et al., 2000), the effect we can relate to difference in metal chelate compounds electron configuration and symmetry. In addition, the influence of metal chelate compound on PU dynamic depends also on the polymer topology. For example, it can be seen the opposite influence of Cu(2+) chelate compounds on the macro chain mobility in LPU and CPU (Table2).

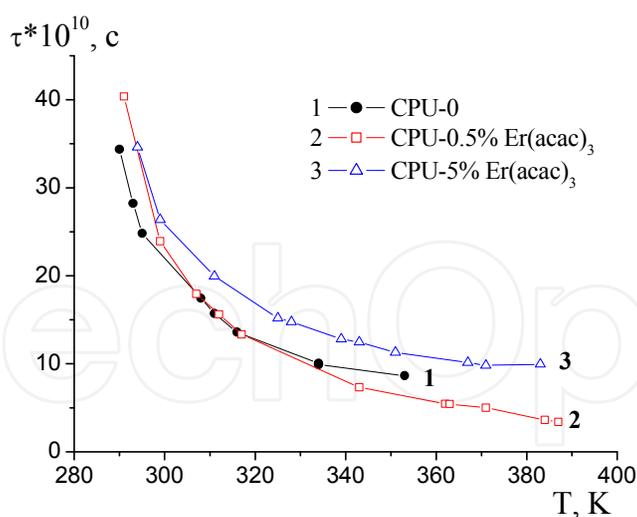
The analysis of SP EPR-spectrum shape and hyperfine splitting (HFS) gives additional information concerned probed medium. In PU matrices that contain metal chelate compounds the EPR spectra of SP have asymmetric shape (Figure 3). In all of the spectra occur essential increasing of central component and broadening of all components as compared with TEMPO spectrum in homogeneous glycerol matrix. In many spectra there is noticeable splitting of low-field and/or high-field components of SP spectrum.

The peculiarities observed are most likely the result of signal superposition of “fast” and “slow” probes located in polymer regions with different mobility. In conformity with above supposition the temperature increasing brings on enhancement of the SP EPR spectra isotropy (Figure 3). Initially asymmetric ESR spectrum becomes more isotropic while heating the sample. The spectrum components narrow and the intensity of central component diminishes.

As a result of heating the equalizing of polymer segments mobility and „unfreezing” of „slow” SP rotation diffusion occurs. The correlation time decreases with the rise of temperature due to increasing of molecular mobility and “softening” of PU matrix. Figure 4 represents the relationship  $\tau(T)$  for CPU.



**Figure 3.** The spectra of the TEMPO introduced in CPU+Er(acac)<sub>3</sub> at the various temperatures: 18 °C (1); 26 °C (2); 44 °C (3) ; 90 °C (4); 114 °C (5); 21 °C (30 min after thermal heating) (6); 18 °C (2 days after thermal heating) (7).

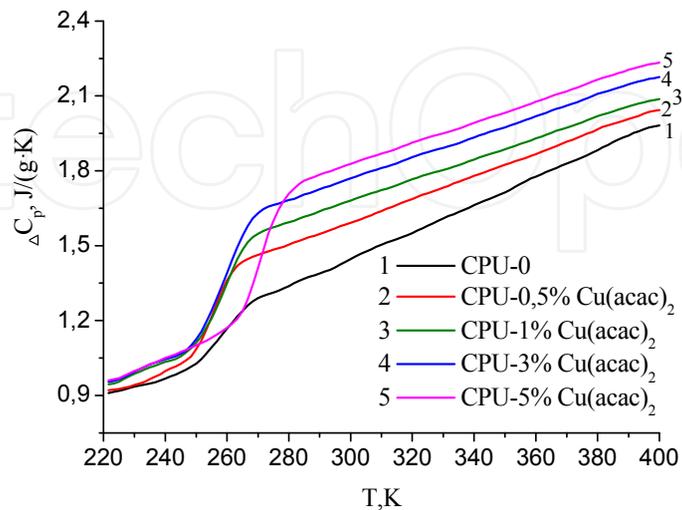


**Figure 4.** The thermal dependence of correlation time of the TEMPO in CPU-0 (1), CPU, modified with 0,5%wt. (2) and 5%wt. (3) of Er(acac)<sub>3</sub>.

### 2.3. Thermodynamic heterogeneity of PU according to DSC data

The PU's thermodynamic heterogeneity is closely associated with above discussed types of heterogeneities. The influence of the metal chelate compounds on the thermodynamic

heterogeneity and thermo-physic properties of PUs was analyzed by DSC. Figure 5 illustrates the temperature dependences of specific heat capacity of CPUs modified with 0,5; 1; 3; 5%wt. of  $\text{Cu}(\text{acac})_2$ . The thermo-physic characteristics of copper-containing CPUs are given in Table 3.



**Figure 5.** Temperature dependence of specific heat capacity for copper-containing CPU.

System	$T_g$ , K	$\Delta T$ , K	$\Delta C_p$ , J/(g·K)	$\frac{\Delta C_p(\text{CPU-Cu})}{\Delta C_p(\text{CPU-0})}$
CPU-0	258	18	0,25	1
CPU-0,5% $\text{Cu}(\text{acac})_2$	256	16	0,38	1,52
CPU-1% $\text{Cu}(\text{acac})_2$	258	18	0,43	1,72
CPU-3% $\text{Cu}(\text{acac})_2$	260	21	0,50	2,00
CPU-5% $\text{Cu}(\text{acac})_2$	271	20	0,55	2,20

**Table 4.** The thermo-physical properties of copper-containing CPU.

It is evident from fig. 5 and table 3 that for the CPUs the specific heat capacity ( $\Delta C_p$ ) grows with increasing of Cu (2+) chelate content from 0,5 to 5% wt. comparing with CPU-0. In addition, the high temperature shifting of glass temperature ( $T_g$ ) and the broadening of the temperature interval of glassing ( $\Delta T$ ) for CPU- 3%Cu and CPU-5%Cu are observed. The similar effect was discussed in (Lipatov et al., 1999) for CPUs, modified with 1%wt of various transition metals chelate compounds. That effect we can relate to formation of coordination bonds between functional groups of CPU and copper (2+) chelate compound.

Thus, growth of  $T_g$  and  $\Delta C_p$  values with increasing of  $\text{Cu}(\text{acac})_2$  amount corresponds to rise of polymer segments with decreased mobility due to complexing.

The ratio of  $\Delta C_p(\text{CPU-Cu})$  to  $\Delta C_p(\text{CPU-0})$  allows estimate the degree of PU's thermodynamic heterogeneity (Bershtein. & Yegorov, 1990) and analyze the influence of metal chelate modifier content on this type of heterogeneity (table 3). As it can be seen the thermodynamic

heterogeneity degree of CPU correlates with modifier amount in the system. This result agrees with X-ray data (section 2.1).

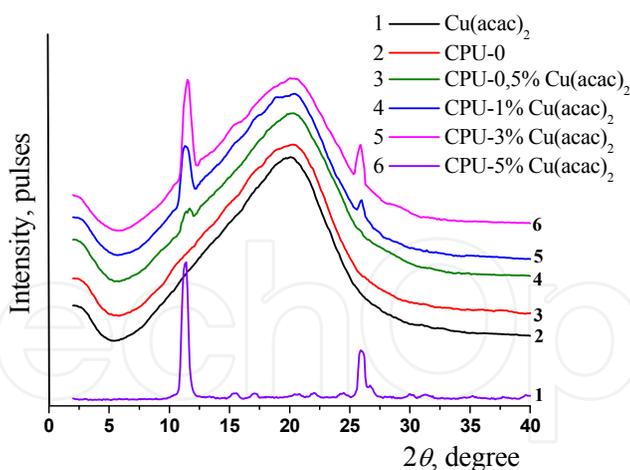
#### 2.4. The formation of ordered micro regions in metal containing PUs

The segregation of metal containing micro crystals in CPU-5% Co and CPU-5%Cr was revealed in (Kozak et al., 2006):. Such unexpected segregation seemed unlikely due to homogeneous dispersion of metal chelate compound solution in reaction mixture (see 2.1) and coordination immobilization of metal chelate compounds in PU matrix. Nevertheless, the further X-ray study of CPU-5%Cu, LPU-5%Cu (fig. 6) and microscopy data (see 2.5) confirm partial segregation of metal-containing sites in PU matrices. This effect can be explained by different complex ability of segmented PU soft and hard components towards metal chelate compound as well as by higher mobility of PU's soft component.

The Scherer's equation (Stempel & Kercha, 2008) for the average diameter ( $L$ ) of crystallite in amorphous media allows estimate dimensions of the particles in metal-containing PU.

$$L = k\lambda / (\beta \cos\theta_m) \quad (9)$$

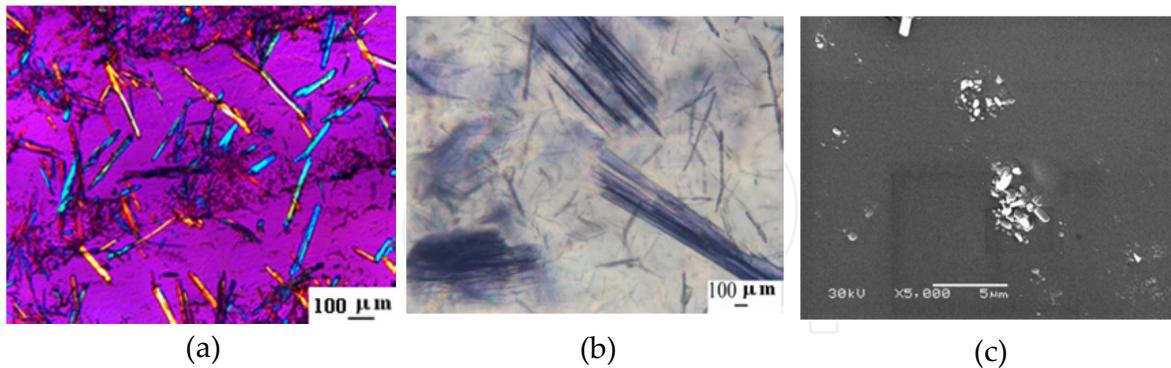
Here X-ray wavelength  $\lambda = 1,54 \text{ \AA}$ ,  $k$  is the shape factor assigned to 0,9,  $L$  is the average diameter of the crystals in angstroms,  $\theta_m$  is the Bragg's angle in degrees, and  $\beta$  is the half-height of diffraction angle in radians. The value of  $L$  is equal to 3 nm for CPU-1%Co, it is equal to 4 nm for CPU-1%Cr and it is equal to 10 nm in LPU-1%Eu. The evaluated dimensions of the aggregates in copper containing PUs are ranged from 8 to 12 nm.



**Figure 6.** The WAXS diffractograms of the CPU-%Cu(acac)<sub>2</sub> films.

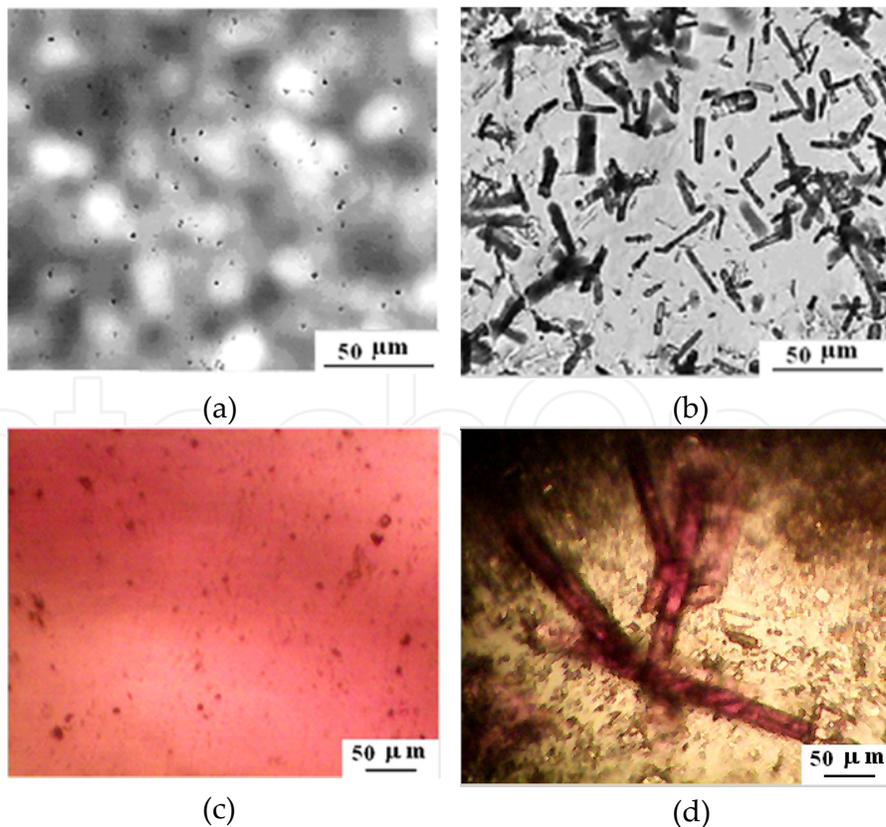
Segregation of the micro crystals detected via WAXS study has been also fixed by optical light transmission microscopy and by the scanning electron microscopy (SEM) (Figure 7). The micro crystals detected by optical microscopy are coloured like metal chelate compounds used as PU modifier. Such colouring indicates enrichment of the crystals with corresponding metal ions. The crystalline regions can be formed by the modifier itself and/or by complexes of modifier with PU chains as macro ligand. The last conclusion agrees

with the X-ray data that register several discrete peaks in  $\text{Cu}(2+)$ ,  $\text{Cr}(3+)$  and  $\text{Co}(3+)$  containing PUs (Figure 6).



**Figure 7.** The optical microscopy (a, b) and SEM microscopy micro images of the LPU-0,5% $\text{Cu}(\text{acac})_2$  (in polarized light) (a), LPU-5% $\text{Cu}(\text{acac})_2$  (b) and CPU-5% $\text{Cr}(\text{acac})_3$ .

Optical microscopy allows obtain information concerning two surfaces of one PU film. One of them formed on the boundary “polymer-support” (the PU’s surface formed on the Teflon support) and another formed on the boundary “polymer-air” (the PU’s surface formed on the air).



**Figure 8.** Micro images of LPU-1% $\text{Eu}(\text{fod})_3$  (a,b) and CPU-1% $\text{Cr}(\text{acac})_3$  (c, d) surfaces formed at the “polymer-air” boundary (a, c) and the “polymer-support” boundary (b, d).

Figure 8 illustrates the typical differences in surfaces of PU films. As it can be seen, at surface formed at the boundary “polymer-support” (fig. 8, *a*) the size and quantity of crystals are larger. Where as, at surface formed at the “polymer-air” boundary (fig. 8, *b*) the size and quantity of crystals are significantly smaller. For example, the mean size of crystals in LPU-1%Eu changes from the one surface to another from 20  $\mu\text{m}$  to 0,5  $\mu\text{m}$ .

Detailed analysis of PUs surface properties depending on the boundary nature can give additional information.

### 3. Influence of metal chelate modifiers on surface properties of polyurethanes

The presence of metal chelate compounds in reaction mixture can influence the surface tension of the formed polyurethane. In (Lipatov, 1997) the surface properties were studied of PU with metal ions introduced through in four different ways. There are filling, metal ion cross-linking, metal ion chain-extending and diffusion of metal chelate compound from its solution to polymer being formed earlier. It has been shown that the surface properties of metal containing PU depend on metal quantity much less than on the way of metal chelate compound introduction in polymer. For example, the  $\gamma_{\text{sg}}$  of PU filled with  $\text{Cr}(\text{acac})_3$  (0.18% wt.) changes up to 8 mN/m. On the contrary the  $\gamma_{\text{sg}}$  of Pb (15% wt) cross-linked PU changes up to 0.3 mN/m as compared with metal free PU.

Obviously, the PU's surface structure depends on the boundary “polymer-support” or “polymer-air”. Data of ESCA and IR-spectroscopy by (Lipatova et al., 1987; Lipatova & Alexeeva, 1988) point on possibility of the chemical unequivalence of the polymer surfaces formed at the different boundaries. In addition in (Kozak et al., 2010) it was observed substantial difference in luminescence intensity at different surfaces of the PU films modified with europium (3+) chelate compounds. Therefore, the surface properties of europium containing LPU and CPU were compared for surfaces formed at the “polymer-air” and “polymer-support” boundary using measurement of contact wetting angle. The data obtained are listed in the table 4.

The values of surface tension of metal containing PU obtained using Wilgelmy method (with water as wetting liquid) (Lipatov et al., 1997) are consistent with values of the surface tension calculated using measurement of contact wetting angle (Table 5) of standard liquid.

The wetting angles at the „polymer-air” boundary for all of CPU and LPU are from 5.5 to 15.5 degrees less than the wetting angles at the „polymer-support” boundary (table 4). The difference between relative values of surface tension ( $\gamma_1-\gamma_2$ ) takes values from 2.18 to 5.59 mN/m. As it is known, the higher compound polarity is the greater surface energy and surface tension it possesses. Obtained results allow conclude that PU surface formed at the „polymer-air” boundary is enriched with more polar groups (e.g. urethane ) and PU surface formed at the „polymer-support” boundary is enriched with less polar groups (e.g. glycol segments).

Concentration of PU less polar groups that form the weak complexes with metal chelate compound at the „polymer-support” boundary can facilitate the partial segregation of metal containing centres at this boundary. That conclusion is consistent with microscopic data and photoluminescence measurements.

System	$\theta$ , degree		$\gamma_{EG-PU}$ , mN/m		$\Delta\theta = \theta_2 - \theta_1$ , degree	$\Delta\gamma = \gamma_1 - \gamma_2$ , mN/m
	$\theta_1$ (the „polymer-air” boundary)	$\theta_2$ (the „polymer-support” boundary)	$\gamma_1$ (the „polymer-air” boundary)	$\gamma_2$ (the „polymer-support” boundary)		
CPU-0	55	65	38,06	34,50	10	3,56
CPU-1% Eu	53	64	38,74	34,67	11	4,07
CPU-3% Eu	51	66	39,39	33,95	15	5,44
CPU-5% Eu	56	64	37,70	34,77	8	2,93
LPU-0	58	70	37,00	32,45	12	4,55
LPU-1% Eu	61	67,5	35,95	33,43	6,5	2,52
LPU-3% Eu	67,5	73	33,43	31,25	5,5	2,18
LPU-5% Eu	59	74,5	36,63*	30,64	15,5	5,99

$\theta_1, \theta_2$  – the wetting angles at the „polymer-air” and the „polymer-support” boundaries, respectively, degree;  
 $\gamma_1, \gamma_2$  – the surface at the „polymer-air” and the „polymer-support” boundaries, respectively, mN/m;  
 \* the unbalanced wetting angles

**Table 5.** The contact wetting angle ( $\theta$ ) and surface tension ( $\gamma$ ) of PU films. The standard liquid is ethylene glycol (EG)  $\gamma_{EG-air} = 48,36$  mN/m.

Varying of the metal containing modifier amount (from 0,5 to 5% wt.) in CPU practically does not affect surface tension. In the contrary, change of metal chelate compound content in LPU from 0,5 to 3%wt. lead to decreasing of both  $\gamma_1$  and  $\gamma_2$ .

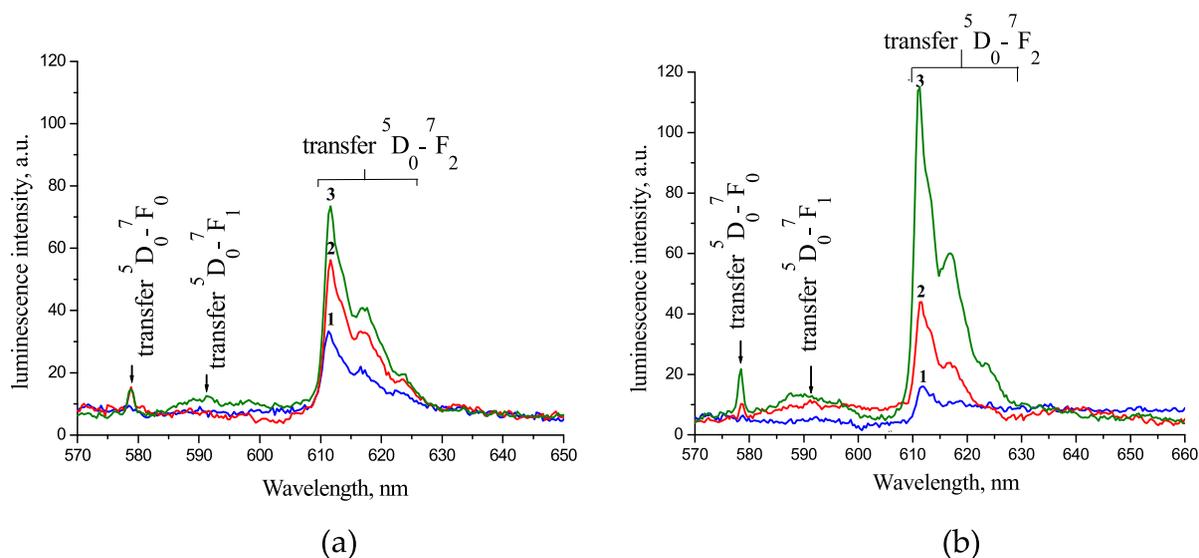
The difference of the tendency in changing of surface tension in LPU and CPU clearly depend on polymer topology. Different PU topology results in different segmental mobility of the polymer, that agrees with DRS data. This effect described detailed in Section 5 and Section 2.4. At that time we can't formulate the certain reason for non monotonous influence of the modifier's amount on the surface tension.

#### 4. The influence of polymer topology and modifier content on the luminescent properties of segmented polyurethanes

According to (Lobko et al., 2010) the PU matrix can intensify the photoluminescence of europium chelate compounds introduced into polymer *in situ*. Taking into account that immobilization *in situ* of metal chelate compounds in polymer matrix can influence both structure and properties of the hybrid system (Nizelskii & Kozak, 2006; Nizelskii et al., 2005) the investigation of rare-earth metal compounds in polymeric environment is a way for creation of new optically active materials.

LPU and CPU modified with Eu(3+) chelates when exposed in 365 nm UV-light demonstrate the intensive photoluminescence in red region. Figure 9 represents the luminescent spectra of LPU and CPU, modified with various amount of Eu(fod)<sub>3</sub>.

The luminescent spectra of europium containing PU are diffuse, while luminescence spectrum of Eu(fod)<sub>3</sub> is enough well-resolved. According to (Poluectov et al., 1989) the luminescence spectra of europium β-diketonate solutions contain bands corresponding to the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>i</sub> -transitions (where *i* = 0,1,2,3,4). The spectra of Eu β-diketonate in PU matrices demonstrate the intensive wide band of photoluminescence in the region of λ=610-635 nm (<sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub>-transition), narrow band λ=660 nm (<sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>3</sub> -transition) and bands of <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>0, 1, 4</sub>-transitions (580, 600,700 nm, accordingly) of low-intensity. It is possible to explain the diffuse spectrum of luminescence of europium containing PU in the region of λ =610-635 nm by distortion of the Eu (3+) chelate geometry in PU due to complex “polymer-metal chelate compound” formation and due macroligand steric hindrances.

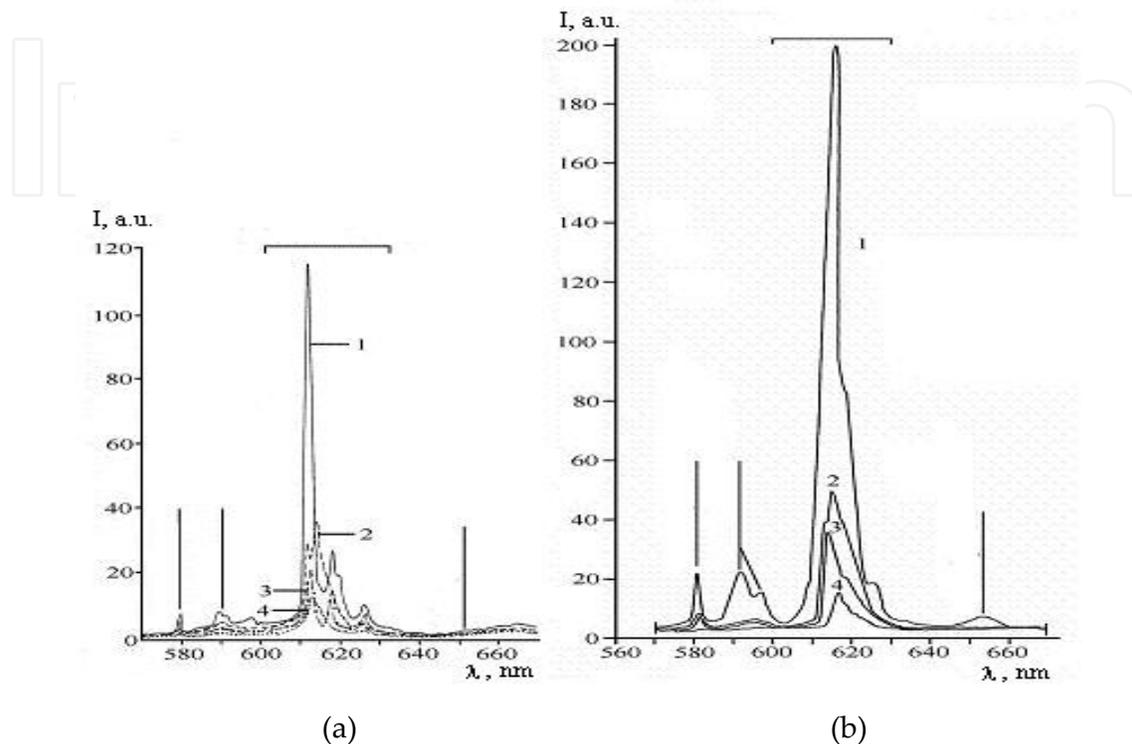


**Figure 9.** The spectra of luminescence of LPU (a) and CPU (b), modified with europium chelate ( $\lambda_{UV} = 365$  nm): (1) 0.5%; (2) 1%; (3) 5%.

The intensity of PU-Eu luminescence depends both on the europium chelate content and polymer topology. The luminescence intensity increases with increasing of europium chelate compound content. The luminescence intensities of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition (λ=612nm) for LPU with 05%, 1% and 5%wt. of Eu(fod)<sub>3</sub>, correspond as 1:1,8:2,4. The relationship of luminescence intensity *vs.* modifier percentage in CPUs is linear (1:3,3:9,2). The CPU-Eu with low modifier content has the lower luminescent intensity as compared with LPU-Eu. Where as CPU-5%Eu luminescence intensity is 1,5 higher, than LPU-5% Eu luminescence intensity. Taking into account data of Sections 2, 3, 6 we can suppose that due to difference in PU topology this effect is associated with higher concentration of polymer photo transmitting sites near the modifier in CPU as compared with LPU.

The tetra coordinated Eu (3+) chelate compounds with different additional ligands in an external coordination sphere were used to analyse the influence of additional coordination

of europium chelate compounds on the intensity of their luminescence. The fig. 10, a illustrates the luminescent spectra of isolated Eu (3+) chelate compounds. The fig. 10, b represents the spectra of luminescence of CPU films, modified with 1%wt. of Eu (3+) compounds.



**Figure 10.** The luminescence spectra ( $\lambda_{ex.} = 365$  nm) of the europium (3+) chelate compounds (a) and of CPU films with 1%wt. of these chelate compounds (b): Eu(TTA)<sub>3</sub>phen (1); Eu(TTA)<sub>3</sub>TPPO (2); Eu(TTA)<sub>3</sub> (3); Eu(fod)<sub>3</sub> (4)

As it can be seen the luminescence of Eu (3+) chelate compounds introduced into PU matrix (only 1%wt.) is more intensive than luminescence of isolated metal chelate compounds (100% wt). In addition, the intensity of luminescence of tetra coordinated Eu(3+) chelate compounds (Eu(TTA)<sub>3</sub>phen and Eu(TTA)<sub>3</sub>TPPO) both isolated and introduced into CPU matrix, considerably exceeds such intensity for 3-coordinated Eu(3+) chelate compound Eu(TTA)<sub>3</sub> that does not contain additional ligands The intensity of photoluminescence of Eu(fod)<sub>3</sub> also is considerably lower.

Estimation of Eu (3+) environment symmetry in various complexes via the coefficient of asymmetry ( $\eta$ ) defined as ratio of intensity of  $^5D_0 \rightarrow ^7F_2$  -transition to intensity of  $^5D_0 \rightarrow ^7F_1$  transition. (Haopeng et al., 2008) shows that the greatest coefficient of asymmetry ( $\eta = 9$ ) has CPU-1%Eu(TTA)<sub>3</sub>phen characterized by the greatest intensity of luminescence. Consequently, the presence of additional ligand in the external coordination sphere of Eu (3+) favours increasing of luminescence intensity. Then increasing of Eu-chelate compounds luminescence intensity in PU can be explained in particular by additional coordination of lanthanide ion with the functional groups of PU and/or by formation of

donor-acceptor complexes between aromatic fragments of PU and quasi-aromatic chelate rings of chelate compounds of rare-earth metals.

### 5. Dielectric relaxation and conductivity

The dielectric properties of PU were studied by broad band DRS measurements in wide range of temperature (-40 to 120 °C). The data are analyzed within the various formalisms. The direct current conductivity was both measured using two-electrode method and was estimated using DRS complex electric resistance  $\sigma_{dc} = d/(AR_{dc})$  and  $Z''(Z')$  isotherms (Cole-Cole diagram). Figure 11-13 illustrate obtained dielectric spectra. Calculated conductivity values are listed in Table 5.

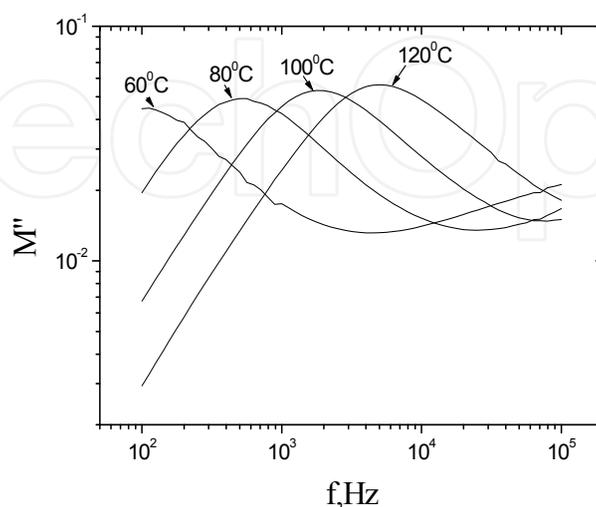
According to two-electrode method the direct current conductivity of PU can drastically change in the presence of some metal chelate compounds. At the room temperature  $\sigma_{dc}$  for the CPU-5%Eu increases by one order as compared with CPU-0. In the presence of polyheteronuclear metal chelate compounds  $\sigma_{dc}$  enlarges from 2 to 3 orders (fig. 13, table 5). DRS analysis of complex dielectric permittivity as well as complex admittance  $\sigma^*$ , complex electrical modulus  $M^*$  and impedances  $Z'$ ,  $Z''$  allows reveal the nature of the observed conductivity.

System	a) $\sigma_{dc}$ , Sm/cm 20°C	b) $\sigma_{dc}$ , Sm/cm 40°C	System	a) $\sigma_{dc}$ , Sm/cm 20°C	b) $\sigma_{dc}$ , Sm/cm 20°C
CPU-0	1,78 $10^{-12}$	1,3 $\cdot 10^{-11}$	LPU-0	4,65 $\cdot 10^{-12}$	4.6 $\cdot 10^{-12}$
CPU-Cu	2,86 $10^{-11}$	2 $\cdot 10^{-9}$	LPU-Cu	4,25 $\cdot 10^{-11}$	3.8 $\cdot 10^{-11}$
CPU-Cu <sub>2</sub> Zn	2,47 $10^{-9}$	0,7 $\cdot 10^{-8}$	LPU-Cu <sub>2</sub> Zn	1,51 $\cdot 10^{-9}$	1.2 $\cdot 10^{-10}$
*CPU <sup>2000</sup> -0	-	1 $\cdot 10^{-10}$	*CPU <sup>2000</sup> -Cu <sub>2</sub> Zn	-	1 $\cdot 10^{-7}$
*CPU <sup>2000</sup> -Cu	-	1 $\cdot 10^{-9}$			

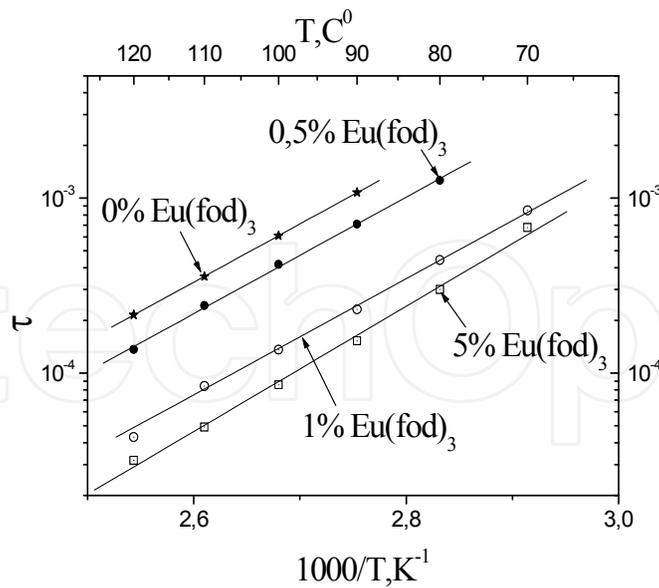
\* The PU films synthesized with PPG-2000

a)  $\sigma_{dc}$  measured using two-electrode method and b)  $\sigma_{dc}$  obtained using DRS data

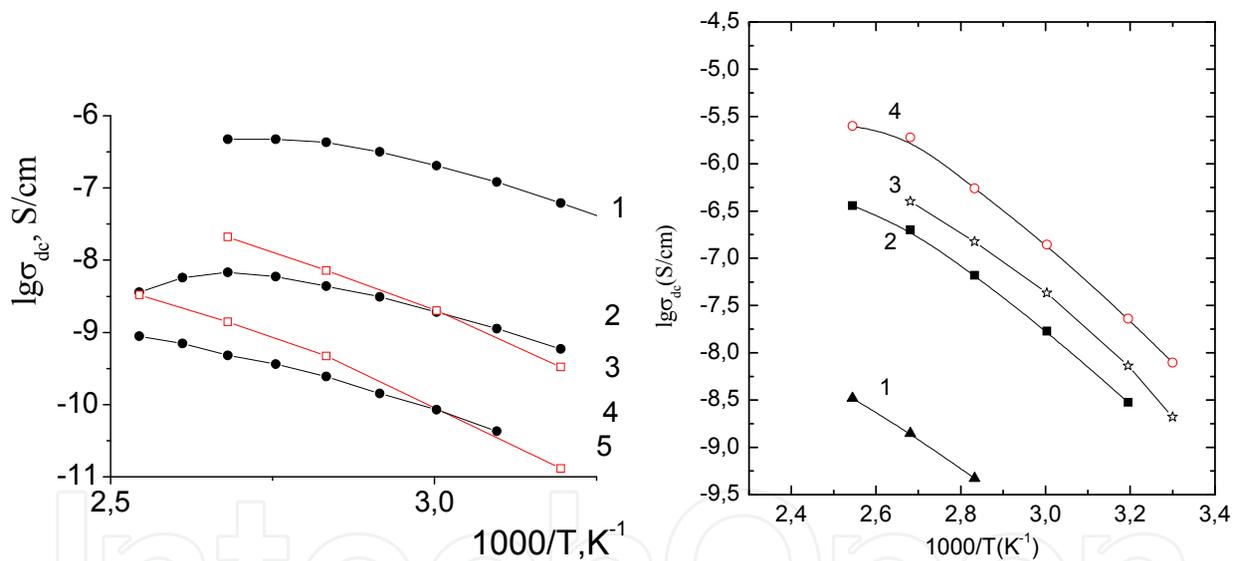
**Table 6.** PUs conductivity at a direct current



**Figure 11.** Log-log plots of the imaginary part of complex electrical modulus  $M''$  vs. frequency for CPU-5%Eu at several temperatures



**Figure 12.** The thermal dependence of the relaxation time ( $\tau_{\max}$ ) for the CPU with various content of Eu (3+) chelate compound.



**Figure 13.** The  $\log \sigma_{dc}$  vs.  $1/T$  for CPU: (a) CPU with various length of flexible component: CPU (PPG-2000) – 1%Cu<sub>2</sub>Zn (1); CPU (PPG-1000) – 1% Cu(eacac)<sub>2</sub> (2); CPU (PPG-2000) – 1% Cu(eacac)<sub>2</sub> (3); CPU (PPG-2000) – 0 (4); CPU (PPG-1000) – 0 (5) and (b) CPU-0 (1) and CPU-Cu<sub>2</sub>Zn formed in the presence of various solvents: 1, 4-dioxane (2); dichloromethane (3) and DMFA (4).

The curves on the fig. 11 have well defined maxima in temperature region of 60 to 120°C. According to (Pathmanatham & Johari, 1990; Kyritsis & Pissis, 1997) these maxima correspond to conductivity relaxation. Increasing of temperature is accompanied with shift of conductivity relaxation maxima to higher frequencies (fig. 11). The fact concerned to increasing of segmental mobility in PU. The metal chelate compounds introduction and increasing of their content in the system result in increasing of PU segmental mobility.

Experimental dependences of relaxation time ( $\tau_{\max} = \frac{1}{2\pi f_{\max}}$ ) in log scale vs.  $1/T$  (fig. 12) for metal-containing PU are linear indicating the Arrhenius-type of temperature dependence of  $\tau_{\max}$ .

Decreasing of  $\tau_{\max}$  value with the increasing of Eu(3+) content in PU confirm increasing of macro chains mobility in metal-containing CPU (Kozak et al., 2006). The activation energy of conductivity relaxation for CPU-0, CPU-0,5%Eu, CPU-1%, CPU-5% are approximately similar. Experimental dependences of  $\log\sigma_{dc}$  vs.  $1/T$  are non-Arrhenius both for PU-0 and metal containing PUs. It fits the theoretical curves of Vogel–Tamman–Fulcher (VTF) equation  $\sigma_{dc} = \sigma_0 \exp(-B/(T-T_0))$  (fig. 13) indicating influence of the PU free volume on charge transport. The results obtained give evidence of significant influence of structural organization in the modified PU on its conductivity level.

As it can be seen PU's direct current ( $\sigma_{dc}$ ) conductivity grows with increasing of temperature and that is characteristic to ionic conductivity. The metal ion participation as current carrier is unlikely because to small amounts of metal ion in the modified PUs (~ 0.025-0.25% wt.). That fact and coordination immobilization of the modifiers in polymer makes unlikely increasing of the conductivity due to the metal chelate compound conductive properties. On the other hand ionic mechanism of conductivity and adequate amount of protons presented in PU matrix as well as observed increasing of polymer chain mobility in modified PU allows us to suppose proton participation in the process of charge transport.

Comparison of direct current conductivity of CPU based on PPG-2000 with conductivity of CPU based on PPG-1000 shows increasing of conductivity at the direct current of such system up to  $10^{-7} \text{Sm/sm}$  at the  $40^\circ\text{C}$  due "softening" of PU. Nevertheless it can be seen that conductivity level of maximum soft LPU is at least one order lower than conductivity of CPU.

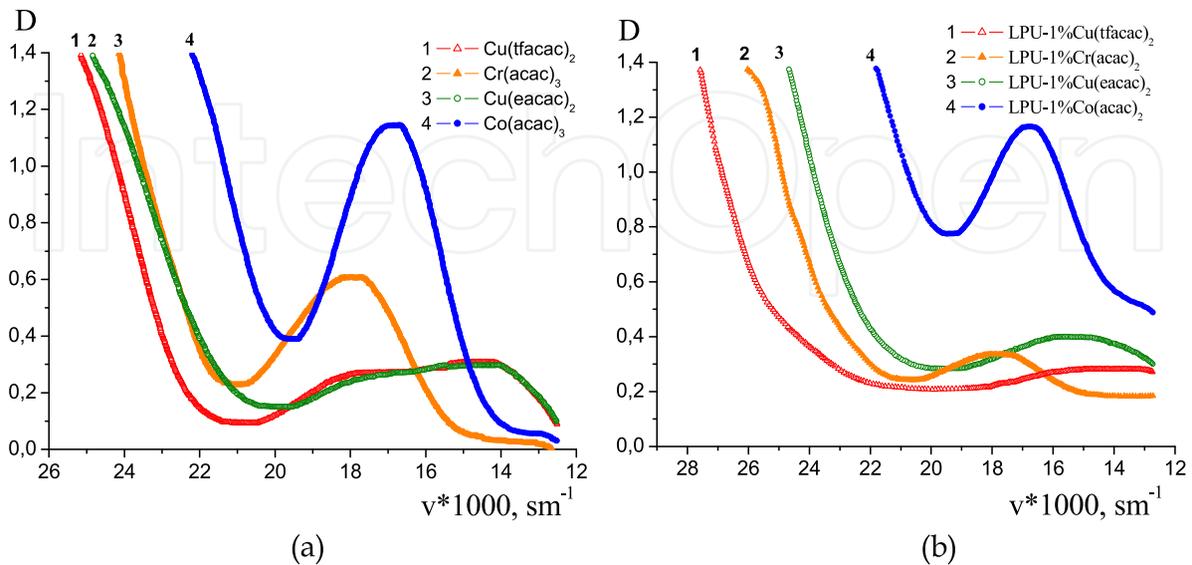
## 6. "Metal chelate compound - polymer" complexing and formation of the additional network of coordination bonds in metal containing PU

Mutual influence of metal chelate compound and polymer matrix due to complex formation is a decisive reason of observed changes of structural, dynamic, relaxation etc. characteristics of the metal contained PU. The complexing of metal chelate compounds with PU matrix was analysed using electron spectroscopy and EPR.

### 6.1. The complexing of the metal chelate compound with PU matrix according to the electron spectroscopy

The electron spectroscopy allows analyse both character of complexing of metal chelate compound with the polymer matrix and state of metal chelate compound in PU. The electron spectra of transition and rare-earth metal chelate compound in PU indicate presence of the band of  $d-d$ -transitions for the transition metal chelate compound introduced into PU (fig.14) and band of  $\pi-\pi$ -transitions for the rare-earth metal chelate compounds

introduced into PU. That points on saving of chelate structure of the complexes in polymer matrix. While the change the band intensity, its broadening and shift to a long-wave region testifies their participation in complexing with PU.



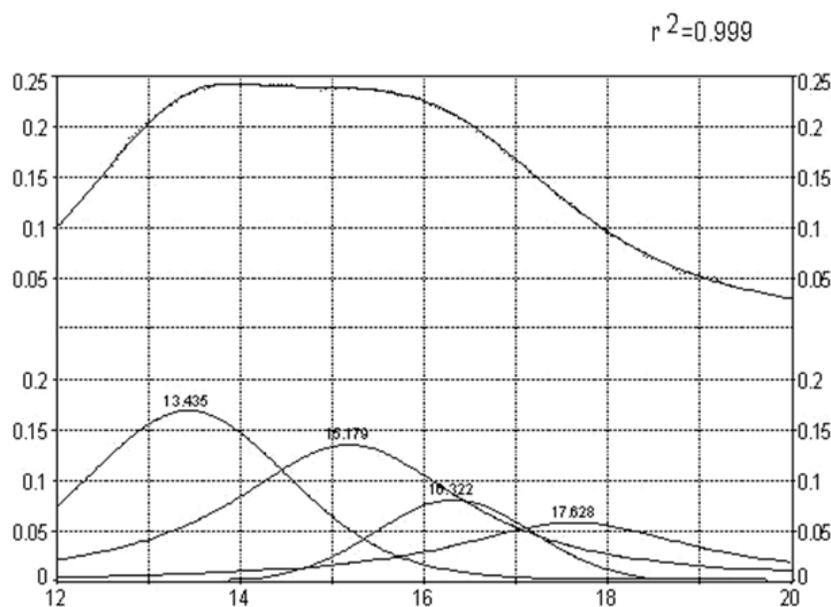
**Figure 14.** The electron spectra of transition metal chelate compounds in dichloromethane (a) and LPU (b):  $\text{Cu}(\text{tfacac})_2$  (1), 1% $\text{Cr}(\text{acac})_3$  (2),  $\text{Cu}(\text{eacac})_2$  (3);  $\text{Co}(\text{acac})_3$  (4); LPU  $\text{Cu}(\text{tfacac})_2$  ( $\epsilon = 28 \text{ l/mol}\times\text{sm}$ ) (1); LPU-1% $\text{Cr}(\text{acac})_3$  ( $\epsilon = 33 \text{ l/mol}\times\text{sm}$ ) (2); LPU-1% $\text{Cu}(\text{eacac})_2$  ( $\epsilon = 40 \text{ l/mol}\times\text{sm}$ ) (3); LPU-1% $\text{Co}(\text{acac})_3$  ( $\epsilon = 117 \text{ l/mol}\times\text{sm}$ ) (4)

Figure 14 represents comparison of electron spectra in the visible region of the LPU films with 1%wt. of transition metal (copper, chrome, cobalt) chelate compounds (fig. 14, a) and the spectra of this metal chelate compounds dissolved ( $c = 10^{-2} \text{ M}$ ) in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) (fig. 14, b).

In addition to described above changes in electron spectra the influence of fluorine on complex ability of metal chelate compound in PU is evident due to, the rise of absorption level ( $\epsilon = 40 \text{ l/mol}\times\text{cm}$ ) and hypsochromic shift of maxima of band of d-d-transitions for LPU - 1%  $\text{Cu}(\text{eacac})_2$  as compared with LPU-1%  $\text{Cu}(\text{tfacac})_2$  that have fluorine in ligand ( $\epsilon = 28 \text{ l/mol}\times\text{cm}$ ). Fig. 15 illustrates the detailed analysis of electron transitions of copper ion in  $\beta$ -diketonates (4 transitions for  $D_{2h}$  symmetry). Calculated maxima positions of Gaussian components of adsorption band corresponding to electron d-d-transitions of copper ion for  $\text{Cu}(\text{tfacac})_2$  and  $\text{Cu}(\text{eacac})_2$  in solution and in PU are listed in the table 6.

System	$\nu, \text{cm}^{-1}$			
	$d_{\text{uH}} \rightarrow d_{z^2}$	$d_{\text{uH}} \rightarrow d_{x^2-y^2}$	$d_{\text{uH}} \rightarrow d_{xz}$	$d_{\text{uH}} \rightarrow d_{yz}$
$\text{Cu}(\text{tfacac})_2$ in $\text{CH}_2\text{Cl}_2$	13658	15386	17930	19579
LPU -1% $\text{Cu}(\text{tfacac})_2$	13435	15179	16322	17628
$\text{Cu}(\text{eacac})_2$ in $\text{CH}_2\text{Cl}_2$	13715	15376	16686	18261
LPU-1% $\text{Cu}(\text{eacac})_2$	12771	14497	16059	17738

**Table 7.** The allocation of Gaussian components of copper chelate compounds adsorption band.



**Figure 15.** The adsorption band of LPU+1%Cu(tfacac)<sub>2</sub> with Gaussian components allocation.

The maxima of  $d_{xz}$  and  $d_{yz}$  transitions of Cu(2+) ion in copper chelate compounds, immobilized in PU matrix are shifted to the long-wave region, as compared to corresponding transitions of copper chelate compounds in solution (table 6). Visible broadening of the  $d_{z^2}$  component of absorption band of Cu (2+) chelate compounds in PU indicates the prevalence of axial coordination of macro ligand in “PU-metal chelate compound” complexes.

## 6.2. Complex formation in the “polymer-modifier” system according to EPR data

The EPR data confirm the complexing between the metal chelate compound and PU functional groups. The state of paramagnetic Cu(2+) containing chelate compounds in PU can be directly analyzed using EPR due to sensitivity of spin-electron parameters  $A_{II}$  and  $g_{II}$  (see table 7) of the tetragonal copper chelate compounds to symmetry and chemical nature of the copper nearest environment.

Decreasing of  $A_{II}$  and increasing  $g_{II}$  of Cu(acac)<sub>2</sub>, Cu(tfacac)<sub>2</sub>, Cu(eacac)<sub>2</sub> and (Cu<sub>2</sub>Zn<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>(HDea)<sub>4</sub>)Br<sub>2</sub> immobilized in PU as compared with undisturbed compounds indicate the participation of the modifiers in the complexing with PU electron donor groups.

Figure 16 illustrates the representative EPR spectra of some copper containing modifiers both isolated and immobilized in PU with different topology (linear and cross-linked). The EPR spectra of polyheteronuclear powdered crystalline samples have anisotropic shape with weakly resolved HFS due to broadening of the spectrum components and possible tetrahedral distortion of the copper ion surrounding in the polyatomic complex. Immobilization of such chelate compounds in a PU network resulted in decreasing of the EPR signal intensity.

System	$g_{\parallel}$	$A_{\parallel} \times 10^{-4}$ $\text{cm}^{-1}$	$g_{\perp}$	$A_{\perp} \times 10^{-4}$ $\text{cm}^{-1}$	$g^0$	$a_0^* \times 10^{-4}$ $\text{cm}^{-1}$
$^1\text{Cu}(\text{tfacac})_2$ *	2,271	187	2,052	23	-	-
CPU-1% Cu(tfacac) <sub>2</sub>	2,275	172	2,059	21	2,131	71
	2,290	151			2,136	64
LPU-1% Cu(tfacac) <sub>2</sub>	2,283	162	2,049	19	2,127	67
	2,302	141			2,133	60
$^1\text{Cu}(\text{eacac})_2$ *	2,276	187	2,055	22	2,128	68
CPU-1% Cu(eacac) <sub>2</sub>	2,249	150	-	-	-	-
LPU-1% Cu(eacac) <sub>2</sub>	2,298	173	-	-	-	-
$^1\text{Cu}(\text{acac})_2$ *	2,250	189	2,052	24	2,118	75
CPU-1% Cu(acac) <sub>2</sub>	2,269	182	-	-	-	-
LPU-1% Cu(acac) <sub>2</sub>	2,254	188	2,052	29	2,119	82
$^2(\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HDea})_4)\text{Br}_2$	2,370	122	-	-	-	-
CPU-1% CuZn	2,370	132	-	-	-	-
	2,300	142				
LPU-1%CuZn	-	-	-	-	-	-

<sup>1</sup>)undisturbed Cu(2+) complex in glassy matrix chloroform/toluene (40/60) (at -196°C)

<sup>2</sup>) powder of polycrystalline sample

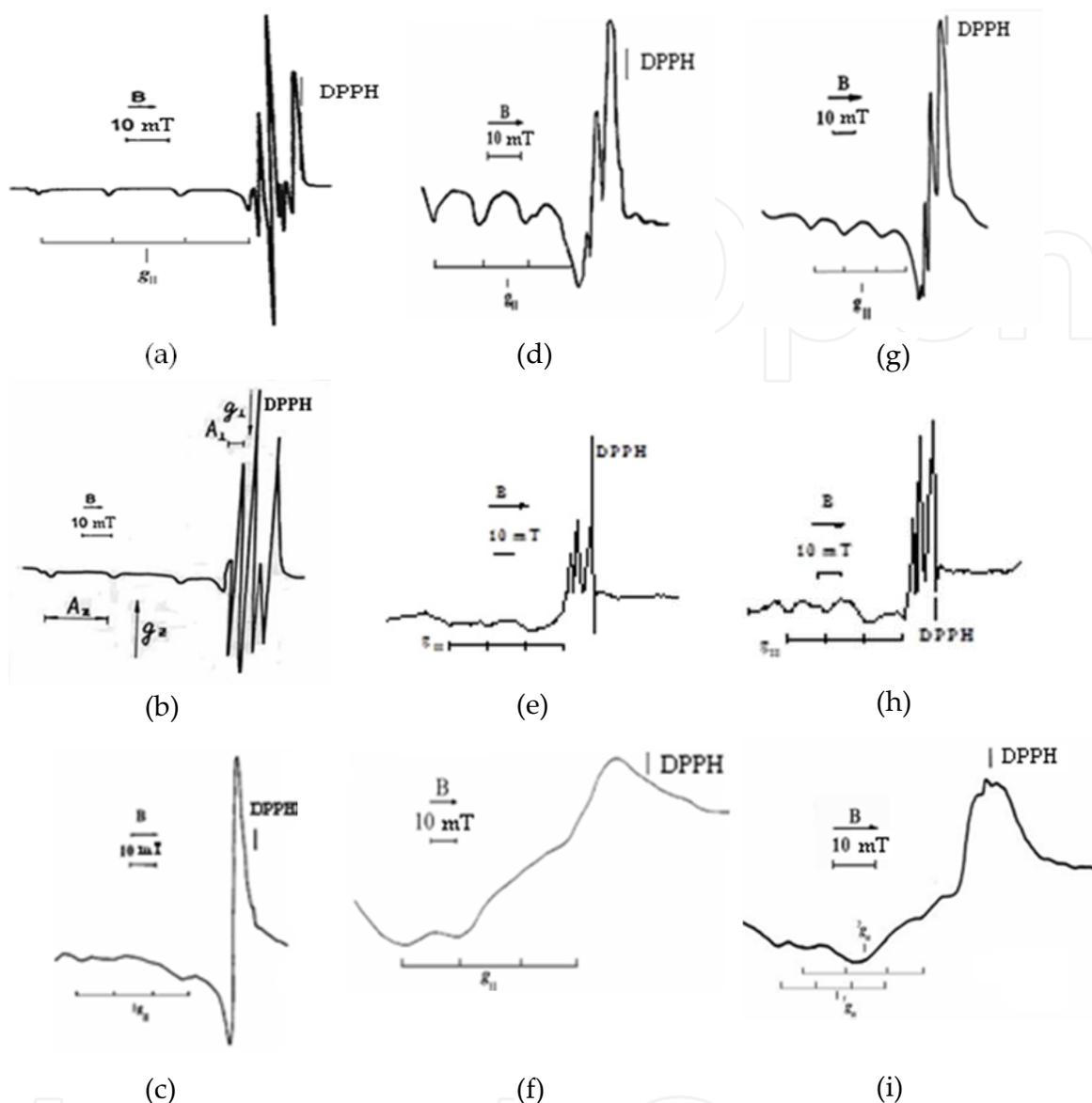
\* (Lipatova & Nizelskii, 1972)

**Table 8.** Electron-spin parameters of isolated and polymer immobilized copper complexes.

The most reasonable explanation for this effect is distortion of the modifier's symmetry or geometry in PU-CuZn. The shape of EPR signal in PU network modified with  $(\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HDea})_4)\text{Br}_2$  indicates formation of complexes of various content and structure.

### 6.3. Low molecular probes dynamic and formation of additional network of the coordination bonds in metal containing polyurethanes

Using QENS and EPR with paramagnetic probes of various natures it was shown that complex formation of metal containing modifier with macro chains results in appearance of additional spatial obstacles for probe diffusion as compared with metal free network. The dynamic of low molecular probes and complex formation in the nanostructured polyurethane network containing Co (3+) chelate compounds immobilized *in situ* were analyzed.



**Figure 16.** EPR – spectra of matrix isolated  $\text{Cu}(\text{eacac})_2$  (a),  $\text{Cu}(\text{acac})_2$  (b),  $(\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HDea})_4)\text{Br}_2$  (c) in chloroform-toluene at  $-196^\circ\text{C}$ ; LPU with 1%wt. of  $\text{Cu}(\text{eacac})_2$  (d),  $\text{Cu}(\text{acac})_2$  (e),  $(\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HDea})_4)\text{Br}_2$  (f) and CPU with 1%wt. of  $\text{Cu}(\text{eacac})_2$  (g),  $\text{Cu}(\text{acac})_2$  (h),  $(\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HDea})_4)\text{Br}_2$  (i).

According to EPR data obtained using complex spin probe (Kozak et al., 2006) it was demonstrated that in cobalt containing CPU the complexes “polymer-metal chelate compound” of two types are formed. The analysis of rotational diffusion of nitroxyl spin probe TEMPO (see table 2) reveals the decreasing of PU segmental mobility due metal chelate compound introduction and/or its content increasing. The dynamic of solvent molecules diffusion in swelled CPU-0, CPU-5%Co films and in probe liquid was analysed to compare the ratio of one-particle and collective modes of the solvent molecules motion.

System	$D \cdot 10^{-6}$ , cm <sup>2</sup> /c	$D^F \cdot 10^{-6}$ , cm <sup>2</sup> /c	$D^L \cdot 10^{-6}$ , cm <sup>2</sup> /c	$D^L/D$ , %
Probe liquid	3,52	3,18	0,35	8,0
The solution of Co(acaca) <sub>3</sub> 5%wt. in the probe liquid	3,33	3,04	0,29	8,7
CPU-0 (CH <sub>2</sub> Cl <sub>2</sub> )	2,71	2,40	0,31	11,5
CPU-Co5% (CH <sub>2</sub> Cl <sub>2</sub> )	1,85	1,32	0,53	28,6
CPU-Co5% (DMF)	1,25	0,89	0,36	28,8

where  $D^F$  – one-particle (“Frenkel”) diffusion coefficient ;  
 $D^L$  – collective (“Lagrangian”) diffusion coefficient.

**Table 9.** The diffusion parameters of the probe molecules in the swelled PU films

The sharp decreasing of both the general and one-particle component of diffusion coefficient for the metal containing PU as compared with the metal-free PU indicates the appearance of the spatial hindrances for the liquid molecule dynamics.

## 7. Conclusion

Immobilization *in situ* mono- and polyheteronuclear chelate compounds of transition and rare-earth metal in linear and cross-linked polyurethanes results in nanoscale structuring of forming polymer and is accompanied with polymer matrix enrichment by the nanosize heteroligand macro complexes of metal formed simultaneously with organic nanosize structures characteristic for metal-free polymer. Nanostructuring of formed in this way polyurethane favours creation of a new hierarchy in structural organization of the polymer as compared with metal free system as well as changes in dynamic, relaxation, optical, dielectric, surface etc. properties of the modified polyurethane.

Analysis of structural heterogeneity of metal-modified polymer indicates existence of two types of nanosize heterogeneities in the bulk of polyurethane. One of them is inherent to segmented PU and another is generated in the presence of transition metal chelate compound. The structural heterogeneity of PU influences the local segmental mobility of macro chains, resulting in “dynamic heterogeneity” as well as in “thermodynamic heterogeneity” of the systems.

The possible origin of the formation of the ordered micro regions is segmental structure of PU containing the soft and hard blocks with different complex ability relative to metal chelate compound. The PU’s surface structure depends on the boundary “polymer-support” or “polymer-air”. Concentration of PU less polar groups that form the weak complexes with metal chelate compound at the „polymer-support” boundary can facilitate the partial segregation of metal containing centres at this boundary.

The essential increasing of luminescence intensity of the rare-earth metal in the polyurethane environment is a way for creation of new optically active materials. The intensity of PU-Eu luminescence depends both on the europium chelate compound content and polymer topology. Contrary to LPU the relationship of luminescence intensity *vs.* modifier percentage in CPUs is linear.

Increasing of the polyurethane conductivity to semi-conducting level is caused by the drastic increasing of macro chain mobility in the presence of polyheteronuclear modifiers. Conductivity level of LPU is at least one order lower than conductivity of CPU.

The results obtained indicate significant influence of structural organization of the modified polyurethane on its properties. The effect is caused by complex formation between metal chelate compound and functional groups of the forming polymer. The analysis of dynamic of low molecular probes and complex formation in the nanostructured polyurethane gives experimental evidence of existence of additional coordination bond network in metal-contained polyurethanes.

## Author details

Nataly Kozak and Eugenia Lobko

*Institute of Macromolecular Chemistry National Academy of Sciences of Ukraine, Ukraine*

## Acknowledgement

We would like to express our sincere gratitude to Professor Svetlana B. Meshkova (A. V. Bogatsky Physic-Chemical Institute of National Academy of Sciences of Ukraine, Odessa) and Professor Vladimir N. Kokozay (Taras Shevchenko Kyiv University) for synthesized heteroligand rare-earth metal's and polyheteronuclear chelate compounds, respectively.

## 8. References

- Bershein, V.A. & Yegorov, V.M. (1990). *Differential Scanning Calorimetry in Polymer Physic.* (in Russ.). Chemistry, ISBN 5-7245-0555-X, St. Petersburg
- Buchachenko, A. L., Wasserman, A.M., Alexandrova, T.A. et al. (1980). Spin Probe Studies in Polymer Solids, In: *Molecular Motions in Polymers by ESR*, R.F. Boyer & S.E. Keinath, (Eds.), 33-42, ISBN 3718600129, Harwood Academic Publisher, Chur, Switzerland
- Bulavin, L.A.; Karmazina, T.V.; Klepko, V.V.; Slisenko, V.I. (2005). Neutron spectroscopy of condensed medium. (in Russ.). *Akademperiodica*, ISBN 966-360-009-8, Kyiv

- Kovarskii, A.L. (1996). Spin Probes and Labels. A Quarter of a Century of Application to Polymer Studies, In: *Polymer Yearbook*, R.A. Pethrick, (Ed.), 113-139, ISBN 9783718659142, Harwood, Switzerland
- Kozak, N.V.; Kosyanchuk, L.F.; Lipatov, Yu.S. et al. (2000). Effect of Zn<sup>2+</sup>, Cr(2+) and Ni<sup>2+</sup> Ions of Cross-linked Segmented Polyurethanes. *Polymer Science*, Ser. A, Vol. 42, № 12, (June-August 2000), pp. 1304-1309, ISSN 0965-545X
- Kozak, N.; Nizelskii, Y.; Mnikh, N. et al. (2006). Formation of Nanostructures in Multicomponent Systems Based on Organic Polymer and Coordination Metal Compound. *Macromolecular Symposia*, Vol. 243, (November 2006), pp. 243-262, ISSN 1521-3900
- Kozak, N.V.; Lobko, Eu.V; Perepelitsina, L.M. et al. (2010). The Surface Characteristics of Polyurethanes, Contained  $\beta$ -diketonate Europium (3+). (in Ukr.). *Ukrainian Chemistry Journal*, Vol. 76, № 8, (June-August 2010), pp. 121-126, ISSN 0041-6045
- Kratky, O.; Pilz, I.; Schmitz, P.J. (1966). Absolute intensity measurement of small-angle x-ray scattering by means of a standard sample. *Journal of Colloid Interface Science*, Vol. 21, №1, pp. 24-34, ISSN 1095-7103
- Kyritsis, A. & Pissis, P. (1997). Dielectric studies of polymer-water interactions and water organization in PEO/water systems. *Journal of Polymer Science: Ser. B, Polymer Physics*, Vol. 35, (July 1997), pp. 1545-1560, ISSN 0965-545X
- Lipatova, T. E. & Nizelskii, Yu.M. (1972). Complex Forming and Mechanism of the Catalysis of the Reaction Urethane Formation in situ  $\beta$ -diketonate of metals. (in Russ.). In: *The Successes of the Polyurethane Chemistry*, Yu. S. Lipatov, pp. 214-244, Naukova Dumka, Kyiv
- Lipatova, T.E.; Shylow, V.V., Alexeeva, T.T.; et al. (1987), The Influence of the Support Character on the Structure of the Linear Polyurethanes Surface. (in Russ.). *Polymer Journal*, Seria B, Vol. 29, № 4, (December 1987), pp. 55-260, ISSN 1560- 0904
- Lipatova, T.E. & Alexeeva, T.T. (1988). The spectroscopy investigated of the surface of segmented polyurethanes. (in Ukr.). *The Ukrainian Chemistry Journal*, Vol. 54, № 6, (June 1988) , pp. 324 – 628, ISSN 0041-6045
- Lipatov, Yu. S.; Kosyanchuck, L. F.; Kozak, N. V et al. (1997). Effect of Metal Compounds on the Surface Properties of the Solid Polyurethanes being Formed in their presence. *Journal of Polymer Materials*, Vol. 14, № 3, (December 1997), pp. 63-268, ISSN 0970-0838
- Lipatov, Yu. S.; Kozak, N. V.; Nizelskii, Yu. M. et al. (1999). Effect of Metal Compounds on the Physical Aging of Poly (urethanes). *Polymer Science*, Series A, Vol. 41, №8, (September 1999), pp. 1308-1315, ISSN 0965-545
- Lobko, Eu.V; Kozak, N.V.; Meshkova, S.B. et al. (2010). The Photoluminescence of Polyurethanes, which Modified by the Chelate Compounds of threes- and tetra coordinated europium (3+). (in Ukr.). *Polymer Journal*, Vol. 32, № 5, (December 2010), pp. 410-415, ISSN 1818-1724

- Nizelskii, Yu. N.; Shtompel, V.I.; Kozak, N.V. et al. (2005) The Nanostructure Heterogeneity of Polyurethane Films, Formed in the Presence of  $\beta$ -diketonate of Metals. *Report of National Academy of Science of Ukraine*, № 10, (October 2005), pp. 142-148, ISSN 1025-6415
- Nizelskii, Yu. & Kozak N. (2006). In Situ Nanostructured Polyurethanes with Immobilized Transition Metal Coordination Complexes. *Journal of Macromolecular Science, Part B*, Vol. 46, (April 2007), pp. 97-110, ISSN 0022-2348
- Pathmanatham, K. & Johari, G.P. (1990) Dielectric and Conductivity Relaxations in Poly (hema) and of Water in its Hydrogel. *Journal of Polymer Science: B*, Vol. 28., Issue 6, (May 1990), pp. 675-689, ISSN 0887-6266
- Pissis, P.; Kanapitsas, A. (1996). Broadband dielectric relaxation spectroscopy at  $10^{-4} - 10^{10}$  Hz. *Journal of the Serbian Chemical Society*, Vol. 61, № 9, pp.703-715, ISSN0352-5139
- Poluectov, N.S.; Kononenko, L.I.; Yefrushyna, N.P. et al. (1989). Spectrometric and Luminescence Methods of lanthanides detection, (in Russ.), Naukova Dumka, ISBN 512000749X, Kyiv
- Porod G. (1982). General theory. In: *Small-angle X-ray Scattering*. O.Glatter & O.Kratky (eds.), 17-51, Academic Press, ISBN 0-12-286280-5, London
- Saunders, J.H. & Frish, K.C., (1962). *Polyurethanes. Chemistry and Technology*. Part 1, Chemistry, Interscience Publisher, John Wiley&Sons, ISBN 0898745616, New York-London
- Skopenko, V.V.; Garnovsky, A.D.; Kokozay, V.M.; et al. (1997). *The direct synthesis of coordination compounds*, (in Russ.), Ventury, ISBN 966-570-025-1, Kiev
- Stompel, V.I. & Kercha, Yu.Yu. (2008) *The Structure of Linear Polyurethanes*, (in Ukr.), Naukova Dumka, ISBN 978-966-00-0699-7, Kyiv, Ukraine
- Schmidt, P.W.; Hight, R.J. (1960). Slit height corrections in small angle x-ray scattering. *Acta Crystallographia*, Vol. 13, (June 1960), pp.480-483, ISSN 0365-110X
- Tavana, H.; Gitiafroz, R.; Hair, M.L. et al. (2004). Determination of solid surface tension from contact angles: the role of shape and size of liquid molecules. *The Journal of Adhesion*, Vol. 80, (August 2004), pp. 705-725, ISSN 0021-8464
- Vasserman, A.M.; Kovarskii, A.L. (1986). *Spin Labels and probes in physical chemistry of polymers*", (in Russ.), Nauka, Moscow, Russia)
- Vinogradova, E.A.; Vassilyeva, O.Yu.; Kokozay, V.N. (2002). An incomplete cube-like array of Cu, Zn, I with O atoms from 2-dimethylaminoethanol formed directly from zero-valent metal powders. *Inorganic Chemistry Communications*, Vol. 5, (May 2001), pp. 19-22, ISSN 1387-7003
- Wirpsza, Z. (1993). *Polyurethanes: chemistry, technology and applications*. Elis Horwood Limited, ISBN 0-13-683186-9, London
- Yang, H.; Zhang, D.; Shi, L. et al. (2008). Synthesis and strong red photoluminescence of europium oxide nanotubes and nanowires using carbon nanotubes as templates. *Acta materialia*, Vol. 56, (March 2008), pp. 955-967, ISSN 13596454

Ying, J. (Ed.) (2002). *Nanostructured Materials: Advances in Chemical Engineering*, Massachusetts Institute of Technology, ISBN 0-12-008527-5, Cambridge

IntechOpen

IntechOpen