

Synthesis and Characterization of Some Polyazomethine-urethane-urea Metal-Complexes

STELIAN VLAD*, ANGELICA VLAD

Institute of Macromolecular Chemistry "Petru Poni", 41-A Aleea Grigore Ghica Voda, 700487 Iasi, Romania

A new type of polyurethane metal-complex was prepared by incorporating the transition metal ions such as copper (II), cobalt (II) and nickel (II), into polyazomethine-urethane-urea, containing functional groups. Polyazomethine-urethane-urea (PAMU) was synthesized from 5,5'-methylene-bissalicylaldehyde (MBS) by reaction with an urethane prepolymer based on polyethylene adipate diol (PEA), hexamethylene diisocyanate (HDI) and ethylene diamine (EDA), in DMF as solvent, using 0.5 wt % dibutyltindilaurate (DBTDL) as catalyst. The polymeric Schiff base was converted to the chelates of the metal salts. This complex was performed by mixing of the polyazomethine-urethane-urea, containing functional groups, with the metal salts in DMF as solvent. The polyurethane metal-complexes were characterized by FT-IR spectroscopy and elemental analysis. The polymer property investigated was their thermal stability which was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The aim of this work is to present a general idea of the various methods of preparation, properties, and applications of metal-containing polyurethanes.

Keywords: polyazomethine-urethane-urea, chelate polymers, metal-polymer complex

In the last decades, the polymer-metal complexes have been of interest to many researchers in the light of their potential applications in various fields and as an interdisciplinary area involving chemistry, electrochemistry, metallurgy, environmental protection, material science, etc., [1-4]. Polymer chemistry provides many opportunities for designing materials with desired properties by the use of selected monomers, different functionalities, and combinations [5-8]. The coordinative binding sites confer the ability to form polymer-metal complexes [9,10].

Many studies of coordination polymers were carried out by Korshak and co-workers [11-13]. In general, the resulting polymers were insoluble in common organic solvents, infusible, or melting only at high temperatures; which impeded their use in certain domains [14]. Polymer complexes may be classified into different groups according to the metal position on the chain, which is designed by the preparation technique. Many organic molecules contain functional groups (ligands) that actively interact with metal ions in solution by adsorption, ion exchange, or chelation/coordination/complexation. Water-soluble organics have limitations as reagents for metal-ion separations from aqueous solutions. However, if the ligand molecule(s) are grafted onto an insoluble matrix, the resulting ligand(s)-containing product becomes useful for separations applications related to metal recovery or remediation.

In the polyurethane field, the structure of a metal-complex system based on different metal salts interaction with a polyurethane matrix was studied by many authors [15,16]. The reaction between the metal ion and the polyurethane matrix depends on the nature of chelating group and the selective behavior of the resin considering the stability of the resultant metal-complexes.

Experimental part

Materials

The basic materials used in this research were: 5,5'-Methylene-bissalicylaldehyde (MBS) was prepared according to a known procedure [17] by the treatment of

salicylaldehyde with trioxane and sulphuric acid in an acetic acid solution (38% yield, mp 131-134°C); polyethylene adipate diol (PEA), Mw 2000 g/mol, C_{OH} 56 mgKOH/g; local market; 4,4'-diphenylmethane diisocyanate (MDI); ethylene diamine (EDA) – Fluka; dimethylformamide (DMF) – Fluka, as solvent; copper acetate monohydrate; nickel acetate tetrahydrate; cobalt acetate tetrahydrate; dibutyltindilaurate (DBTDL) – Fluka; as a catalyst; and dioxane- Fluka;

PEA was checked for the content of moisture and, if it would be necessary, dried under a vacuum until the content of water was below 0.03%. All the chemicals were used as such, without further purification.

Measurements

Infrared spectra of the samples were recorded with a Vertex 7 spectrometer equipped with a Golden Gate single reflection ATR (Attenuated Total Reflection) accessory, spectrum range 600-4000 cm⁻¹.

Elemental analysis

The thermal stability of polyurethanes was performed on a Derivatograf Q-1500 D apparatus (Hungary). The rate of the TGA scans was 10°C/min in air atmosphere. The initial weight of the samples was about 100 mg and the temperature range 30-700°C.

A Perkin-Elmer DSC-7 was used for thermal analysis and was operated under a nitrogen atmosphere at a heating rate of 10 °C/min and temperature range of -60°C to +150 °C. The glass transition temperature was determined from the midpoint of the DSC-curve.

Results and discussion

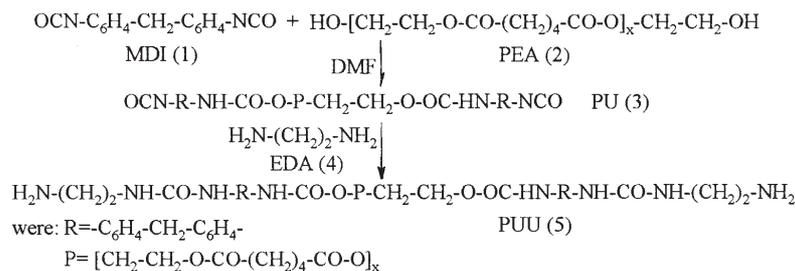
Procedure

The PUU (5) was synthesized via a standard two-step process as shown in scheme 1. The polyester (PEA) was dried under vacuum for 3 h at 80°C temperature. The MDI (1) and PEA (2) with a NCO:OH molar ratio of 2:1 were mixed in anhydrous DMF solvent in a three-necked reaction flask under dry nitrogen purge and then heated to 80 °C to react. The NCO content in the mixture was periodically measured by the di-*n*-butylamine titration [18] until

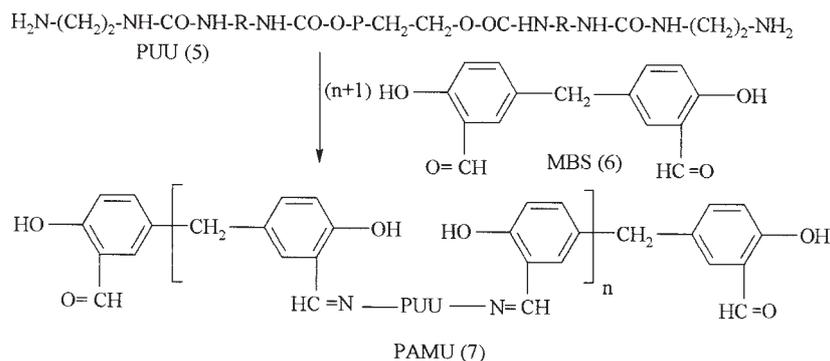
* email: vladus@icmpp.ro

decreased to half of the initial amount. The chain extender was carried out by slowly adding EDA (4) to the isocyanate-terminated prepolymer (3) until 1:1 molar ratio of NCO:OH,

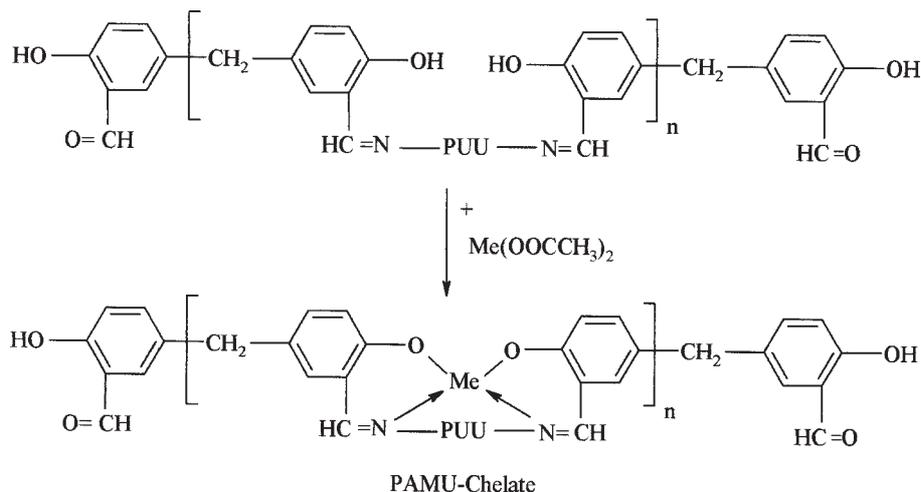
using 0.5 wt % dibutyltin dilaurate as a catalyst. The mixture reacted at 80 °C until no unreacted isocyanate groups remained.



Scheme 1



Scheme 2



Scheme 3

In the polyurethane-urea solution formed by (32 g PUU and 100 g DMF) was added 3 g MBS. The PAMU (7) was synthesized from MBS (6) by reaction with PUU (5) according to scheme 2.

The polymer metal chelate films were prepared by mixing metal salts with PAMU, which contain functional groups according to scheme 3, resulting a polyazomethine-urethane-urea-chelate. The complexation reaction is very simple by mixing of the reaction partners PAMU and the metal salts. The PAUU solution (135 g) was split in three portions and in each was added 0.5 g copper acetate, 0.48 g cobalt acetate and respectively 0.48 g nickel acetate.

When the ligand contains a great number of atoms between the chelate groups it is expected to obtain crosslinking structures. However, in this case close of the ring of coordination on same ligand is possible due to the high chain flexibility of polyurethane and because the reaction was made in solvent at great dilution. In this condition, the intramolecular contact polymer-polymer is

favourable and the macromolecular chains are curled. The hydroxyl groups are oriented to the polar solvent, so it is possible to be implicating in the same chelate cycle.

Film casting

The polymer was shredded and dissolved at 80°C in dioxane up to a concentration of weight 2.0 % for 3 h. After the dissolution of the polymer, the solution was poured into a Petri dish. The solvent was evaporated at 60 °C for 3 h. To complete the drying the films were placed in a vacuum oven at 50 °C for 24 h. The films of polyazomethine-urethane-urea metal-complexes were characterized using conventional spectroscopic methods and elemental analysis.

Results from elemental analysis, FT-IR spectroscopy, and determination of stability by thermal analysis (TGA and DSC) were studied carefully to characterize the polyazomethine-urethane-urea metal-complexes.

Elemental Analysis

Table 1
ELEMENTAL ANALYSIS OF THE POLYAZOMETHINE-URETHANE-UREA METAL-COMPLEXES

Sample	C%	N%	H%	O%	Cu%	Ni%	Co%
	Fnd/calcd	Fnd/calcd	Fnd/calcd	Fnd/calcd	Fnd/calcd	Fnd/calcd	Fnd/calcd
PAMU-Cu	49.54/49.5	3.48/3.55	9.77/9.65	35.23/35.12	1.97/2.15	-/-	-/-
PAMU-Ni	48.8/49.00	3.42/3.40	9.81/9.76	36.17/36.00	-/-	1.79/1.83	-/-
PAMU-Co	48.8/48.90	3.42/3.44	9.81/9.75	36.17/36.10	-/-	-/-	1.8/1.81

The amount (%) of carbon, hydrogen, oxygen, nitrogen and metals in the polyazomethine-urethane-urea metal-complexes, found by elemental analysis, was in agreement with the one calculated (table 1). The results from elemental analysis suggested that the polyazomethine-urethane-urea metal-complex structures proposed is in accordance with the reaction scheme.

FT-IR spectroscopy

The peak at 3335–3328 cm^{-1} is due to N-H stretching, at 2944–2951 cm^{-1} of CH_2 stretching. The carbonyl stretching frequency due to the urethane groups is seen at 1740 cm^{-1} . The peaks between 1651–1608 cm^{-1} are attributed to the aromatic C=C stretching. The carboxylate ion gives two broad peaks between 1597–1540 and 1470–1420 cm^{-1} . The C-H out of plane bending vibrations of aromatic system is seen at 771–740 cm^{-1} . The FTIR spectrum of polyazomethine-urethane-urea (PAMU) without metal salts was showed in figure 1.

Thermal properties

Thermogravimetric analysis (TGA) has been used to examine the thermal stability of the polyazomethine-urethane metal complex (example for sample PUNi, fig. 2).

The results are presented in table 2. The initial decomposition temperatures of the polyazomethine-urethane-urea metal complexes are in the range between 185 and 227°C, which are lower than those of blank polyazomethine-urethane-urea (PAMU). This result indicates that the metal acts as a catalyst and facilitates the first stage of decomposition. All the polymers show multiple-stage decompositions. The residual weights at 700°C correspond to metal oxides (CuO, NiO, and CoO) formed by degradation of the polyazomethine-urethane-urea metal complexes. According to the global activation energy decomposition values it can be concluded that the thermal stability decreases in the following order:

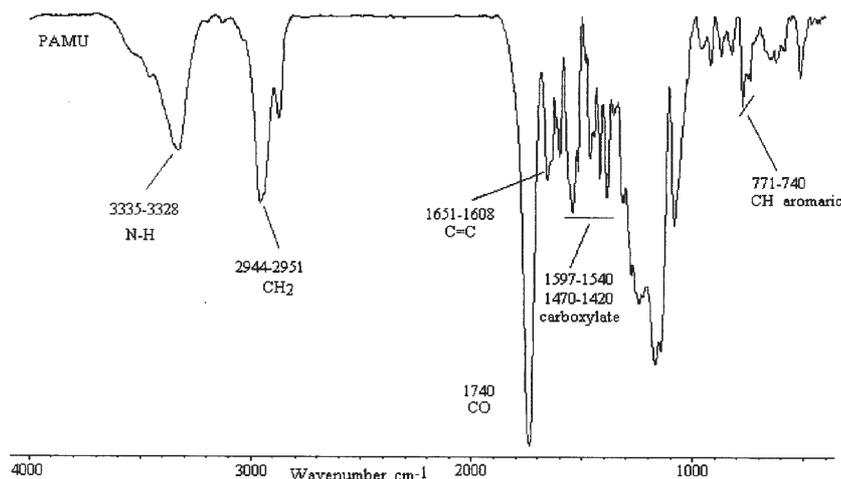


Fig. 1. FT-IR spectrum of polyazomethine-urethane-urea (PAMU)

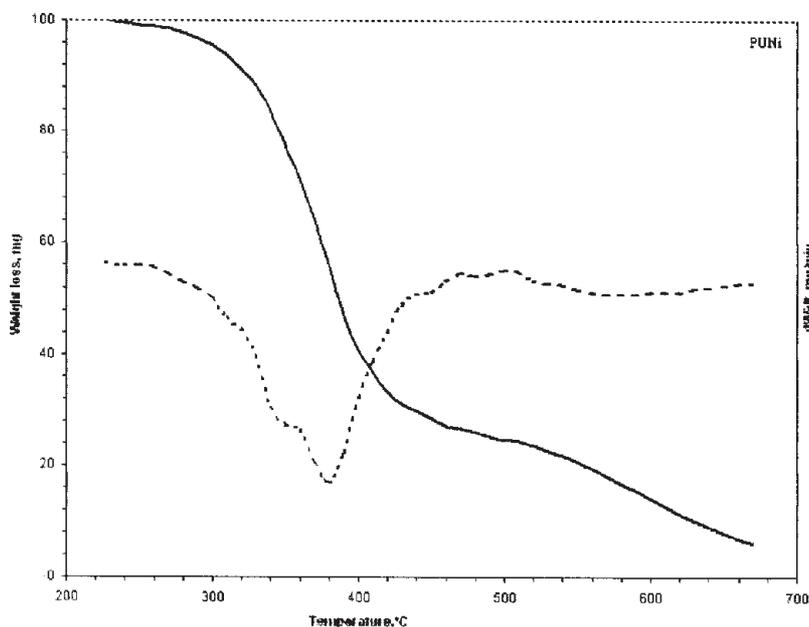


Fig. 2. Thermogravimetric analysis for sample PUNi

Table 2
THERMAL STABILITY OF METAL COMPLEX POLYURETHANES

Code	Reaction order*	Weight losses / decomposition temperature ranges				Activation energy * KJ/mol	T_g ** (°C)	T_{melt} ** (°C)
		Residue %	Step I % / °C	Step II % / °C	Step III % / °C			
PAMU	0.5	8.0	0.1(205-285)	81.9(285-480)	10(480-660)	55.80	-28.12	46.18
PU-Co	0.5	24.0	0.4(185-210)	61.6(210-480)	14(480-640)	54.24	-31.24	49.41 121.24
PU-Ni	0.7	24.0	0.4(188-227)	59.6(227-480)	16(480-680)	80.77	-31.30	46.25 118.13
PU-Cu	0.6	23.2	0.4(185-212)	57.2(212-480)	19.2(480-670)	67.35	-29.87	43.96 136.46

* Calculated through Reich-Levi method – global reaction order and global activation energy [20]

**Calculated by DSC

Ni>Cu>Co which corresponds to the decrease of metal electronegativity (Allred-Rochow Electronegativity Scale- $Ni \geq Cu > Co$) [19].

Polyazomethine-urethane-urea metal-complexes analyzed decomposed in three steps and the temperature interval where the weight losses were greatest is 210-480°C (step II).

From overall kinetic parameters of thermooxidative decomposition we have represented the dependence of the activation energy versus conversion (fig. 3). It can be seen that the energy of activation decreases until a conversion $\alpha=0.1-0.15$, after that it increases till $\alpha = 0.7-0.75$, as final to decrease again. For $\alpha < 0.15$ it appears an important depression in activation energy values versus conversion. This suggests that at the beginning, the reaction have an autocatalytic behaviour. In connection with this, it

should be noted that the oxygen traces in the polymer act as a catalyst for the decomposition process.

Thermal properties of the samples were studied by means of DSC, as well figure 4. DSC measurements can be recorded to 200 °C without degradation of the polymers. Polyazomethine-urethane-urea metal-complexes exhibit single T_g between -31.30 and -29.87°C. In negative domain the samples do not present the crystallization temperature, but in positive domain present two melting endotherms temperature, first between 43.96 and 49.41 °C and second between 118.13-136.46°C. For T_g and lower melting temperature is responsible the soft segments, and for second melting endothermic temperature the hard segments. The soft segment is typically a polyether or polyester and the hard segment unit is normally a diisocyanate, which is extended with diol or diamine to form urethane or urethane-urea segment.

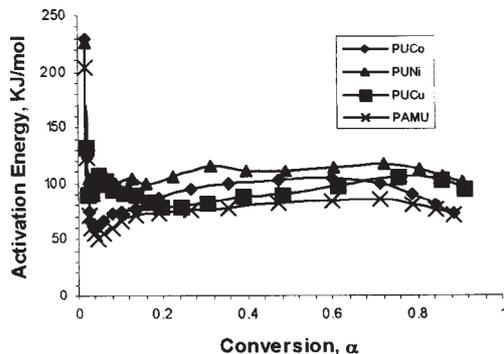


Fig. 3. Activation energy vs. conversion of PAMU and metal complex polyurethanes

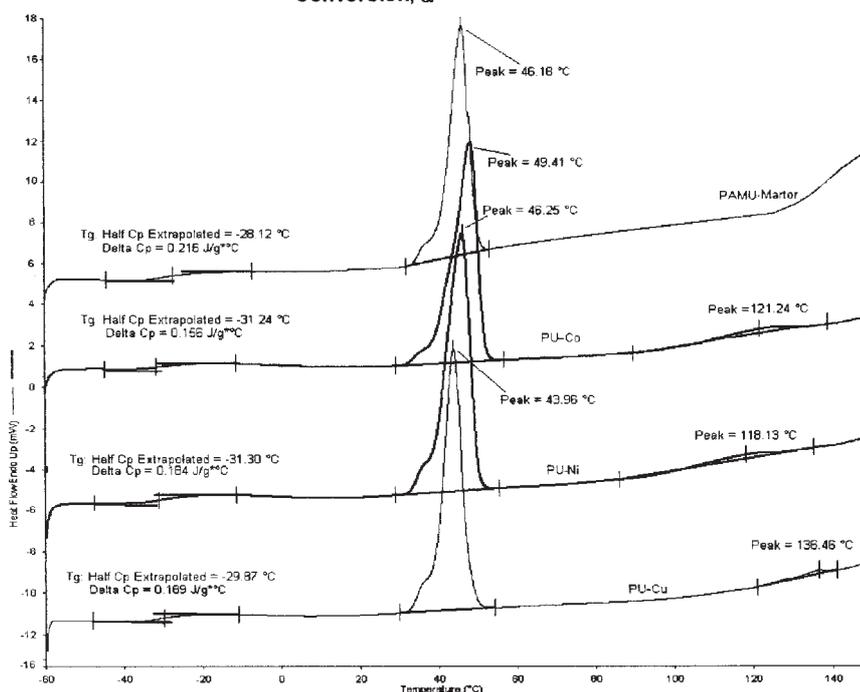


Fig. 4. DSC traces of metal-complex polyurethane

Conclusions

A new type of polyurethane metal-complex was prepared by incorporating the transition metal ions such as copper (II), cobalt (II) and nickel (II), into polyazomethine-urethane-urea, containing functional groups. Metal-complexes based on polyazomethine-urethane-urea were prepared by mixing of the PAMU with metal salt. Thermal properties of polyurethanes metal complexes were found to improve by the introduction of metal ions into the polymer chain. Incorporation of metal into polyurethanes has led to wide application as aqueous thickeners, impregnates, textile sizers, adhesives, additives, resins, and catalysts.

Acknowledgment: We acknowledge the financial support of this work by the Ministry of Education and Research, Grant CNCSIS 76GR/2007

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Manuscript received: 30.10.2007