Transition Metal-Ions Incorporated PEG₃₀₀ and TDI Based Hydroxy-Terminated Polyurethanes

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Abstract

Present work reports the synthesis of polyethylene glycol, PEG 300 (soft segment) and toluene 2,4-diisocyanate, TDI (hard segment) based hydroxy-terminated polyurethane ligands (HTPU₃₀₀) for the first time to the best of our knowledge. The effect of 3d transition metal ions with different 3d electrons within HTPU (M(II)-HTPU₃₀₀, M= Mn, Co, Ni, and Zn) was evaluated by their physical and antibacterial studies of the final complex polymeric unit. M(II) HTPU₃₀₀ and was conveniently synthesized in appreciable yields following a facile and one-pot addition polymerization reaction scheme. Foremost the thermal stability of all the M(II)-HTPU₃₀₀ polymeric materials were evaluated using TGA, DSC, and IPDT calculations. FTIR technique was used to ascertain the structure of M(II)-HTPU₃₀₀, while SEM/EDX and XRD techniques were used to study their morphology, elemental analysis, and crystalline nature of the material, respectively. Further, the *in-vitro* antimicrobial activity of the PU was investigated against gram-positive (*Staphylococcus aureus*, *Bacillus subtilis*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacterial strains. The comparatively moderate efficacy against bacterial stain supports the possible application of such PU as thermally stable bacterial resistant materials constructed out of degradable PEG.

Introduction

In metal ion-containing polymers synthesis, the selection of both polymers as well as metal ions plays a key role in deciding their overall physical, chemical, thermal, and antimicrobial properties. A small change in core structure would lead to considerable changes in the resulting materials[1]. The monomers or polymers that have been used in recent times include crown ether [2], epoxy resins[3], macrocycles[4], Schiff bases[5], porphyrins, N-heterocycles[6], polyureas[7], and polyurethanes (PUs)[8]. The chemical and structural properties of PUs can easily be modulated to generate tailored polymers with predetermined features[9]. PUs generally comprises a linear copolymer having flexible components called as soft segments well as relatively polar, a stiff component called a hard segment. The PUs are one of the most versatile classes of polymeric materials as they find applications in various emerging fields like catalysis[10], drug delivery[11], gas storage,[12] luminescence[13], non-linear optics[14], adsorption[6], photo-physical studies[15], antimicrobial agents[16], material[17], pollutant sequestration[18], and biomedical fields. The chemical and structural properties of PUs can be varied by: (i) Changing the chemical structure of diisocyanate and/or diols[19], (ii) Changing the chemical structure or length of chain extenders having α , ω -alkane di-ols[20], (iii) Altering the ratio of diisocyanate/diols, (iv) Changing the polymerization procedure and processing conditions. Moreover, it is also observed that the structure of aliphatic and aromatic diols and diisocyanate plays a key role in elucidating the overall properties and successive applications of the resulting PU. Further, to develop new and advanced PUs with relatively improved or value-added functionalities, incorporation of secondary additives like macromolecules, bio-actives, pharmaceuticals, nanogels, nanoparticles, and metal ions, is very general, however, the concentration, compatibility, and toxicity of such additives plays a big role while the formulation of metal ion-containing PUs[21].

Among various diols, PUs synthesized with polyethylene glycol (PEG₃₀₀) (as a soft segment), which is a water-soluble polymer has attracted greater interest due to increasing health/ environment awareness, and its superior properties owing to the controllable transition temperature, improved degradation rate, high biocompatibility, low toxicity[22], molecular structure, contact angle measurements, hydrophilic nature,[23] shorter synthesis timings, room temperature stability, adhesive properties, absence of immunogenicity[24], and facile anion polymerization methodology. Thus, PEG has been used as a monomer of choice for the synthesis of PUs in the present study. A review of the literature reveals only a handful of reports about the interaction between the PUs and metal ions[25]. Matsuda, synthesized the metal coordinating PUs by interacting the Toluene diisocyanate (TDI) and Hexamethylene diisocyanate (HMDI) with Ca and Mg salts of mono(hydroxyl-ethyl) phthalate for 6 h. They reported that metal incorporation into the polymeric ligand enhances the thermal decomposition of the polymer[26]. N. Senthilkumar et al prepared the metal-containing PU by the polyaddition reaction of poly (oxytetramethylene) glycol-2000 with 4, 4-methylene bis (phenyl isocyanate) for 11-13 h to develop PU with improved thermal and mechanical properties[27]. Hasnain et al. synthesized the metal chelated PUs by reacting the metal chelated bi-functional monomer and TDI for 5-7 h to report the enhancement of studied properties due to metal coordination[7]. Khan et al. derived cardanol formaldehyde-based polyurethane by the addition of divalent metal ions through the green route[28]. Laxmi et al. synthesized the coordination polymer derived by the reaction of metal ions with hydroxyl-terminated PU as a ligand to formulate PU with good adsorption abilities[29]. Although, metal ions can strongly interact with the planar polymeric backbone which results in limited solubility, use of harmful solvents in huge quantities, multi-step synthesis process, and longer reaction times during[30]. However, to the best of our understanding, there is no report dealing with the synthesis of metal-containing PU by using the nontoxic monomer, *i.e.*, polyethylene glycol. In the present work, we attempted to synthesize metal coordinated polyurethane via a feasible approach, with minimum use of harmful solvents, having shorter reaction times, and with additive properties.

We have fabricated PEG₃₀₀ and TDI-based hydroxy-terminated polyurethane, HTPU₃₀₀, and their hybrid with divalent metal ions (Mn, Co, Ni, and Zn) to form metal ion-containing polymer, M(II)-HTPU₃₀₀ with synergic properties of the polymeric unit as well as a metallic ion. M(II)-HTPU₃₀₀ polymers were characterized by analytical techniques such as FTIR, SEM/EDX, and XRD, along with detailed thermal studies. The M(II)-HTPU₃₀₀ were also screened for their plausible antibacterial activity against gram-positive and gram-negative bacteria.

Methods And Materials

Polyethylene glycol (PEG; Mol. Wt. 300gm/mole), Toluene diisocyanate (TDI), and p-Toluene sulphonic acid (pTsOH) were purchased from S. D. Fine Chem Ltd. India. Manganese (II) acetate tetrahydrate (Mol. Wt. 245.09g/mol) Cobalt(II) acetate tetrahydrate [Mol. Wt. 249.08g/mol] , Nickel(II) acetate tetrahydrate [Mol. Wt. 248.84g/mol] (Merck India) , Zinc(II) acetate dihydrate [Mol. Wt. 219.49 g/mol] (Qualigens Fine Chemicals and dibutyltin dilaurate (DBTDL) were procured from Loba Chemie Pvt. Ltd. Mumbai. Solvents

such as DMSO, Diethyl ether, Ethanol, Methanol, and acetone were obtained from Merck, India. All the chemicals are used as received without further purification. Double distilled water was used throughout the work.

Synthesis

Synthesis of M(II)-HPU₃₀₀

Metal-containing polymers were synthesized *via*, a facile route as shown in Scheme 1. Briefly, the 2:1 stoichiometric ratio of PEG₃₀₀ and TDI were dissolved in 30 ml DMSO separately. They were mixed in a three-necked round bottom flask equipped with a mechanical stirrer, thermometer, reflux condenser, and temperature controller. 1-2 drop of DBTDL catalyst was added in the reaction mixture by using a microsyringe. The mixture was allowed to stir for 2-3 minutes at room temperature until a color change was observed. Subsequently, methanolic solution of stoichiometric amount 1:1 (HTPU₃₀₀:M(CH₃COO)₂.nH₂O (M= Mn, Co, Ni, and Zn) was slowly added under constant stirring. After 5 min of uniform mixing, p-TsOH (0.1%) was added which catalyzes the incorporation of metal ions as well as helps in dehydrating the reaction mixture. The reaction mixture was refluxed until viscosity increases and color change was observed. The addition of 15% DMSO to the reaction mixture at this stage is to adjust the viscosity which facilitates the filtration and processing of the PU. The filtrate was filtered into double distilled water where the product gets precipitated. The PU was then separated by decantation of non-precipitated reaction products, washed with distilled water, acetone, and diethyl ether. The final product was dried in a vacuum.

Synthesis of HTPU₃₀₀

HTPU₃₀₀ was synthesized by following the same method as followed during the fabrication of M(II)-HTPU₃₀₀ excluding the addition of metal salt to study the effect of metal incorporation.[30]

CHARACTERIZATIONS

The solubility was checked by dissolving 20 mg of sample in 5 ml of different solvents (polar and non-polar). Digital conductivity meter, PICO⁺, Lab India Instrument, Pvt. Ltd was used to record the electrical conductivity. Bruker Tensor 37 spectrophotometer (Germany, 4000 to 400 cm⁻¹, KBr pellet mode) was used to analyze FT-IR spectra of the samples. The diffractogram of samples was obtained from an X-ray diffractometer, Ultima IV model, Rigaku cooperation, Japan. (10-80° range at the scan rate of 1 °/min with CuK_α radiations). ZEISS EVO 50 Series instrument was used to analyze FESEM/ EDX for determining surface morphology and chemical composition of the surface of the samples. The thermal analysis (TGA/DTA/DSC) was carried out under N₂ atmosphere using Mettler Toledo AG, Analytical CH8603, Schwerzenbach, Switzerland. Doyle method was used to calculate the IPDT values from the thermal data[31]. In-vitro antibacterial activities of HTPU₃₀₀ and M(II)-HTPU₃₀₀ were carried out by agar diffusion

method[29] against gram-positive(*Staphylococcus aureus*, *Bacillus subtilis*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacterial strains as using the standard drug Ampicillin.

Results And Discussion

Chemistry of HTPU₃₀₀ and M(II)-HTPU₃₀₀

The synthesis of HTPU₃₀₀ was carried out by reacting diols with di-isocyanates *via* a single pot addition polymerization in presence of DBTDL as a catalyst. The synthesis of HTPU₃₀₀ was followed by condensation polymerization of HTPU₃₀₀ with metal acetates, yielding colored M(II)-HTPU₃₀₀ (Table 1) that seemed to be new materials having huge potential and value-added properties[32]. The successful formulation of the metal ion incorporated PU was confirmed by the change in solubility, conductivity, functional properties, and thermal properties of the final material. The obtained PU was dried and then subjected to solubility studies to ascertain the effect of metal-induced coordination.

The synthesized HTPU₃₀₀ was easily soluble in DMSO, DMF, and pyridine. Interestingly, the incorporation of the divalent metal ions led to the restricted solubility of Zn(II)-HTPU₃₀₀ to DMSO only. Most probably the interaction of the electronegative functional heads in the HTPU₃₀₀ has resulted in increased rigidity and higher crosslinking density of the M(II)-HTPU₃₀₀. [33] The percentage yield of M(II)-HTPU₃₀₀ was found to be significant and ranges from 79-82% (Table 1).

Electrical Conductivity

The conductivity of HTPU₃₀₀ and M(II)-HTPU₃₀₀ depends directly on the degree of ionization and vice-versa. The HTPU₃₀₀ showed a comparatively lower conductivity value than M(II)-HTPU₃₀₀ (10^{-6} Scm^{-1}) in DMSO. Although, the incorporation of metal ions did increase the conductivity the range of conductivity is in the lower range which indicates possible semi-conducting nature[34] of the metal incorporated PU, as shown in Table 2. Since the amount of metal ions used is mostly incorporated within the HTPC₃₀₀ polymeric matrix which restricts the overall conductivity of the PU.

FTIR spectral analysis

FTIR spectral data of HTPU₃₀₀ and Zn(II)-HTPU₃₀₀ are shown in Figure 1, and the rest of the characteristic peaks of other M(II)-HTPU₃₀₀ have been summarized in Table 3. A comparative study implies the successful synthesis of proposed M(II)-HTPU₃₀₀. The characteristics peaks of HTPU₃₀₀ were recorded at $3532\text{-}3215 \text{ cm}^{-1}$ corresponding to -OH group of aliphatic alcohol[35], while the peaks appearing at 3055 can be ascribed due to $(\text{Ar C}=\text{C-H } \nu)$ and 2988 cm^{-1} may be assigned to aliphatic -CH_2 , CH_3 symmetric, and asymmetric stretching vibration[36]. The strong band observed at 1658 cm^{-1} may be attributed to >C=O stretching vibration of urethane[37], while the bands at 1533 cm^{-1} may be assigned to N-H out of

plane bending in urethane[38], while the band at 1043 cm^{-1} may be corroborated to C-O-C stretching vibration.[39]

The spectral data of $M(\text{II})\text{-HTPU}_{300}$ [where, $M = \text{Mn}(\text{II})\ d^5$, $\text{Co}(\text{II})\ d^7$, $\text{Ni}(\text{II})\ d^8$ and $\text{Zn}(\text{II})\ d^{10}$] can be extensively discussed. The peak centered between $3277\text{-}3300\text{ cm}^{-1}$ may be ascribed to -NH stretching vibration while the strong peak appearing between $1696\text{-}1712\text{ cm}^{-1}$ may be assigned to $>\text{C}=\text{O}$ stretching vibration of urethane groups.¹⁵ The peak lying in between $1541\text{-}1536\text{ cm}^{-1}$ may be due to the N-H out-of-plane bending of urethane. Similarly, the peak observed between $896\text{-}916\text{ cm}^{-1}$ may be due to rocking and wagging vibrations in $\text{M-H}_2\text{O}$, [7] while the new peak appearing in between $752\text{-}773\text{ cm}^{-1}$ in $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$ may be due to the presence of coordinated water molecules.[40] Also, the weak bands lying between $448\text{-}459\text{ cm}^{-1}$ may be conveniently assigned to M-O stretching bonds[29]. The main changes observed after the coordination of the metal ions to HTPU_{300} are summarized as follows:

- i. The broad band of -OH of HTPU_{300} disappears and a sharp N-H band surfaces in between the $3277\text{-}3300\text{ cm}^{-1}$ range.
- ii. A downfield shift in -NH bending of $M(\text{II})\text{-HTPU}_{300}$ of about $10\text{-}15\text{ cm}^{-1}$, was observed illustrating the coordination of lone pair of -NH to with metal ions[41] in $M(\text{II})\text{-HTPU}_{300}$.
- iii. The shifting of strong carbonyl frequency peak in the region $1698\text{-}1709\text{ cm}^{-1}$ in $M(\text{II})\text{-HTPU}_{300}$ might be due to coordination of lone pair of -NH to metal ions and thus cannot delocalize into the carbonyl group[42]
- iv. Medium intensity peaks were observed at $752\text{-}773\text{ cm}^{-1}$ in $\text{Mn}(\text{II})/\text{Co}(\text{II})/\text{Ni}(\text{II})\text{-HTPU}_{300}$ might be due to the presence of coordinated water molecules, thereby supporting the octahedral geometry[43]. However, this peak was found to be absent in $\text{Zn}(\text{II})\text{-HTPU}_{300}$ thus, supporting our assignment of tetrahedral geometry for the $\text{Zn}(\text{II})$ ion.

Morphological Studies

XRD

XRD is a well-established technique to evaluate the structural (amorphous, semi-crystalline, and crystalline) arrangement of building units in any material. Here, XRD of HTPU_{300} and $M(\text{II})\text{-HTPU}_{300}$ was performed in the 2θ range from 10° to 60° . The XRD pattern of HTPU_{300} demonstrates a broad peak over the 2θ value of 20° to 22° (Fig.2). This hump can be attributed to the presence of carbon in amorphous form and mostly confirms the presence of organic components [44]. However, after incorporation of the metal ions to form $M(\text{II})\text{-HTPU}_{300}$, the broadness of the peak decreases around 22° and new humps were observed around 24° , 26° and in $\text{Mn}(\text{II})\text{-HTPU}_{300}$, 23° in case of $\text{Ni}(\text{II})\text{-HTPU}_{300}$, 23.5° in $\text{Co}(\text{II})\text{-HTPU}_{300}$ and 21° in $\text{Zn}(\text{II})\text{-HTPU}_{300}$. Although these additional humps won't be able to verify any particular

arrangement, the sharpness (22°) along with these peaks indicates the formation of some uniform structural arrangement. Therefore, the incorporation of metal ions does lead to complexity and denser structural arrangement for the metal incorporated PU. These values are in proximity with the semi-crystalline behavior of the synthesized Zn(II)-HTPU₃₀₀ compared to amorphous HTPU₃₀₀[29].

A degree of crystallinity is generally achieved in metal decorated, dispersed, or metal coordinated polymers, however, this cannot be achieved due to the presence of random arrangement of methyl groups of TDI adjacent to the urethane linkages within the polyurethane chain, inhibiting the crystalline behavior. [34] The encapsulation of the metal ions within the polyurethane chains further affects the detection of crystalline behavior due to the presence of metal ions in M(II) HTPU₃₀₀.

FE-SEM and EDX

FE-SEM was used to examine the generic surface morphology and any possible new surface variations that arise due to the incorporation of metal ions in PU. The FE-SEM micrographs of Zn(II)-HTPU₃₀₀ are shown in Figure 3. FE-SEM micrographs of Zn(II)-HTPU₃₀₀ showed nano-roughness with some cage-like arrangement on the surface. Possibly the coordination of the metal ions to the polymeric chain of HTPU₃₀₀ may have resulted in the secondary arrangement within the PU[7]:[29]. EDX technique was utilized to examine the composition of HTPU₃₀₀ and Zn(II)-HTPU₃₀₀ as displayed in Fig. 4, (a-b). The presence of elements like C, O, and N in HTPU₃₀₀ revealed the construction of the polymer using only organic moieties (PEG and TDI), whereas the presence of Zn into the polymeric chain was confirmed by the strong peak around 1.0 eV for Zn L α in Zn(II)-HTPU₃₀₀ along with the other organic components[29]. The atomic percentage calculated for each metal component was found to be Zn(II): 1.34, confirming the incorporation of the respective inorganic part (metal ions) into a polymeric chain of organic moiety (HTPU₃₀₀).

Thermal studies

The thermal decomposition behavior of HTPU₃₀₀ and M(II)-HTPU₃₀₀ were investigated by the TGA/DTG (Figure 5) and DSC (Figure 6) along with IPDT calculation (Table 4). TGA/DTG results reveals the three steps degradation pattern in both HTPU₃₀₀ and M(II)-HTPU₃₀₀. The first, initial weight loss (5 wt %) for HTPU and Zn(II)-HTPU₃₀₀ was observed at a range of 50-180 °C (Centred at 105 °C) correlates with the evaporation of entrapped moisture/solvent molecules[45]. The second weight loss (5-15 wt %) at 180-255 °C (Centred at 222°C) in both cases, can be due to the urethane linkage scission to their components, isocyanate, and hydroxyl components³⁴ along with further decomposition of hydroxyl components[46]. The third major weight loss occurring in between 255-560 °C (Centred at 355 °C) in all cases can be corroborated by the volatilization of formerly decomposed derivatives (hydrocarbons). The TGA/DTG thermograms results showed comparable thermal stability.[28]

The Integral decomposition temperature (IPDT), reported by the Doyle[31] relates the volatile part of the HTPU₃₀₀ and Mn(II)HTPU₃₀₀ with thermal stability of the same[29]. In this work, the IPDT was examined on the basis of following equations:

$$(a) \text{ IPDT } (^{\circ}\text{C}) = A^*K^*(T_f - T_i) + T_i$$

$$(b) A^* = S_1 + S_2 / S_1 + S_2 + S_3$$

$$(c) K^* = S_1 + S_2 / S_1$$

where, T_i = Initial experimental temperature and T_f = Final experimental temperature

A^* and K^* were calculated by the use of S_1 , S_2 , and S_3 , reported in earlier work[47].

The IPDT values (Table 4) as evaluated from the TG thermograms are found to be 591 °C for HTPU₃₀₀ and 738 °C for Zn(II)-HTPU₃₀₀. The examined results imply that the incorporation of metal ions into the Zn(II)-HTPU matrix enhances the thermal stability of native HTPU₃₀₀ due to the development of a better-crosslinked unit.

DSC

The DSC thermograms of HTPU₃₀₀ and Zn(II)-HTPU₃₀₀ was studied up to 400 °C in Figure 6, (a-b). The results obtained from endothermic peaks may be correlated to the data determined in TGA/DTA curves. The T_g observed for HTPU₃₀₀ was around 89 °C, whereas for, Zn(II)-HTPU₃₀₀ at 80 °C. The observed T_g values indicate possible coordination of the polymeric ligand with the metal ions where metal acts as catalyst.[48] There are following endotherms which are discussed as follows: (i) The first endotherm, ranging from 60 °C to 120°C noticed in HTPU₃₀₀ and Zn(II)-HTPU₃₀₀ can be assigned to the evaporation of entrapped moisture and solvents, (ii) The second endotherm, ranging from 160 to 200 °C found in Zn(II)-HTPU₃₀₀ might be due to the crystalline water which supports their possible octahedral geometry, (iii) the main endotherm, ranging from 300 to 340 °C obtained in both the polymers may correspond to the urethane linkage scission.[34] The observed results support the data obtained in TGA/DTA up to 400 °C.

In-vitro antimicrobial assay

The preliminary antibacterial activity of samples, HTPU₃₀₀ and M(II)HTPU₃₀₀ was assessed based on the zone of inhibition against bacterial growth around the wells(Fig.7). These antibacterial activities are compared with the standard antibiotic drug, Ampicillin using disk diffusion assay (Kirby Bauer method). The data (Table 5) indicates that different polymers perform differently against gram-positive [*Staphylococcus aureus*, MTCC 902 and *Bacillus substilis*, MTCC 736] and gram-negative bacteria [*Escherichia coli*, MTCC 443 and *Pseudomonas aeruginosa*, MTCC 2453]. The results revealed moderate

activity by HTPU₃₀₀ and M(II)HTPU₃₀₀ against all the gram-positive and gram-negative bacteria as compared to the standard drug. All the synthesized polymers inhibit the growth of *B. subtilis*, *E. coli*, and *S. aureus* but do not show any effect on *P. aeruginosa*. Nothing particular was observed due to the incorporation of the metal ions with different 3d electrons. So, it can be predicted that the obtained antimicrobial activity exhibited by the synthesized polymers may not be entirely due to the presence of metal ions but it may be due to the donor atoms present within the polymeric chain. These atoms inhibit enzyme production as reported in earlier studies[41].

Conclusion

The M(II)HTPU₃₀₀ have been successfully synthesized by reacting the HTPU₃₀₀ with divalent metal ions [Mn(II) '*half filled*', Co(II), Ni(II) '*partially filled*' and Zn(II) '*full filled*'] via *in situ* single pot addition polymerization reaction. The constructive effect of divalent metal ions was observed on the structure, geometry, surface morphology, thermal and antibacterial properties of HTPU₃₀₀. The metal ion incorporation results in a slight increase in conductivity and semi-crystalline behavior of the M(II)-HTPU₃₀₀ polymers. The surface roughness and formation of crosslinked structures may have been responsible for improved thermal stability. Moderate antibacterial activity was observed in the case of *B. subtilis*, *E. coli*, and *S. aureus*. Although, a big difference in the thermal stability of the PU polymers was observed, possibly due to variation in available 3d electrons and their ability to crosslink particular ligands the same could not be ascertained in antibacterial properties. The overall outcome indicates a potential for the formulation of PU using degradable PEG and metal incorporated polymers.

Declarations

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Tables

Table 1. Sample designation and reaction conditions for the synthesis of HTPUs and M(II)-HTPU₃₀₀

Polymers	Yield (%)	Color	Solubility in DMSO (min)	Reaction time (min)	Reaction temperature (°C)
HTPU ₃₀₀	82	White	1	5-15	15± 5
Zn(II)-HTPU ₃₀₀	79	Light yellow	2	70	110± 5
Mn(II)-HTPU ₃₀₀	82	Dark brown	2	60	110± 5
Ni(II)-HTPU ₃₀₀	81	Mustered	2	65	110± 5
Co(II)-HTPU ₃₀₀	80	Light Brown	2	67	110± 5

Table 2. Electrical conductance for HTPU₃₀₀ and M(II)-HTPU₃₀₀

Polymer No.	Polymer's code	Elec. Cond. (10 ⁻⁶ Scm ⁻¹)
1	HTPU ₃₀₀	5.4
2	Zn(II)-HTPU ₃₀₀	5.9
3	Mn(II)-HTPU ₃₀₀	8.6
4	Ni(II)-HTPU ₃₀₀	7.7
5	Co(II)-HTPU ₃₀₀	8.1

Table 3. FTIR spectrum data of HTPU₃₀₀ and M(II)-HTPU₃₀₀

Polymers	Urethane NH	Urethane C=O	Isocyanate C=O	OH	Aliphatic CH ₂	M-O	M-H ₂ O	-NH bending
HTPU ₃₀₀	3360	1658	-	3532-3215	2992-2892	-	-	1540
Zn(II)-HTPU ₃₀₀	3277	1709	-	-	3032-2946	459	773	1537
Mn(II)-HTPU ₃₀₀	3289	1698	-	-	3008-2921	448	762	1535
Ni(II)-HTPU ₃₀₀	3300	1706	-	-	3012-2930	456	756	1525
Co(II)-HTPU ₃₀₀	3293	1702	-	-	3003-2932	452	752	1527

Table 4. Thermal behavior data of HTPU₃₀₀ and Zn(II)-HTPU₃₀₀

Polymer code	T ₀	T _f	S ₁	S ₂	S ₃	A*	K*	IPDT (°C)
HTPU ₃₀₀	25	800	21529	11658	37321	0.51	1.40	591
Zn(II)-HTPU ₃₀₀	25	800	27765	16619	33060	0.57	1.59	738

Table 5. Zone of Inhibition (in mm) of the HTPU and M(II)-HTPU₃₀₀ against bacteria's

Polymer Code	<i>E.coli</i>	<i>S.aureus</i>	<i>B. subtilis</i>	<i>P.aeruginosa</i>
HTPU ₃₀₀	7	7	9	0
Zn(II)-HTPU ₃₀₀	8	8	7	0
Mn (II)-HTPU ₃₀₀	9	7	9	0
Co(II)-HTPU ₃₀₀	9	7	8	0
Ni(II)-HTPU ₃₀₀	10	8	0	0
Ampicillin	28	27	35	15

Scheme

Scheme 1 is available in the Supplementary Files section.

Figures

Figure 1

FTIR spectrum of (a) HTPU300 (b) Zn(II)-HTPU300

Figure 2

XRD micrograph of (a) HTPU300 and (b) Zn(II)-HTPU300

Figure 3

FE-SEM images at different magnification of Zn(II)-HTPU300

Figure 4
EDX surface scanning of (a) HTPU300 and (b) Zn(II)-HTPU300

Figure 5

TGA/DTA thermograms of (a) HTPU300 (b) Zn(II)-HTPU300

Figure 6

DSC thermogram of (a) HTPU300 and (b) Zn(II)-HTPU300

Figure 7

Zone of Inhibition (in mm) of (a) HTPU300, (b) Zn(II)-HTPU300, (c) Mn(II)-HTPU300, (d) Co(II)-HTPU300 and (e) Ni(II)-HTPU300

Supplementary Files

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- [Scheme1.png](#)