SYNTHESIS OF COPOLYURETHANE-UREAS CONTAINING NICKEL AND ZINC 4,4′-DIHYDROXYSALTRIEN COMPLEXES IN THE PRESENCE OF DIALCOHOLS OR DIAMINES

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Abstract

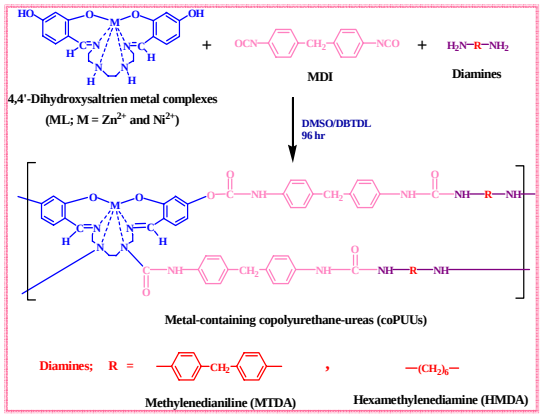
Synthesis of copolyurethane-ureas containing nickel and zinc 4,4′ - dihydroxysaltrien complexes in the presence of dialcohols or diamines were done by polymerization of 4,4′ -dihydroxysaltrien metal complexes (ML, Where M = Zn and Ni), 4,4′ - methylene*bis*(phenyl isocyanate) (MDI) and various diamines or dialcohols. The diamines used were methylenedianiline (MTDA) and hexamethylenediamine (HMDA). The dialcohols employed were bisphenol A (BA) and 1,6-hexanediol (HD). Dibutyltin dilaurate (DBTDL) was used as a catalyst. The polymers were characterized by using IR, NMR and solubility. Thermal properties were determined by thermogravimetric analysis (TGA).

Introduction

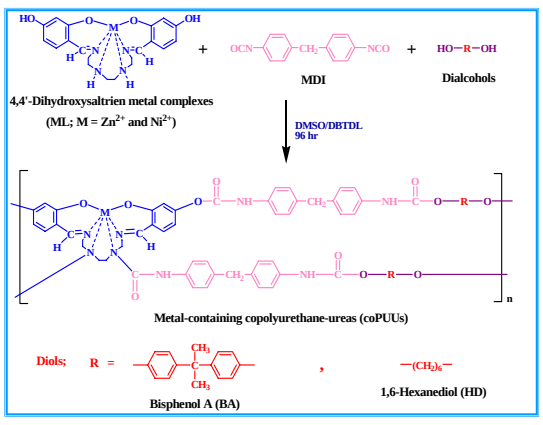
Polyurethanes-ureas possess excellent mechanical and physical properties, high combustion resistance and high wear resistance. These polymers are widely applicable to a number of industrial products including elastomers, fibers, foams, adhesives, coatings and paints etc. The incorporation of metals into the polymer backbone results in a considerable increase in thermal stability of the polymer. This research involves the synthesis of polyurethane-ureas and copolyurethane-ureas containing nickel and zinc 4,4′-dihydroxysaltrien complexes in the presence of diamines or dialcohols.

Methodology

Synthesis of copolyurethane-ureas containing nickel and zinc 4,4′ - dihydroxysaltrien complexes in the presence of dialcohols or diamines were done by the reaction between metal complexes (ML) with MDI and diamines or dialcohols as shown in Schemes 1 and 2, respectively. Metal containing copolyurethane-ureas were synthesized from different compositions by taking the molar ratio of ML: MDI: dialcohols or diamines as 1:2:0 0.5:3:1.5, 1:3:1 and 1.5:3:0.5 to study the thermal property of copolymers.



Scheme 1 Synthesis of coPUUs from the reaction between ML, MDI and diamines



Scheme 2 Synthesis of coPUUs from the reaction between ML, MDI and dialcohols

Results and Discussion

Metal-containing polyurethane-ureas and copolyurethane-ureas were obtained in 57-87% yields. The polymers were chalacterized by IR, NMR, Solubility and TGA.

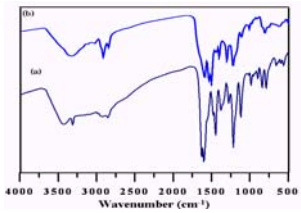


Figure 1 IR spectrum of (a) ZnL (b) ZnL-MDI

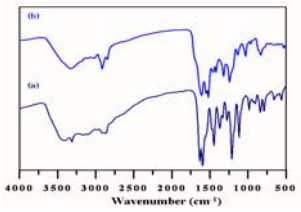


Figure 2 IR spectrum of (a) NiL (b) NiL-MDI

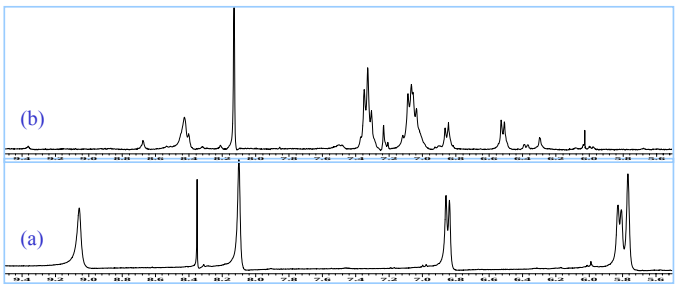


Figure 3 ^{1}H-NMR of (a) ZnL (b) ZnL-MDI

Thermogravimetric analysis result showed that nickel-containing polymer have higher thermal stability than zinc-containing polymers. The solubility of metal containing copolymer increases with addition dialcohols in the copolymers. The copolymers ZnL-MDI-BA (1.0: 3:1.0) and ZnL-MDI-HD (1.0: 3: 1.0) showed the best thermal stability at 600°C. Initial decomposition temperature (IDT) of metal containing copolymers were compared to that of the metal-containing polymers without diamines or dialcohols which were synthesized from the reaction between metal complexes and MDI. The result showed that when adding dialcohols or diamines in the polymerization, the polymers exhibited better IDT.

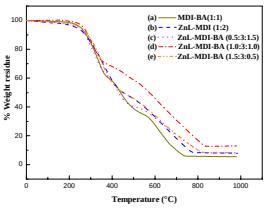


Figure 4 TGA thermograms of ZnL-MDI-BA

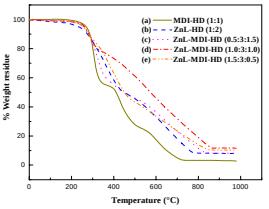


Figure 5 TGA thermograms of ZnL-MDI-HD

Polymer code	IDT (°C)	Char yield at 600 (°C)	Solubility (mg)
NiL-MDI (1:2)	227.8	55	56
MDI-MTDA (1:1)	270.0	34	5
NiL-MDI-MTDA (1:3:1)	288.5	51	37
MDI-HMDA (1:1)	302.5	19	30
NiL-MDI-HMDA (1:3:1)	252.2	51	40
MDI-BA (1:1)	262.0	28	5
NiL-MDI-BA (1:3:1)	262.1	47	54
MDI-HD(1:1)	278.9	18	90
NiL-MDI-HD (1:3:1)	232.0	47	125

Polymer code	IDT (°C)	Char yield at 600 (°C)	Solubility (mg)
ZnL-MDI (1:2)	241.2	33	92
MDI-MTDA (1:1)	270.0	34	5
ZnL-MDI-MTDA (1:3:1)	271.8	33	75
MDI-HMDA (1:1)	302.5	19	30
ZnL-MDI-HMDA (1:3:1)	260.9	35	88
MDI-BA (1:1)	262.0	28	5
ZnL-MDI-BA (1:3:1)	257.5	54	132
MDI-HD(1:1)	278.9	18	90
ZnL-MDI-HD (1:3:1)	256.4	54	225

Conclusion

The metal containing copolyurethane-ureas showed high thermal stability and good solubility. All polymers were soluble in polar solvents such as DMF and DMSO.

Acknowledgement

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