

Thermally Stable Polyurethane-Ureas and Copolyurethane-Ureas Containing Zinc and Nickel Dihydroxysaltriene Complexes

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Received 16 May 2007; accepted 5 October 2007

DOI 10.1002/app.27554

Published online 27 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New 4,4'-dihydroxysaltriene metal complexes, (MOHSal₂trien, where M = Zn and Ni) were synthesized and used for the synthesis of metal-containing polyurethane-ureas and copolyurethane-ureas. MOHSal₂trien underwent polymerization reaction with two diisocyanates, namely 4,4'-diphenylmethane diisocyanate (MDI) and isophorone diisocyanate (IPDI) to yield polyurethane-ureas. Copolyurethane-ureas were synthesized by the reaction between MOHSal₂trien, MDI, and diamines or dialcohols. The diamines or dialcohols employed were 4,4'-methylene-dianiline (MDA), hexamethylenediamine (HMA), bisphenol A (BPO), and hexamethylene glycol (HMO). The polymers were characterized by IR, NMR, elemental analysis, XRD, solubility, and viscosity. Thermal stability and flammability of polymers were studied by thermogravimetric analysis (TGA) in air and by measuring limiting oxygen index (LOI)

values, respectively. It was found that the resulting metal-containing polyurethane-ureas and copolyurethane-ureas exhibited good thermal stability. Among all metal-containing polyurethane-ureas, NiOHSal₂trien-MDI was the most thermally stable polymer with char yield of 55% at 600°C. Solubility in DMSO of zinc-containing copolyurethane-ureas based on dialcohols was greatly improved when compared with those of zinc- and nickel-containing polyurethane-ureas. ZnOHSal₂trien-MDI-BPO and ZnOHSal₂trien-MDI-HMO gave high char yield of 46% at 600°C, which is almost comparable with that of NiOHSal₂trien-MDI. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 245–255, 2008

Key words: polyurethane-ureas; metal-containing polymers; thermally stable polymers; thermogravimetric analysis

INTRODUCTION

Polyurethane-ureas are unique copolymers with a wide range of physical and chemical properties such as good toughness, high extensibility, and abrasion resistance. Because of these properties, polyurethane-ureas are one of the major important commercial polymers. The properties provided by these polyurethane-ureas make them useful for a wide variety of applications such as textile fibers, sealing gaskets, and elastomers used in automotive industry. However, the polyurethane-ureas have poor thermal stability. Therefore, the synthesis of thermally stable polyurethane-ureas by introduction of metal into a polymer backbone has received interest, since it is known that the resulting metal-containing polymers

possess useful properties such as high thermal stability and flame retardancy.

Several works concerning the synthesis of metal-containing polyurethanes, polyureas polyurethane-ureas, and other copolyurethanes have been reported. These metal-containing polymers were obtained by the polymerization of metal salts or metal complexes with different diisocyanates.^{1,2} For example, metal-containing polyurethanes and polyurethane-ureas were synthesized by use of mono(hydroxyalkyl)phthalate salts such as mono(hydroxyethyl)phthalate,³ mono(hydroxybutyl)phthalate,^{4–6} mono(hydroxypentyl) phthalate,^{7–9} mono(hydroxyethoxyethyl)phthalate,^{10–15} and mono(hydroxybutyl)hexolate.¹⁶ Another type of metal complex used in the synthesis of metal-containing polyurethane was 1,2-bis[4-(2-hydroxy)ethoxy-2-hydroxyphenyl]methyl ketimino]ethane metal complexes.¹⁷ In many cases, the thermal stability of the metal-containing polymers is not superior to that of the pure polymer at low temperature, however, the char yield of the modified metal-containing polymers is higher than that of the pure polymer at high temperature. Metal-containing polyureas having ionic link in the main chain were synthesized by the

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Contract grant sponsors: Chulalongkorn University Ratchadaphisek Somphot, Chulalongkorn University Graduate School Grants.

Journal of Applied Polymer Science, Vol. 108, 245–255 (2008)
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polymerization of 2,4-tolylene diisocyanate with mixtures of 4,4'-diaminodiphenylmethane and divalent metal salts of *p*-aniline sulfonic acid¹⁸ and *p*-aminobenzoic acid.¹⁹ It was found that the metal-containing polyureas based on *p*-aniline sulfonic acid showed an increase in thermal stability.

From the work previously done by our group, thermally stable metal-containing polyureas²⁰ and polyurethane-ureas²¹ were synthesized from the reaction of hexadentate Schiff base metal complexes with diisocyanates and diisocyanate-terminated prepolymers, respectively. Therefore, we became interested in the synthesis of polyurethane-ureas using a new metal complex, 4,4'-dihydroxysaltrien metal complex (MOHSal₂trien). In this metal complex, there are two amine groups and two hydroxyl groups which are able to undergo polymerization reaction with isocyanates to give metal-containing polyurethane-ureas, and it is expected that the polymers should exhibit good thermal stability. In this article, we describe the synthesis and characterization of metal-containing polyurethane-ureas and metal-containing copolyurethane-ureas containing hydroxysaltrien metal complex in the polymer chain. Thermal stability of the obtained polymers is investigated.

EXPERIMENTAL

Materials

All chemicals were used as received from Aldrich and Fluka without purification. DMSO was dried over calcium hydride and distilled under reduced pressure before its use.

Analytical methods

IR spectra were obtained using a Nicolet Impact 410 FTIR spectrophotometer with KBr disc method. The NMR spectra were recorded in CDCl₃ and DMSO-*d*₆ solution on Varian Mercury 400 MHz and JEOL JNM-A 500 MHz NMR instruments. Elemental analyses were carried out using a Perkin Elmer 2400 CHN analyzer. MALDI-TOF mass spectra were obtained on a Bruker Biflex mass spectrometer using α -cyanocinnamic acid as a matrix. XRD experiments were performed on a Bruker D8 Discover diffractometer using Ni-filtered Cu K α radiation (40 kV, 40 mA) with scanning rate of 1°/min.

Inherent viscosity (η_{inh}) of the polymers was determined using a Cannon-Fenske viscometer at a concentration of 0.5 g/100 mL in DMSO at 40°C. Solubility of polymers was tested in various polar and nonpolar solvents by addition of 10 mg samples to 2 mL of a solvent and kept overnight.

TGA was carried out in a Netzsch STA 409C thermal analyzer at a heating rate of 20°C/min in air

atmosphere. The limiting oxygen index (LOI) data were obtained on an apparatus following ASTM-D 2863-70 and using a modified procedure as described in the literature.²²

Preparation of 4,4'-dihydroxysaltrien zinc complex (ZnOHSal₂trien)

A solution of triethylenetetramine (0.165 mL, 1.11 mmol) in methanol (10 mL) was added dropwise to a solution of 2,4-dihydroxybenzaldehyde (0.309 g, 2.22 mmol) and zinc (II) acetate dihydrate (0.244 g, 1.11 mmol) in methanol (25 mL) at 0°C, and the mixture was stirred for 15 min. A solution of 1N potassium carbonate (1.11 mL, 1.11 mmol) was added and stirred at 0°C for 30 min. The pink powder, which precipitated immediately after addition of potassium carbonate, was separated by filtration. The filtrate was allowed to stand at room temperature for 6 h. ZnOHSal₂trien precipitated from the solution and was subsequently isolated by filtration and dried *in vacuo*. ZnOHSal₂trien was obtained as yellow solid (0.19 g, 34%). IR (KBr, cm⁻¹); 3313 (NH), 2895, 1630 (C=N), 1601, 1449, 1378, 1278, 1121, 980, 902, 843, 785, 660, 629, 563. ¹H NMR (400 MHz, DMSO-*d*₆ + CDCl₃, ppm); δ 9.06 (s, 2H, OH), 8.10 (s, 2H, CH=N), 6.85 (d, 2H, ArH, *J* = 8.0 Hz), 5.82 (d, 2H, ArH, *J* = 8.0 Hz), 5.77 (s, 2H, ArH), 3.70–3.65 (m, 2H, CH₂), 3.20–3.10 (m, 2H, CH₂), 3.00–2.90 (m, 2H, CH₂), 2.85–2.75 (m, 2H, CH₂), 2.60–2.50 (m, 2H, CH₂, overlap with DMSO-*d*₆), 2.45–2.35 (m, 2H, CH₂). ¹³C NMR (125 MHz, DMSO-*d*₆, ppm); δ 173.6, 165.8 (CH=N), 161.5, 136.2, 113.6, 106.4, 101.2, 54.4, 45.7, 43.4. MALDI-TOF MS (*m/z*) 450.1 (C₂₀H₂₄O₄N₄Zn). Anal. Calcd. for (C₂₀H₂₄O₄N₄Zn) · 3H₂O: C 47.67; H 6.00; N 11.12; found C 48.25; H 5.93; N 11.62.

Synthesis of 4,4'-dihydroxysaltrien nickel complex (NiOHSal₂trien)

NiOHSal₂trien was synthesized in the same manner as ZnOHSal₂trien using nickel (II) acetate tetrahydrate (0.281 g, 1.13 mmol). NiOHSal₂trien was obtained as green solid (0.34 g, 67%). IR (KBr, cm⁻¹); 3314 (NH), 2855, 1634 (C=N), 1601, 1450, 1374, 1333, 1278, 1215, 1118, 988, 937, 905, 840, 790, 660, 559. MALDI-TOF MS (*m/z*) 443.5 (C₂₀H₂₄O₄N₄Ni). Anal. Calcd. for (C₂₀H₂₄O₄N₄Ni) 3H₂O: C 48.32; H 6.08; N 11.27; found C 48.26; H 6.22; N 11.55.

Synthesis of metal-containing polyurethane-ureas from the reaction between MOHSal₂trien and diisocyanates

Polyurethane-ureas were synthesized from MOHSal₂trien (where M = Zn and Ni) and diisocyanates. The diisocyanates used were 4,4'-diphenylmethane

diisocyanate (MDI) and isophorone diisocyanate (IPDI). The mole ratio of MOHSal₂trien : diisocyanate employed was 1 : 2. The general procedure for the synthesis of metal-containing polyurethane-ureas is as follows: A solution of diisocyanate (0.680 mmol) in DMSO (2 mL) was added to the solution of MOHSal₂trien (0.340 mmol) in DMSO (1 mL) under nitrogen atmosphere at room temperature. Dibutyltin dilaurate (0.04 mL, 0.067 mmol) was then added. The reaction mixture was heated at 90°C for 96 h. Finally, the reaction mixture was allowed to cool and poured into a large quantity of distilled water to precipitate the polymer. The polymer was filtered, washed several times with methanol, and dried *in vacuo* for 24 h. Zinc- and nickel-containing polymers were obtained as red-orange and red-brown powder, respectively. The yields obtained for metal-containing polyurethane-ureas were 65–90%.

Coding for various reactants is as follows: MSa-OH₂trien refers to metal complexes. MDI and IPDI represent 4,4'-diphenylmethane diisocyanate and isophorone diisocyanate, respectively.

ZnOHSal₂trien-MDI: IR (KBr, cm⁻¹); 3322 (NH), 2922, 2854, 1693 (C=O), 1601, 1512, 1445, 1411, 1309, 1228, 1122, 1019, 947, 851, 816, 754, 625, 506. ¹H NMR (400 MHz, DMSO-*d*₆ + CDCl₃, ppm); δ 8.43 (s, 2H, CH=N, overlaps with NH), 7.25–7.40 (m, 8H, MDI ArH), 7.23 (s, 2H, ZnOHSal₂trien ArH), 6.95–7.15 (m, 8H, MDI ArH), 6.86 (d, 2H, ZnOHSal₂trien ArH, *J* = 8.2 Hz), 6.52 (d, 2H, ZnOHSal₂trien ArH, *J* = 8.2 Hz). The peaks in aliphatic region could not be clearly observed due to the large peak of H₂O and DMSO. Anal. Calcd. for C₅₀H₄₄ N₈O₇Zn; C 64.27; H 4.75; N 11.99; found C 63.82, H 5.04, N 8.93.

ZnOHSal₂trien-IPDI: IR (KBr, cm⁻¹); 3379 (NH), 2923, 1693 (C=O), 1625, 1543, 1485, 1452, 1400, 1384, 1365, 1302, 1223, 1182, 1124, 1021, 983, 954, 851, 793, 614.

NiOHSal₂trien-MDI: IR (KBr, cm⁻¹); 3333 (NH), 2922, 1693 (C=O), 1603, 1542, 1512, 1449, 1410, 1310, 1232, 1126, 1017, 951, 819. Anal. Calcd. for C₅₀H₄₄ N₈O₇Zn; C 64.74; H 4.78; N 11.08; found C 64.00, H 5.05, N 10.80.

NiOHSal₂trien-IPDI: IR (KBr, cm⁻¹); 3386 (NH), 2950, 2921, 1693 (C=O), 1637, 1552, 1461, 1384, 1357, 1334, 1302, 1229, 1123, 1069, 983, 843, 765, 649.

Synthesis of copolyurethane-ureas from MOHSal₂trien, MDI, and diamines or dialcohols

The mole ratio of MOHSal₂trien : MDI : diamines or dialcohols employed were 0.5 : 3.0 : 1.5, 1.0 : 3.0 : 1.0, and 1.5 : 3.0 : 0.5. Diamines employed were 4,4'-methylenedianiline (MDA) and hexamethylenediamine (HMA). Dialcohols employed were bisphenol A (BPO) and hexamethylene glycol (HMO). The general procedure for the synthesis of metal-containing

copolyurethane-ureas is as follows: MOHSal₂trien and MDI were dissolved in dried DMSO. Diamines or dialcohols in dried DMSO was rapidly added into the mixture followed by addition of DBTDL as a catalyst under nitrogen atmosphere. The reaction mixture was stirred at 90°C for 96 h. Eventually, the hot solution was poured into distilled water to precipitate the polymer. The polymer was separated by filtration, washed with distilled methanol several times, and dried *in vacuo* for 24 h. Zinc-containing copolymers were obtained as yellow powder in 57–87% yield and nickel-containing copolymers were obtained as light brown powder in 57–74% yield.

Coding for various reactants is as follows: MOHSal₂trien represents metal complexes. MDI represents 4,4'-diphenylmethane diisocyanate. MDA, HMA, BPO, and HMO refer to 4,4'-methylenedianiline, hexamethylenediamine, bisphenol A, and hexamethylene glycol, respectively. The last three digits refer to the mole ratios of the copolymer compositions.

The copolymers obtained from different mole ratios have similar IR spectra, therefore, only the IR data of copolymers obtained from mole ratio of 1.0 : 3.0 : 1.0 are shown as follows:

ZnOHSal₂trien-MDI-MDA: IR (KBr, cm⁻¹); 3376 (NH), 2922, 2851, 1708 (C=O), 1600, 1542, 1512, 1411, 1310, 1233, 1116, 1014, 816, 763, 508.

ZnOHSal₂trien-MDI-HMA: IR (KBr, cm⁻¹); 3337 (NH), 2923, 2854, 1716 (C=O), 1600, 1543, 1513, 1410, 1309, 1232, 1123, 1018, 812, 760, 508.

ZnOHSal₂trien-MDI-BPO: IR (KBr, cm⁻¹); 3342 (NH), 2921, 2851, 1720 (C=O), 1600, 1544, 1513, 1411, 1309, 1231, 1116, 1014, 816, 754, 506.

ZnOHSal₂trien-MDI-HMO: IR (KBr, cm⁻¹); 3321 (NH), 2922, 2851, 1718 (C=O), 1600, 1543, 1512, 1410, 1309, 1231, 1116, 1011, 816, 758, 629, 508.

NiOHSal₂trien-MDI-MDA: IR (KBr, cm⁻¹); 3369 (NH), 2918, 2851, 1694 (C=O), 1600, 1536, 1510, 1409, 1308, 1231, 1116, 1014, 812, 758, 508.

NiOHSal₂trien-MDI-HMA: IR (KBr, cm⁻¹); 3336 (NH), 2923, 2851, 1710 (C=O), 1600, 1542, 1515, 1410, 1309, 1232, 1116, 1014, 808, 761, 512.

NiOHSal₂trien-MDI-BPO: IR (KBr, cm⁻¹); 3330 (NH), 2921, 2859, 1720 (C=O), 1600, 1548, 1512, 1410, 1309, 1232, 1112, 1014, 812, 765, 508.

NiOHSal₂trien-MDI-HMO: IR (KBr, cm⁻¹); 3342 (NH), 2924, 2848, 1710 (C=O), 1601, 1540, 1509, 1411, 1310, 1232, 1116, 1014, 816, 758, 641, 512.

Synthesis of polymers without metal complexes (reference polymers) from the reaction between MDI and diamines or dialcohols

MDI and diamines or dialcohols were dissolved in DMSO. The mole ratio of diamines or dialcohols employed was 1 : 1. Dibutyltin dilaurate was added as a catalyst, and the reaction was heated at 90°C

under nitrogen atmosphere for 96 h. When the reaction mixture was completed, it was poured into distilled water to precipitate the polymer. The polymer was filtered, washed with distilled methanol, and dried *in vacuo*. The polymer was obtained as white powder. The yield obtained for the polymer was 45–77%.

MDI-MDA: IR (KBr, cm^{-1}); 3308 (NH), 2918, 2848, 1644 (C=O), 1598, 1545, 1512, 1410, 1307, 1236, 1112, 1018, 812, 649, 505.

MDI-HMA: IR (KBr, cm^{-1}); 3319 (NH), 2926, 2855, 1648 (C=O), 1598, 1551, 1513, 1408, 1309, 1236, 1108, 1011, 816, 761, 652, 508.

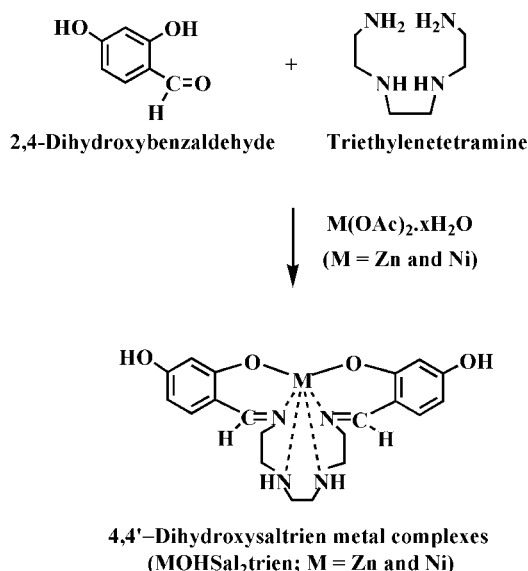
MDI-BPO: IR (KBr, cm^{-1}); 3308 (NH), 2910, 2840, 1645 (C=O), 1597, 1545, 1511, 1410, 1308, 1234, 1108, 1011, 812, 649, 508.

MDI-HMO: IR (KBr, cm^{-1}); 3323 (NH), 2930, 2851, 1706 (C=O), 1599, 1528, 1412, 1410, 1311, 1228, 1069, 816, 769, 508.

RESULTS AND DISCUSSION

Synthesis and characterization of 4,4'-dihydroxysaltrien metal complexes (MOHSal₂trien)

ZnOHSal₂trien and NiOHSal₂trien were synthesized by a one-pot reaction as shown in Scheme 1. The metal complexes contain two amine and two hydroxyl groups capable of undergoing polymerization with diisocyanates to give metal-containing polyurethane-ureas, which should give the polymer with good thermal stability. Both ZnOHSal₂trien and NiOHSal₂trien are soluble in DMF and DMSO, but insoluble in CH₂Cl₂, CHCl₃, CH₃CN, THF, and CH₃OH.



Scheme 1 Synthesis of 4,4'-dihydroxysaltrien zinc and nickel complexes (MOHSal₂trien).

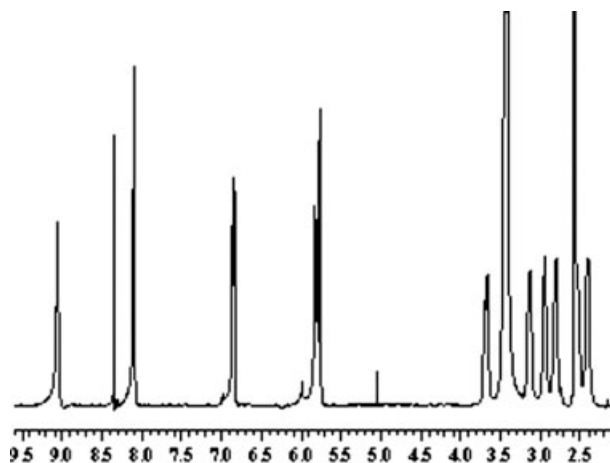
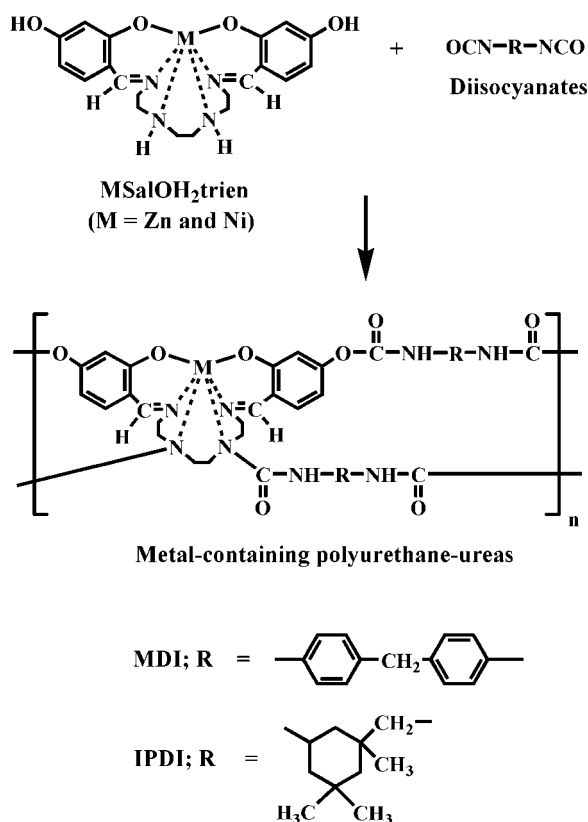


Figure 1 ¹H NMR spectrum of ZnOHSal₂trien.

The structure of metal complexes was confirmed by spectroscopic methods and elemental analysis. The IR spectra of ZnOHSal₂trien and NiOHSal₂trien show important bands of C=N stretching at 1630 and 1634 cm^{-1} , respectively. ¹H and ¹³C NMR data, which can be obtained only for ZnOHSal₂trien also support its structure. ¹H NMR spectrum of ZnOHSal₂trien (Fig. 1) show the characteristic imine —CH=N— and phenolic —OH protons at 8.10 and 9.06 ppm, respectively. The imine —CH=N— carbon of ZnOHSal₂trien is observed at 165.8 ppm in ¹³C NMR spectrum. MS data of both zinc and nickel complexes give the corresponding molecular formula. Elemental analysis data show that the experimentally determined percentage values of carbon, hydrogen, and nitrogen of both ZnOHSal₂trien and NiOHSal₂trien are within the calculated values.

Synthesis of metal-containing polyurethane-ureas from metal complexes and diisocyanates

The polymerization was carried out in DMSO, since the metal complexes are soluble in this solvent. Metal-containing polyurethane-ureas were synthesized from the reaction between MOHSal₂trien and diisocyanates (Scheme 2) at the mole ratio of MOHSal₂trien : diisocyanate = 1 : 2 with dibutyltin dilaurate as a catalyst. This mole ratio of 1 : 2 was employed since MOHSal₂trien contains four functional groups, i.e., two —NH— and two —OH groups, which can undergo polymerization with diisocyanates. The polymerization mechanism is the —NH— and —OH groups in MOHSal₂trien undergo reactions with isocyanate groups to give urea and urethane linkages, respectively. When the mole ratio of MOHSal₂trien : diisocyanate employed in the polymerization was 1 : 1, low yields of the polymers were obtained.



Scheme 2 Synthesis of metal-containing polyurethane-ureas from MOHSal₂trien and diisocyanates.

The solubility of zinc- and nickel-containing polyurethane-ureas was tested in various polar and non-polar solvents. The polymers based on MDI, namely ZnOHSal₂trien-MDI and NiOHSal₂trien-MDI are soluble in polar solvents such as DMF and DMSO and insoluble in CH₂Cl₂, CHCl₃, CH₃CN, THF, and CH₃OH. However, the polymers based on IPDI, namely ZnOHSal₂trien-IPDI and NiOHSal₂trien-IPDI, are slightly soluble in DMSO and most part of these polymers remain insoluble after heating. This solubility data suggest that the structure of MDI-based polymers should be a linear polymer while that of IPDI-based polymers might contain both linear and crosslinked polymers.

Characterization of metal-containing polyurethane-ureas

Infrared spectroscopy

All zinc- and nickel-containing polyurethane-ureas show similar IR spectra. The important characteristic absorption bands are observed at 3322–3386 cm⁻¹ (N–H stretching), and the carbonyl of urethane and urea appear as a shoulder in the range 1688–1699 cm⁻¹ with the center around 1693 cm⁻¹.

NMR spectroscopy

¹H NMR spectrum can be obtained only for ZnOHSal₂trien-MDI as shown in Figure 2. The ¹³C NMR spectrum of ZnOHSal₂trien-MDI could not be obtained because of the poor solubility of the polymer. ¹H NMR spectrum of ZnOHSal₂trien-MDI shows the aromatic protons of ZnOHSal₂trien at 7.23, 6.86, and 6.52 ppm. The aromatic protons of MDI are observed at 7.25–7.40 and 6.95–7.15 ppm. The integration ratio of aromatic protons in ZnOHSal₂trien and MDI units indicates that one ZnOHSal₂trien molecule reacts with two MDI molecules. Comparing between the chemical shifts of the same aromatic protons of ZnOHSal₂trien in ZnOHSal₂trien metal complex and ZnOHSal₂trien-MDI, it is found that they show the same pattern but their positions are different. The aromatic protons of ZnOHSal₂trien metal complex show resonance signals at 5.77–6.85 ppm, while these protons in ZnOHSal₂trien-MDI shift downfield and their signals are observed at 6.52–7.23 ppm. This is because the hydroxyl groups of ZnOHSal₂trien complex change into the urethane groups of ZnOHSal₂trien-MDI. The effect on aromatic protons of ZnOHSal₂trien metal complex resulting from hydroxyl groups is electron donating, while urethane groups show electron withdrawing effect. The spectrum of ZnOHSal₂trien-IPDI could not be obtained because of the poor solubility of the polymer in DMSO.

Elemental analysis

The chemical structure of metal-containing polyurethane-ureas was confirmed by elemental analysis. For ZnOHSal₂trien-MDI and NiOHSal₂trien-MDI, the elemental analysis data show that the experimentally determined percentage values of carbon, hydrogen, and nitrogen are within the calculated values. For

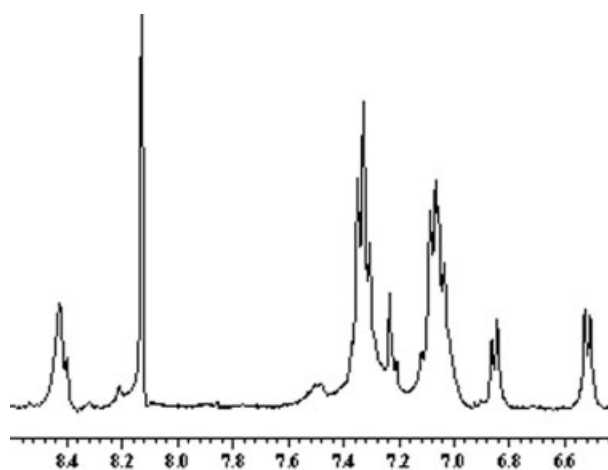


Figure 2 ¹H NMR spectrum of ZnOHSal₂trien-MDI.

TABLE I
Yield, Inherent Viscosity, Solubility, Thermal, and LOI Data of Metal-Containing Polymers and Reference Polymers

Polymers	Yield (%)	η_{inh} (dL/g)	IDT (°C)	Weight of residue at 600°C (%)	LOI	Solubility in DMSO ^a
ZnOHSal ₂ trien-MDI	90	0.1648	241	33	22.6	++
ZnOHSal ₂ trien-IPDI	68	nd ^b	278	14	21.4	-
NiOHSal ₂ trien-MDI	83	0.1566	228	55	22.3	++
NiOHSal ₂ trien-IPDI	65	nd ^b	284	27	21.4	-
ZnOHSal ₂ trien-MDI-MDA (0.5 : 3.0 : 1.5)	69	0.1361	275	34	23.6	+++
ZnOHSal ₂ trien-MDI-MDA (1.0 : 3.0 : 1.0)	67	0.1409	272	33	23.3	++
ZnOHSal ₂ trien-MDI-MDA (1.5 : 3.0 : 0.5)	86	0.1184	253	36	22.8	++
ZnOHSal ₂ trien-MDI-HMA (0.5 : 3.0 : 1.5)	80	0.1012	263	30	23.4	++
ZnOHSal ₂ trien-MDI-HMA (1.0 : 3.0 : 1.0)	57	0.1012	261	35	23.1	++
ZnOHSal ₂ trien-MDI-HMA (1.5 : 3.0 : 0.5)	79	0.1275	258	39	22.8	+++
ZnOHSal ₂ trien-MDI-BPO (0.5 : 3.0 : 1.5)	70	0.1565	257	32	23.1	+++
ZnOHSal ₂ trien-MDI-BPO (1.0 : 3.0 : 1.0)	69	0.1465	258	46	22.2	+++
ZnOHSal ₂ trien-MDI-BPO (1.5 : 3.0 : 0.5)	65	0.1390	263	34	22.8	+++
ZnOHSal ₂ trien-MDI-HMO (0.5 : 3.0 : 1.5)	80	0.1539	255	36	22.7	++++
ZnOHSal ₂ trien-MDI-HMO (1.0 : 3.0 : 1.0)	77	0.1688	256	46	22.5	++++
ZnOHSal ₂ trien-MDI-HMO (1.5 : 3.0 : 0.5)	87	0.1625	255	34	22.4	++++
NiOHSal ₂ trien-MDI-MDA (0.5 : 3.0 : 1.5)	68	0.1150	301	53	23.5	+
NiOHSal ₂ trien-MDI-MDA (1.0 : 3.0 : 1.0)	65	0.1145	289	51	23.4	+
NiOHSal ₂ trien-MDI-MDA (1.5 : 3.0 : 0.5)	66	0.0980	246	49	22.2	+
NiOHSal ₂ trien-MDI-HMA (0.5 : 3.0 : 1.5)	74	0.1390	240	35	22.2	+
NiOHSal ₂ trien-MDI-HMA (1.0 : 3.0 : 1.0)	72	0.1545	252	51	22.6	+
NiOHSal ₂ trien-MDI-HMA (1.5 : 3.0 : 0.5)	70	0.1130	248	54	22.1	+
NiOHSal ₂ trien-MDI-BPO (0.5 : 3.0 : 1.5)	60	0.1700	268	37	22.2	++
NiOHSal ₂ trien-MDI-BPO (1.0 : 3.0 : 1.0)	57	0.1390	262	47	22.5	++
NiOHSal ₂ trien-MDI-BPO (1.5 : 3.0 : 0.5)	82	0.1110	253	42	22.1	+
NiOHSal ₂ trien-MDI-HMO (0.5 : 3.0 : 1.5)	63	0.1513	248	44	21.8	+++
NiOHSal ₂ trien-MDI-HMO (1.0 : 3.0 : 1.0)	59	0.1654	232	47	21.6	+++
NiOHSal ₂ trien-MDI-HMO (1.5 : 3.0 : 0.5)	69	0.1540	240	54	22.2	+++
MDI-MDA	77	0.0940	270	34	^b nd	+
MDI-HMA	73	0.1000	303	19	^b nd	+
MDI-BPO	45	0.1156	262	28	^b nd	+
MDI-HMO	76	0.1390	279	18	^b nd	++

^a Solubility was determined based on the amount of polymer that is soluble in 1 mL of DMSO at room temperature as follows: +, 0–50 mg; ++, 51–100 mg; +++, 101–150 mg; +++++, 201–250 mg; -, insoluble.

^b Could not be determined.

ZnOHSal₂trien-IPDI and NiOHSal₂trien-IPDI, the elemental analysis was not done since these polymers are not soluble in organic solvents.

Inherent viscosity

The inherent viscosity of all polyurethane-ureas was measured at 40°C in DMSO (Table I). The viscosity of ZnOHSal₂trien-MDI is slightly higher than that of NiOHSal₂trien-MDI. The viscosity of ZnOHSal₂trien-IPDI and NiOHSal₂trien-IPDI could not be obtained since these polymers are not completely soluble in DMSO.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) thermograms of zinc- and nickel-containing polyurethane-ureas are shown in Figures 3 and 4. Thermal stability of the polymers is evaluated by the IDT value and weight of residue at different temperatures. IDT of IPDI-

based polymers is higher than that of MDI-based polymers. Considering wt % loss of the polymers, there is not much different in the initial wt % loss that occurs in the temperature range 200–300°C,

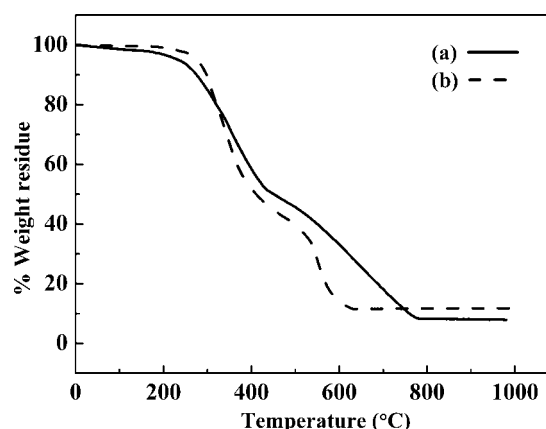


Figure 3 TGA thermograms of (a) ZnOHSal₂trien-MDI; (b) ZnOHSal₂trien-IPDI.

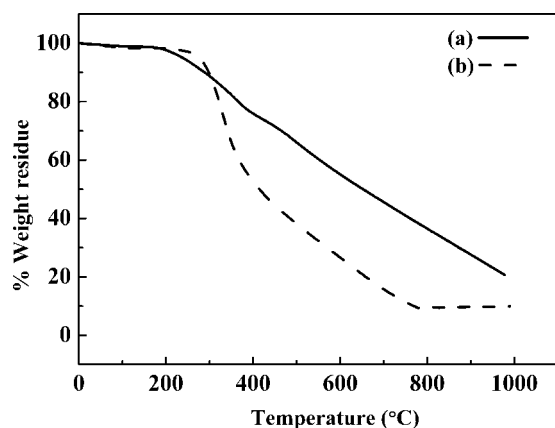


Figure 4 TGA thermograms of (a) NiOHSal₂trien-MDI; (b) NiOHSal₂trien-IPDI.

whereas an appreciable difference in wt % loss in the range 350–700°C could be observed. Considering the wt % loss of polymers at 600°C, the MDI-based polymers are more thermally stable than the polymers based on IPDI. Nickel-containing polymers show better thermal stability than zinc-containing polymers. Among all polymers, NiOHSal₂trien-MDI is the most thermally stable polymers with char yield of 55% at 600°C.

Flame retardancy

Flame-retardant property of zinc- and nickel-containing polyurethane-ureas was compared from the LOI values as shown in Table I. Zinc- and nickel-containing polymers based on MDI and IPDI show almost the same LOI value in the range 21.4–22.6.

XRD

Figure 5 shows the XRD patterns of ZnOHSal₂trien-MDI and NiOHSal₂trien-MDI. These polymers show broad peak and therefore they are amorphous in nature, which is supported by the solubility test of polymers that they are soluble in DMF and DMSO.

Synthesis of metal-containing copolyurethane-ureas from the reaction between of MOHSal₂trien, MDI, and diamines or dialcohols

Metal-containing copolyurethane-ureas were synthesized from MOHSal₂trien, MDI, and diamines or dialcohols as shown in Scheme 3. MDI was chosen as diisocyanate in the synthesis since TGA data of the MDI-based polyurethane-ureas indicate that these polymers are thermally stable when compared with IPDI-based polymers. By addition of diamines during the polymerization, the urea linkage in the polymer structure is increased and it is expected that the polymers should have improved thermal stability

because of more hydrogen bonding from the urea linkage. Addition of dialcohols resulted in the increase in urethane linkage and therefore improve the polymer solubility. The reaction between MOHSal₂trien, MDI, and diamines or dialcohols at variable mole ratios of MOHSal₂trien : MDI : diamines or dialcohols = 0.5 : 3.0 : 1.5, 1.0 : 3.0 : 1.0, and 1.5 : 3.0 : 0.5 was carried out in DMSO with DBTDL as a catalyst. For the reaction between MOHSal₂trien, MDI, and diamines, MDI can undergo reactions with both MOHSal₂trien and diamines. When MOHSal₂trien, MDI, and dialcohols was employed, MDI can also undergo reactions with both MOHSal₂trien and dialcohols. When the mole ratio of MOHSal₂trien : MDI : diamines or dialcohols = 1.0 : 3.0 : 1.0 was employed, it was expected that two moles of MDI reacted with MOHSal₂trien and another one mole of MDI reacted with diamines or dialcohols. Other two mole ratios of MOHSal₂trien : MDI : diamines or dialcohols, 0.5 : 3.0 : 1.5 and 1.5 : 3.0 : 0.5, was employed to study the effect of starting material compositions on the polymer properties.

Characterization of metal-containing copolyurethane-ureas

All metal-containing copolyurethane-ureas have similar IR spectra. The important characteristic absorption bands are 3376–3321 cm⁻¹ (N–H stretching). The carbonyl of urethane and urea are observed as a shoulder in the range 1720–1694 cm⁻¹.

Solubility test shows that metal-containing copolyurethane-ureas are soluble in DMF and DMSO. These copolymers are insoluble in CH₂Cl₂, CHCl₃, CH₃CN, THF, and CH₃OH. The solubility data of copolymers, which are determined from the amount of polymer that is soluble in 1 mL of DMSO at room temperature (Table I) indicate that zinc-containing copolymers show better solubility than nickel-containing copolymers. Most of metal-containing copolyurethane-ureas are more soluble in DMSO as compared with metal-containing polyurethane-ureas. The copolymers based on dialcohol exhibit higher solubility than diamine-based copolymers. This might

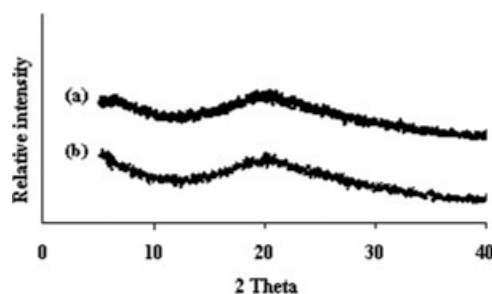
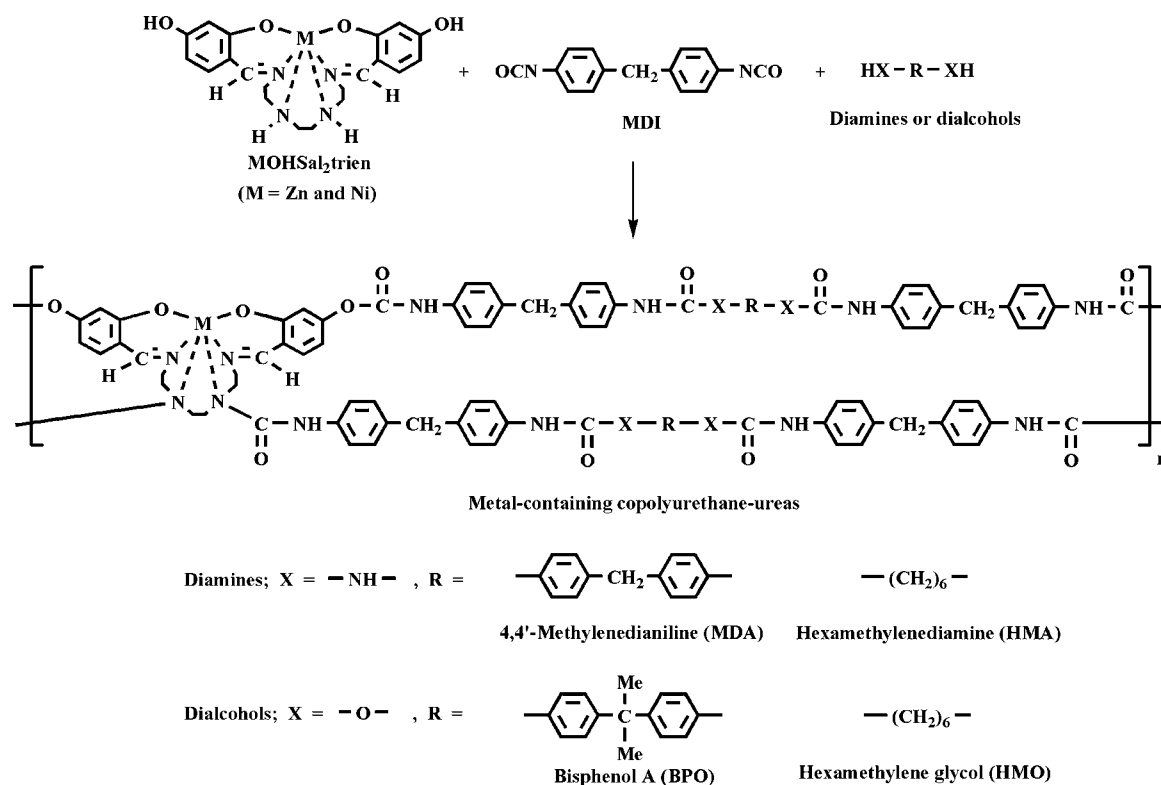


Figure 5 XRD of (a) ZnOHSal₂trien-MDI; (b) NiOHSal₂trien-MDI.



Scheme 3 Synthesis of metal-containing copolyurethane-ureas from MOHSal₂trien, diisocyanates, and diamines or dialcohols.

be due to the increase in urethane linkage in the dialcohol-based copolymers. The aliphatic dialcohol-based copolymers show higher solubility than the copolymers based on aromatic dialcohols-based copolymers. This might be due to the higher flexibility of the aliphatic part in HMO.

Inherent viscosity of the copolymers (Table I) is found to be in the range between 0.1012 and 0.1688 dL/g for

zinc-containing copolyurethane-ureas and 0.0980–0.1700 dL/g for nickel-containing copolyurethane-ureas. The viscosity of metal-containing copolyurethane-ureas is higher than that of reference polyurethane-ureas which do not contain metal complexes in both Zn and Ni series.

For the amine-based copolymers, TGA results of ZnOHSal₂trien-MDI-MDA and NiOHSal₂trien-MDI-

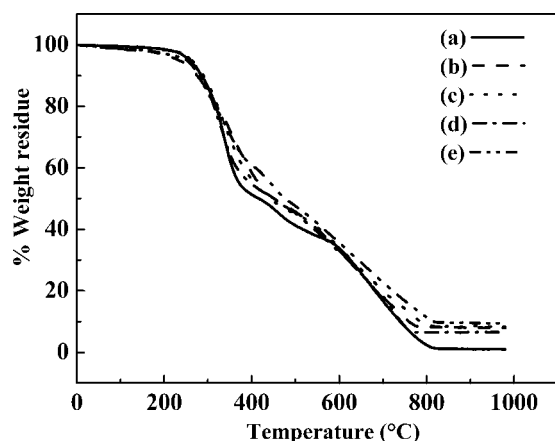


Figure 6 TGA thermograms of (a) MDI-MDA; (b) ZnOH-Sal₂trien-MDI; (c) ZnOHSal₂trien-MDI-MDA (0.5 : 3.0 : 1.5); (d) ZnOHSal₂trien-MDI-MDA (1.0 : 3.0 : 1.0); (e) ZnOHSal₂trien-MDI-MDA (1.5 : 3.0 : 0.5).

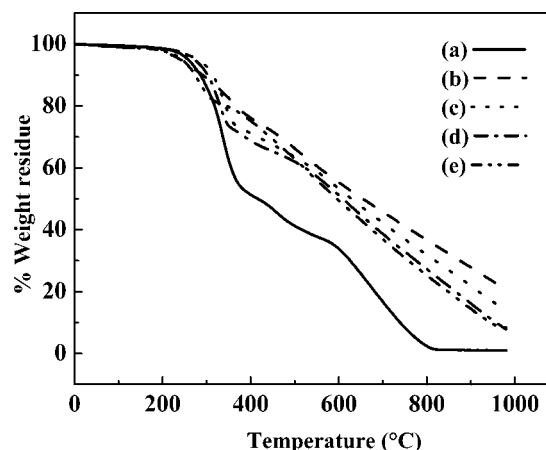


Figure 7 TGA thermograms of (a) MDI-MDA; (b) NiOH-Sal₂trien-MDI; (c) NiOHSal₂trien-MDI-MDA (0.5 : 3.0 : 1.5); (d) NiOHSal₂trien-MDI-MDA (1.0 : 3.0 : 1.0); (e) NiOHSal₂trien-MDI-MDA (1.5 : 3.0 : 0.5).

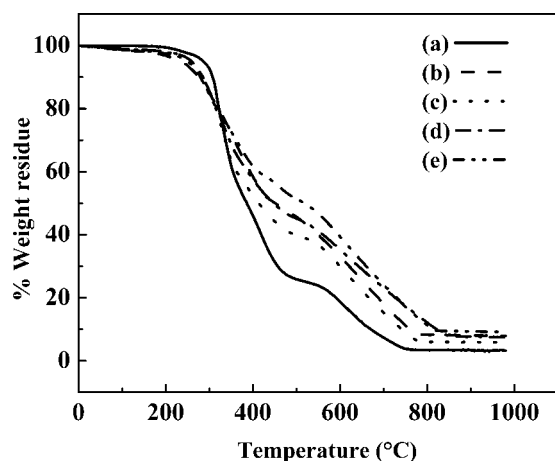


Figure 8 TGA thermograms of (a) MDI-HMA; (b) ZnOH-Sal₂trien-MDI; (c) ZnOHSal₂trien-MDI-HMA (0.5 : 3.0 : 1.5); (d) ZnOHSal₂trien-MDI-HMA (1.0 : 3.0 : 1.0); (e) ZnOHSal₂trien-MDI-HMA (1.5 : 3.0 : 0.5).

MDA copolymers (Figs. 6 and 7) show that the variable amount of MDA in zinc- and nickel-containing copolyurethane-ureas does not affect their char yields at 600°C when compared with those of ZnOHSal₂trien-MDI and NiOHSal₂trien-MDI. Except for NiOHSal₂trien-MDI-MDA (1.5 : 3.0 : 0.5), which has slightly less char yield than NiOHSal₂trien-MDI. For ZnOHSal₂trien-MDI-HMA and NiOHSal₂trien-MDI-HMA (Figs. 8 and 9), the presence of HMA in ZnOHSal₂trien-MDI-HMA (1.5 : 3.0 : 0.5) slightly increases the char yield at 600°C when compared with that of ZnOHSal₂trien-MDI, while the char yield at 600°C of NiOHSal₂trien-MDI-HMA (0.5 : 3.0 : 1.5) is much lower than that of NiOHSal₂trien-MDI. IDTs of ZnOHSal₂trien-MDI-MDA, NiOHSal₂trien-MDI-MDA, ZnOHSal₂trien-MDI-HMA, and NiOH-

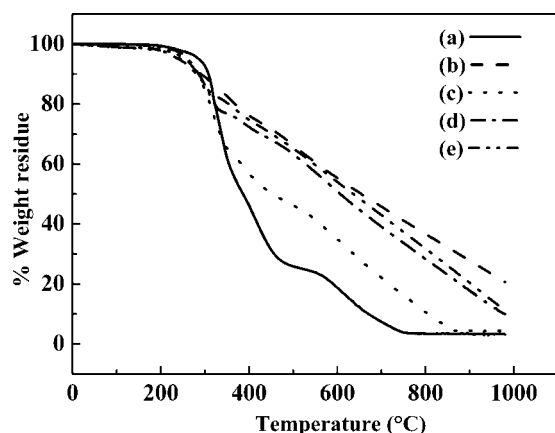


Figure 9 TGA thermograms of (a) MDI-HMA; (b) NiOH-Sal₂trien-MDI; (c) NiOHSal₂trien-MDI-HMA (0.5 : 3.0 : 1.5); (d) NiOHSal₂trien-MDI-HMA (1.0 : 3.0 : 1.0); (e) NiOHSal₂trien-MDI-HMA (1.5 : 3.0 : 0.5).

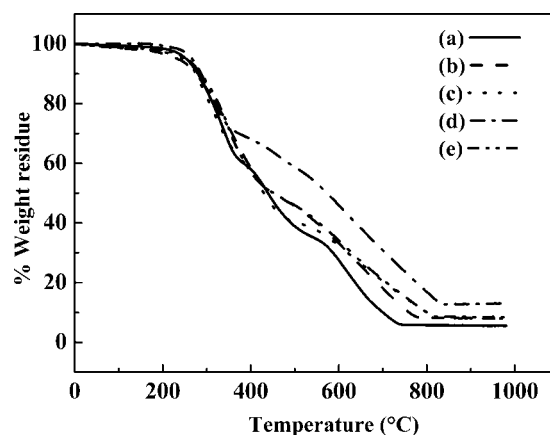


Figure 10 TGA thermograms of (a) MDI-BPO; (b) ZnOH-Sal₂trien-MDI; (c) ZnOHSal₂trien-MDI-BPO (0.5 : 3.0 : 1.5); (d) ZnOHSal₂trien-MDI-BPO (1.0 : 3.0 : 1.0); (e) ZnOHSal₂trien-MDI-BPO (1.5 : 3.0 : 0.5).

Sal₂trien-MDI-HMA are in the range are in the range 253–275, 246–301, 258–263, and 240–252°C, respectively, which are higher than those of the polymers synthesized without MDA and HMA, namely ZnOHSal₂trien-MDI and NiOHSal₂trien-MDI. The IDTs of all copolymers, except NiOHSal₂trien-MDI-HMA, increase with increasing amount of MDA and HMA in the copolymers.

In the case of alcohol-based copolymers, TGA results show that the char yields at 600°C of ZnOH-Sal₂trien-MDI-BPO (1.0 : 3.0 : 1.0) (Fig. 10) and ZnOH-Sal₂trien-MDI-HMO (Fig. 12) are higher than that of ZnOHSal₂trien-MDI. For NiOHSal₂trien-MDI-BPO (Fig. 11) and NiOHSal₂trien-MDI-HMO (Fig. 13), their char yields at 600°C decrease by introducing BPO and HMO into the polymers. The IDTs of ZnOHSal₂-

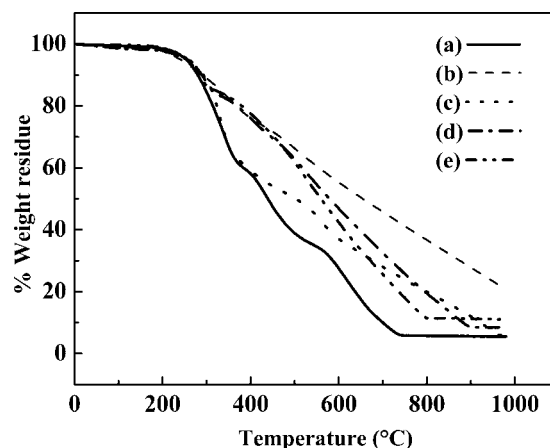


Figure 11 TGA thermograms of (a) MDI-BPO; (b) NiOH-Sal₂trien-MDI; (c) NiOHSal₂trien-MDI-BPO (0.5 : 3.0 : 1.5); (d) NiOHSal₂trien-MDI-BPO (1.0 : 3.0 : 1.0); (e) NiOHSal₂trien-MDI-BPO (1.5 : 3.0 : 0.5).

trien-MDI-BPO, ZnOHSal₂trien-MDI-HMO, NiOHSal₂trien-MDI-BPO, and NiOHSal₂trien-MDI-HMO are in the range 257–263, 255–256, 253–268, and 232–248°C, respectively, which are higher than those of their corresponding polymers synthesized without BPO and HMO, namely ZnOHSal₂trien-MDI and NiOHSal₂trien-MDI. ZnOHSal₂trien-MDI-BPO shows slight increase in IDT when the amount of BPO is decreased. The amount of HMO in ZnOHSal₂trien-MDI-HMO has no effect on the IDT of the copolymers. The IDTs of NiOHSal₂trien-MDI-BPO and NiOHSal₂trien-MDI-HMO increase with increasing amount of BPO and HMO in the copolymers.

Comparing between metal-containing copolyurethane-urea and its corresponding reference polymer which does not contain MOHSal₂trien in the polymer chain, the reference polymer shows higher IDT than metal-containing copolyurethane-urea, but the rate of decomposition is higher than that of metal-containing copolyurethane-urea.

Flame-retardant property of zinc- and nickel-containing copolyurethane-ureas was compared from their LOI values. All metal-containing copolyurethane-ureas show almost the same LOI value in the range 21.6–23.4.

CONCLUSIONS

Hexadentate Schiff base metal complexes, ZnOHSal₂trien and NiOHSal₂trien, were synthesized and used in the synthesis of metal-containing polyurethane-ureas and copolyurethane-ureas. All polymers are soluble in DMF and DMSO. Zinc-containing polymers show better solubility than nickel-containing polymers. Among all metal-containing polyurethane-

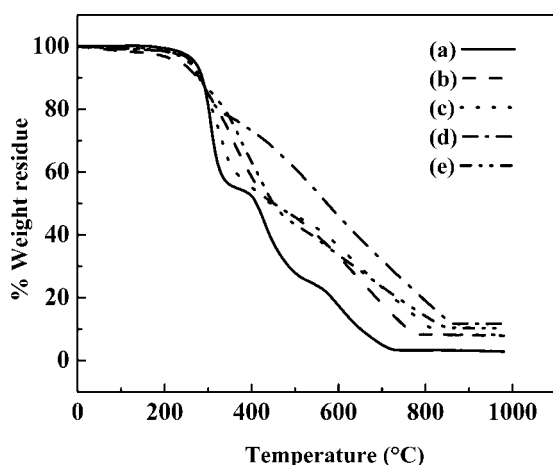


Figure 12 TGA thermograms of (a) MDI-HMO; (b) ZnOHSal₂trien-MDI; (c) ZnOHSal₂trien-MDI-HMO (0.5 : 3.0 : 1.5); (d) ZnOHSal₂trien-MDI-HMO (1.0 : 3.0 : 1.0); (e) ZnOHSal₂trien-MDI-HMO (1.5 : 3.0 : 0.5).

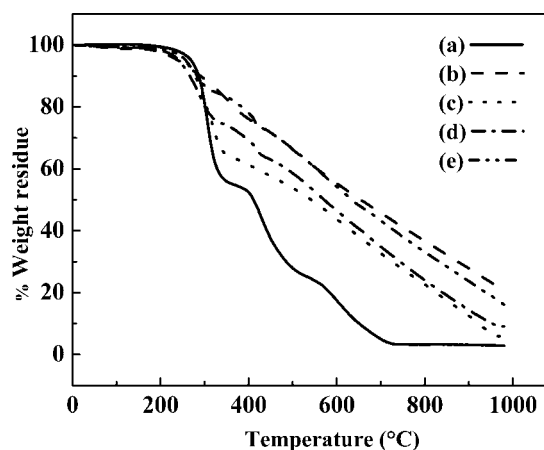


Figure 13 TGA thermograms of (a) MDI-HMO; (b) NiOHSal₂trien-MDI; (c) NiOHSal₂trien-MDI-HMO (0.5 : 3.0 : 1.5); (d) NiOHSal₂trien-MDI-HMO (1.0 : 3.0 : 1.0); (e) NiOHSal₂trien-MDI-HMO (1.5 : 3.0 : 0.5).

ureas, NiOHSal₂trien-MDI is the most thermally stable polymer with the highest char yield of 55% at 600°C. Copolyurethane-ureas were synthesized by the reaction between MOHSal₂trien, MDI, and diamines or dialcohols. It is found that the IDT of both zinc- and nickel-containing copolymers increases upon addition of diamines or dialcohols in the polymerization. Solubility in DMSO and char yield at 600°C of zinc-containing copolyurethane-ureas is improved upon the addition of dialcohols. The char yield at 600°C of both ZnOHSal₂trien-MDI-BPO (1.0 : 3.0 : 1.0) and ZnOHSal₂trien-MDI-HMO (1.0 : 3.0 : 1.0) is 46%, which is almost comparable to that of NiOHSal₂trien-MDI.

The authors thank the Institute of Biotechnology and Genetic Engineering, Chulalongkorn University for MALDI-TOF MS data.

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