

# Thermally Stable Polyureas and Poly(urea-imide)s Containing Zinc and Nickel Naphthrien Complexes

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**ABSTRACT:** Two new naphthrien metal complexes, MNaph<sub>2</sub>trien; where M = Zn and Ni, were synthesized and used for the synthesis of metal-containing polyureas and poly(urea-imide)s. MNaph<sub>2</sub>trien underwent polymerization reaction with two diisocyanates, namely, 4,4'-diphenylmethane diisocyanate and isophorone diisocyanate to yield polyureas. Poly(urea-imide)s were obtained by the synthesis of metal-containing isocyanate-terminated polyurea prepolymers from the reaction between MNaph<sub>2</sub>trien and excess diisocyanates, which could then undergo further reaction with different dianhydrides. The dianhydrides used were pyromellitic dianhydride and benzophenone-3,3',4,4'-tetracarboxylic dianhydride. The polymers were characterized by infrared, nuclear magnetic resonance, elemental analysis, X-ray diffraction, solubility, and viscosity. Glass transition temperature of the polymers was obtained from differential

scanning calorimetry and dynamic mechanical thermal analysis. Thermal stability of polymers was studied by thermogravimetric analysis in air. It was found that the resulting metal-containing polymers exhibited good thermal stability. Initial decomposition temperatures of the polymers depend on the amount of MNaph<sub>2</sub>trien in the polymer composition. Char yields of metal-containing poly(urea-imide)s are higher than those of metal-containing polyureas. Most metal-containing polymers show good solubility in organic solvents. Shore D hardness test indicates that metal-containing poly(urea-imide)s are hard materials. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3945–3954, 2009

**Key words:** polyureas; poly(urea-imide)s; metal-containing polymers; thermally stable polymers; thermogravimetric analysis

## INTRODUCTION

Polyureas have received much interest because they have unique properties such as high toughness, good chemical and abrasion resistance. Because of these properties, polyureas are one of the commercial polymers being used successfully for many applications. The introduction of metal into polyurea backbones to obtain thermally stable polymers has received interest and several approaches have been reported such as synthesis of phosphorus-containing polyureas,<sup>1</sup> heterocyclic polyureas,<sup>2–4</sup> and poly(urea-imide)s.<sup>5–14</sup>

The works concerning the synthesis of metal-containing polyureas have been reported. 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. For example, polymerization of 2,4-tolylene diisocyanate with mixtures of 4,4'-diaminodiphenylmethane and divalent metal salts of *p*-aniline sulfonic acid<sup>15</sup> and *p*-aminobenzoic acid<sup>16</sup> gave polyureas with ionic links in the main chain. 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 in our group, thermally stable metal-containing polyureas<sup>17</sup> were synthesized from the reaction of hexadentate Schiff-base metal complexes with diisocyanates. To increase thermal stability of metal-containing polyureas, we became interested in the synthesis of polymers using the new naphthrien metal complexes (MNaph<sub>2</sub>trien), which contain naphthalene rings as thermally stable polymers containing naphthalene units have been reported.<sup>18,19</sup> The two amine groups in MNaph<sub>2</sub>trien could undergo polymerization reaction with diisocyanates to give metal-containing polyureas. The structures of these metal-containing

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polyureas can be further modified to improve their thermal stability by addition of imide group into the polymer structure because poly(urea-imide)s are known as thermally stable polymers. These metal-containing polymers can be synthesized from MNaph<sub>2</sub>trien, diisocyanates, and dianhydrides by using the reaction of isocyanate-terminated polyurea prepolymer with acid anhydride. Therefore, the resulting metal-containing polymers should possess good thermal stability because of the properties of both metal-containing polyureas and polyimides. In this article, we describe the synthesis and characterization of polyureas and poly(urea-imide)s containing MNaph<sub>2</sub>trien in the polymer chain. Thermal stability of the obtained polymers is investigated.

## EXPERIMENTAL

### Materials

The following chemicals were used as received from Aldrich without purification and their purity percentages were as follows: 4,4'-diphenylmethane diisocyanate (MDI, 98%), isophorone diisocyanate (IPDI, 98%), pyromellitic dianhydride (PMDA, 97%), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA, 98%), nickel(II) acetate tetrahydrate (98%), and 2-hydroxy-1-naphthaldehyde (technical grade). Zinc(II) acetate dihydrate (99%) and triethylenetetramine (technical grade) were obtained from Fluka and used as received. *N*-methyl-2-pyrrolidinone (NMP) was used as received. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were dried over calcium hydride and distilled before their use.

### Measurements

Fourier transform infrared (FTIR) spectra were obtained using a Nicolet Impact 410 FTIR spectrophotometer with potassium bromide (KBr) disk method. Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-*d*<sub>6</sub> 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. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Biflex mass spectrometer using  $\alpha$ -cyanocinnamic acid as a matrix. X-ray diffraction (XRD) experiments were performed on a Bruker D8 Discover diffractometer using Ni-filtered Cu K $\alpha$  radiation (40 kV, 40 mA) with scanning rate of 1°/min. Differential scanning calorimetry (DSC) was carried out using a Netzsch DSC 204F1 thermal analyzer at a heating rate of 20°C/min in nitrogen atmosphere. Dynamic mechanical thermal analysis (DMTA) was

performed on a Netzsch DMA 242 thermal analyzer using penetration mode at a frequency of 0.5 Hz and a heating rate of 3°C/min over the temperature range of -50 to 240°C in nitrogen atmosphere. The sample thickness was 3 mm. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 409C thermal analyzer at a heating rate of 20°C/min in air atmosphere. Initial decomposition temperature (IDT) was taken at the temperature where 5 wt % loss of the polymer occurred. Inherent viscosity ( $\eta_{inh}$ ) 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 5 mg samples to 1 mL of a solvent. Shore D hardness tests were performed using a Zwick 3100 durometer on a shore D scale according to ASTM D-2240. The polymer samples for DMTA and hardness testing were obtained by solution-cast from NMP solutions by heating in an oven at 100°C.

### Synthesis of naphthtrien zinc complex

A solution of triethylenetetramine (0.149 mL, 1.0 mmol) in methanol (10 mL) was added dropwise to solution of 2-hydroxy-1-naphthaldehyde (0.344 g, 2.0 mmol) and zinc(II) acetate dihydrate (0.220 g, 1.0 mmol) in methanol (25 mL) at 0°C, and the mixture was stirred for 10 min. A solution of 2M sodium hydroxide (1 mL, 2.0 mmol) was added and the mixture was stirred at 0°C for 30 min. The solution was allowed to stand at room temperature for 6 h. Naphthtrien zinc complex (ZnNaph<sub>2</sub>trien) precipitated from the solution and was subsequently isolated by filtration and dried under vacuum. ZnNaph<sub>2</sub>trien was obtained as yellow solid (0.363 g, 70%). IR (KBr, cm<sup>-1</sup>): 3340 (NH), 3312, 3043, 2894, 2850, 1619 (C=N), 1533, 1500, 1463, 1171, 972, 828, 750, 649, 513. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm);  $\delta$  9.23 (2H, s, CH=N), 8.06 (2H, d, Ar-H, *J* = 8.8 Hz), 7.52 (2H, d, Ar-H, *J* = 7.2 Hz), 7.46 (2H, d, Ar-H, *J* = 9.2 Hz), 7.23–7.37 (2H, m, Ar-H), 7.02 (2H, t, Ar-H, *J* = 7.2 Hz), 6.62 (2H, d, Ar-H, *J* = 9.2 Hz), 3.83–3.93 (2H, m, CH<sub>2</sub>), 3.60–3.69 (2H, m, CH<sub>2</sub>), 3.12–3.26 (4H, m, NH, and CH<sub>2</sub>), 2.78–2.87 (2H, m, CH<sub>2</sub>), 2.52–2.62 (2H, m, CH<sub>2</sub>), 2.37–2.45 (2H, m, CH<sub>2</sub>). <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>, ppm);  $\delta$  172.60, 161.50, 135.98, 132.86, 128.40, 127.91, 126.46, 124.40, 119.60, 118.00, 107.44, 55.78, 46.16, 43.46. MALDI-TOF MS (*m/z*) 518.78. Anal. Calcd. for C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>Zn 1/2H<sub>2</sub>O: C 63.81; H 5.55; N 10.63; found C 63.47; H 5.33; N 10.44.

### Synthesis of naphthtrien nickel complex

Naphthtrien nickel complex (NiNaph<sub>2</sub>trien) was synthesized in the same manner as ZnNaph<sub>2</sub>trien using

nickel(II) acetate tetrahydrate (0.249 g, 1.0 mmol). NiNaph<sub>2</sub>trien was obtained as brown solid (0.435 g, 85%). IR (KBr, cm<sup>-1</sup>); 3438 (NH), 3319, 3044, 2900, 2851, 1623 (C=N), 1533, 1500, 1463, 1175, 965, 828, 750, 649, 552. MALDI-TOF MS (*m/z*) 511.14. Anal. Calcd. for C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>Ni 1/2H<sub>2</sub>O: C 64.64; H 5.63; N 10.77; found C 64.61; H 5.52; N 11.02.

#### Synthesis of metal-containing polyureas from the reaction between MNaph<sub>2</sub>trien and diisocyanates

Polyureas were synthesized from MNaph<sub>2</sub>trien (where M = Zn and Ni) and diisocyanates. The diisocyanates used were MDI and IPDI. The mole ratio of MNaph<sub>2</sub>trien : diisocyanate used was 1 : 1. The general procedure for the synthesis of metal-containing polyureas was as follows: A solution of MNaph<sub>2</sub>trien (1.0 mmol) and diisocyanate (1.0 mmol) in dried CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was heated at reflux under nitrogen atmosphere. The reaction times of MNaph<sub>2</sub>trien with MDI and IPDI were 4 and 24 h, respectively. Finally, the reaction mixture was allowed to cool and poured into a large quantity of distilled water to precipitate the polymer. The polymer was separated by filtration, washed several times with methanol, and then dried under vacuum for 48 h. Zinc- and nickel-containing polyureas were obtained as yellow and brown powder, respectively. The yields obtained for metal-containing polyureas were 53–85%.

Coding for various reactants is as follows: MNaph<sub>2</sub>trien refers to metal complexes. MDI and IPDI represent 4,4'-diphenylmethane diisocyanate and isophorone diisocyanate, respectively.

#### ZnNaph<sub>2</sub>trien-MDI

IR (KBr, cm<sup>-1</sup>); 3400 (NH), 3035, 2923, 1703 (C=O), 1616 (C=N), 1532, 1514, 1462, 1416, 1356, 1307, 1243, 1186, 965, 828, 749. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm); δ 9.09–9.28 (m, CH=N), 8.49–8.58 (m, NH), 7.91–8.19 (m, Ar-H), 7.57–7.66 (m, Ar-H), 7.42–7.48 (m, Ar-H), 7.22–7.42 (m, Ar-H), 6.93–7.21 (m, Ar-H), 6.80–6.87 (m, Ar-H), 6.66–6.80 (m, Ar-H), 6.58–6.64 (m, Ar-H), 6.42–6.52 (m, Ar-H), 4.82–4.87 (m, NH), 3.96–4.16 (m, CH<sub>2</sub>), 3.83–3.94 (m, CH<sub>2</sub>), 2.81–3.73 (m, CH<sub>2</sub>), 3.44–3.71 (m, CH<sub>2</sub>), 3.10–3.25 (m, CH<sub>2</sub>), 2.77–2.86 (m, CH<sub>2</sub>), 2.69–2.75 (m, CH<sub>2</sub>), 2.38–2.45 (m, CH<sub>2</sub>). Anal. Calcd. for C<sub>43</sub>H<sub>38</sub>N<sub>6</sub>O<sub>4</sub>Zn: C 67.23; H 4.99; N 10.94; found C 65.87; H 5.54; N 10.54.

#### ZnNaph<sub>2</sub>trien-IPDI

IR (KBr, cm<sup>-1</sup>); 3360 (NH), 2941, 2923, 1692 (C=O), 1623 (C=N), 1543, 1463, 1434, 1394, 1358, 1304, 1245, 1189, 1040, 963, 831, 749. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm); δ 9.08–9.31 (m, CH=N), 7.99–8.16

(m, Ar-H), 7.54–7.65 (m, Ar-H), 7.49–7.54 (m, Ar-H), 7.43–7.48 (m, Ar-H), 7.26–7.41 (m, Ar-H), 7.04–7.16 (m, Ar-H), 6.98–7.04 (m, Ar-H), 6.70–6.79 (m, Ar-H), 6.59–6.64 (m, Ar-H), 5.34–5.98 (m, NH), 4.37–4.62 (m, NH), 3.73–3.94 (m, aliphatic-H), 3.46–3.73 (m, aliphatic-H), 3.11–3.24 (m, aliphatic-H), 2.55–2.91 (m, aliphatic-H), 0.65–1.82 (m, aliphatic-H). Anal. Calcd. for C<sub>40</sub>H<sub>46</sub>N<sub>6</sub>O<sub>4</sub>Zn: C 64.90; H 6.26; N 11.35; found C 64.98; H 6.31; N 11.34.

#### NiNaph<sub>2</sub>trien-MDI

IR (KBr, cm<sup>-1</sup>); 3397 (NH), 3036, 2923, 1702 (C=O), 1618 (C=N), 1532, 1514, 1462, 1416, 1356, 1307, 1243, 1186, 1085, 972, 945, 892, 828, 749. Anal. Calcd. for C<sub>43</sub>H<sub>38</sub>N<sub>6</sub>O<sub>4</sub>Ni: C 67.82; H 5.03; N 11.04; found C 68.10; H 5.97; N 10.56.

#### NiNaph<sub>2</sub>trien-IPDI

IR (KBr, cm<sup>-1</sup>); 3378 (NH), 2924, 2855, 1699 (C=O), 1623 (C=N), 1547, 1457, 1436, 1400, 1357, 1314, 1250, 1197, 1124, 1028, 961, 827, 750. Anal. Calcd. for C<sub>40</sub>H<sub>46</sub>N<sub>6</sub>O<sub>4</sub>Ni: C 65.50; H 6.32; N 11.46; found C 63.57; H 8.30; N 12.14.

#### Synthesis of poly(urea-imide)s from MNaph<sub>2</sub>trien, diisocyanates, and dianhydrides

Poly(urea-imide)s were synthesized from MNaph<sub>2</sub>trien (where M = Zn and Ni), diisocyanates, and dianhydrides. The diisocyanates used were MDI and IPDI. The dianhydrides used were PMDA and BTDA. The mole ratios of MNaph<sub>2</sub>trien : diisocyanate : dianhydride used were 1 : 2 : 0.5 and 1 : 2 : 1. General procedure for the synthesis of poly(urea-imide)s are as follows: A solution of diisocyanate (2.0 mmol) in DMSO (5 mL) was added to the solution of MNaph<sub>2</sub>trien (1.0 mmol) in DMSO (2 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 24 h to give isocyanate-terminated polyurea prepolymers. The reaction was cooled to room temperature. Dianhydride (0.5 mmol or 1.0 mmol) in DMSO (1 mL) was added, followed by stirring at room temperature for 30 min. The reaction mixture was then heated to 90°C and stirred for 2 h. Carbon dioxide gas evolution was observed at this temperature. The temperature of the reaction was raised to 110°C and maintained for 24 h. The solution was poured into methanol to precipitate the polymer. The polymer was filtered, washed several times with methanol, and then dried under vacuum for 48 h. Zinc- and nickel-containing poly(urea-imide)s were obtained as yellow and brown powder, respectively.



The yields obtained for metal-containing poly(urea-imide)s were 52–97%.

As the copolymers obtained from different mole ratios of MNaph<sub>2</sub>trien : diisocyanate : dianhydride have similar IR and <sup>1</sup>H-NMR spectra, therefore, only the IR and <sup>1</sup>H-NMR data of copolymers obtained from mole ratio of 1 : 2 : 1 are shown as follows:

#### ZnNaph<sub>2</sub>trien-MDI-PMDA

IR (KBr, cm<sup>-1</sup>); 3422 (NH), 2924, 2854, 1773 (C=O), 1721 (C=O), 1617 (C=N), 1539, 1511, 1459, 1429, 1390, 1363, 1313, 1207, 1181, 1123, 1040, 1017, 974, 914, 825, 749. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm); 9.53–9.61 (m, CH=N), 8.36–8.61 (m, NH), 7.81–7.90 (m, Ar-H), 7.67–7.80 (m, Ar-H), 7.44–7.58 (m, Ar-H), 7.21–7.40 (m, Ar-H), 7.09–7.15 (m, Ar-H), 6.89–6.98 (m, Ar-H), 6.83–6.89 (m, Ar-H), 6.72–6.83 (m, Ar-H), 6.35–6.50 (m, Ar-H), 4.67–4.94 (m, NH), 3.82–3.93 (m, CH<sub>2</sub>), 3.70–3.79 (m, CH<sub>2</sub>), 3.58–3.66 (m, CH<sub>2</sub>), 2.92–2.98 (m, CH<sub>2</sub>), 2.62–2.73 (m, CH<sub>2</sub>), 2.28–2.37 (m, CH<sub>2</sub>).

#### ZnNaph<sub>2</sub>trien-IPDI-PMDA

IR (KBr, cm<sup>-1</sup>); 3380 (NH), 2922, 2855, 1775 (C=O), 1716 (C=O), 1622 (C=N), 1546, 1461, 1430, 1391, 1296, 1245, 1187, 1139, 1096, 1023, 951, 838, 748, 726. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm); 9.01–9.30 (m, CH=N), 7.96–8.25 (m, Ar-H), 7.87–7.95 (m, Ar-H), 7.78–7.85 (m, Ar-H), 7.67–7.76 (m, Ar-H), 7.57–7.66 (m, Ar-H), 7.34–7.49 (m, Ar-H), 7.07–7.27 (m, Ar-H), 6.64–6.76 (m, Ar-H), 5.45–5.99 (m, NH), 3.71–4.10 (m, aliphatic-H), 2.61–3.03 (m, aliphatic-H), 2.27–2.35 (m, aliphatic-H), 1.66–1.85 (m, aliphatic-H), 1.27–1.66 (m, aliphatic-H), 0.71–1.27 (m, aliphatic-H).

#### ZnNaph<sub>2</sub>trien-MDI-BTDA

IR (KBr, cm<sup>-1</sup>); 3350 (NH), 2921, 2851, 1775 (C=O), 1716 (C=O), 1662, 1617 (C=N), 1539, 1511, 1463, 1387, 1304, 1239, 1184, 1118, 1096, 1021, 952, 828, 746, 724. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm); 9.51–9.64 (m, CH=N), 8.30–8.64 (m, NH), 8.30–7.64 (m, Ar-H), 7.90–8.25 (m, Ar-H), 7.80–7.89 (m, Ar-H), 7.61–7.77 (m, Ar-H), 7.44–7.57 (m, Ar-H), 7.22–7.41 (m, Ar-H), 6.98–7.20 (m, Ar-H), 6.90–6.98 (m, Ar-H), 6.84–6.88 (m, Ar-H), 6.38–6.51 (m, Ar-H), 3.54–4.06 (m, CH<sub>2</sub>), 3.16–3.27 (m, CH<sub>2</sub>), 2.90–3.01 (m, CH<sub>2</sub>), 2.63–2.71 (m, CH<sub>2</sub>).

#### ZnNaph<sub>2</sub>trien-IPDI-BTDA

IR (KBr, cm<sup>-1</sup>); 3405 (NH), 2925, 2860, 1775 (C=O), 1716 (C=O), 1625 (C=N), 1549, 1496, 1426, 1391, 1363, 1294, 1244, 1187, 1153, 1123, 1094, 1021, 952, 840, 725. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm); 9.02–

9.60 (m, CH=N), 7.90–8.36 (m, Ar-H), 7.55–7.88 (m, Ar-H), 7.33–7.50 (m, Ar-H), 7.10–7.28 (m, Ar-H), 6.64–7.02 (m, Ar-H), 5.38–5.98 (m, NH), 3.83–4.19 (m, aliphatic-H), 3.57–3.83 (m, aliphatic-H), 3.44–3.57 (m, aliphatic-H), 2.97–3.01 (m, aliphatic-H), 2.60–2.88 (m, aliphatic-H), 1.30–1.82 (m, aliphatic-H), 0.55–1.27 (m, aliphatic-H).

#### NiNaph<sub>2</sub>trien-MDI-PMDA

IR (KBr, cm<sup>-1</sup>); 3380 (NH), 2924, 2855, 1772 (C=O), 1722 (C=O), 1617 (C=N), 1543, 1513, 1456, 1406, 1370, 1313, 1230, 1185, 1124, 1015, 962, 826, 749, 723.

#### NiNaph<sub>2</sub>trien-IPDI-PMDA

IR (KBr, cm<sup>-1</sup>); 3410 (NH), 2925, 2855, 1766 (C=O), 1717 (C=O), 1622 (C=N), 1547, 1459, 1353, 1248, 1204, 1148, 1113, 1035, 970, 827, 747, 726.

#### NiNaph<sub>2</sub>trien-MDI-BTDA

IR (KBr, cm<sup>-1</sup>); 3365 (NH), 2923, 2848, 1775 (C=O), 1717 (C=O), 1670, 1607 (C=N), 1539, 1512, 1434, 1407, 1372, 1308, 1235, 1195, 1118, 1095, 1022, 953, 853, 826, 751, 723.

#### NiNaph<sub>2</sub>trien-IPDI-BTDA

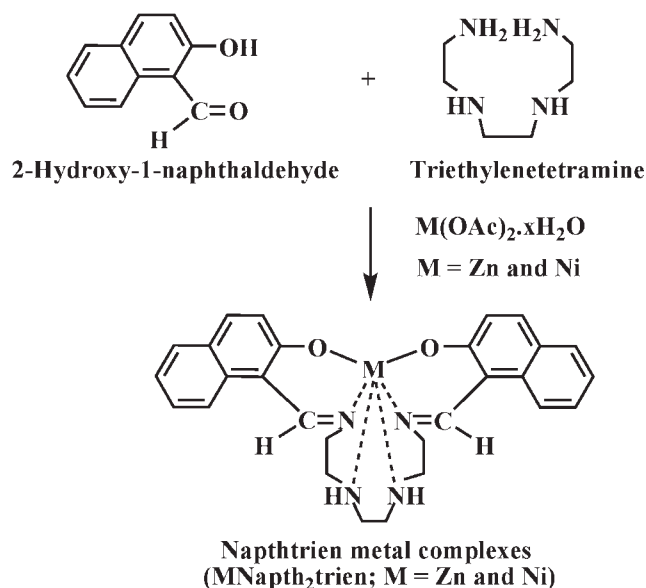
IR (KBr, cm<sup>-1</sup>); 3482 (NH), 2951, 2856, 1773 (C=O), 1713 (C=O), 1625 (C=N), 1547, 1456, 1436, 1387, 1364, 1299, 1247, 1198, 1155, 1125, 1102, 1038, 992, 965, 833, 746, 726.

## RESULTS AND DISCUSSION

### Synthesis and characterization of MNaph<sub>2</sub>trien

ZnNaph<sub>2</sub>trien and NiNaph<sub>2</sub>trien were synthesized by a one-pot reaction as shown in Scheme 1. The metal complexes contain two amine groups capable of undergoing polymerization with diisocyanates to give metal-containing polyureas. Both ZnNaph<sub>2</sub>trien and NiNaph<sub>2</sub>trien are soluble in CH<sub>2</sub>Cl<sub>2</sub>, chloroform (CHCl<sub>3</sub>), acetonitrile (CH<sub>3</sub>CN), tetrahydrofuran (THF), methanol (CH<sub>3</sub>OH), DMF, and DMSO.

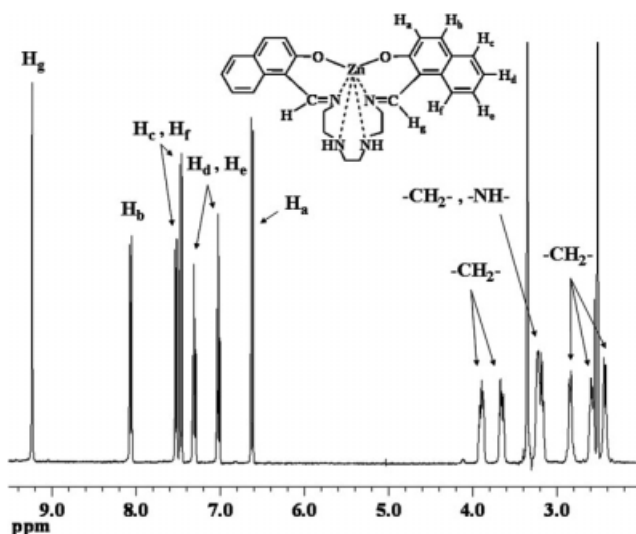
The structure of metal complexes was confirmed by spectroscopic methods and elemental analysis. IR spectra of ZnNaph<sub>2</sub>trien and NiNaph<sub>2</sub>trien show important bands of C=N stretching at 1619 and 1623 cm<sup>-1</sup>, respectively. <sup>1</sup>H- (Fig. 1) and <sup>13</sup>C-NMR spectra of ZnNaph<sub>2</sub>trien show the characteristic imine —CH=N— proton and carbon at 9.21 and 172.60 ppm, respectively. The aromatic protons and carbons are observed at 6.62–8.06 and 107.44–161.50 ppm, respectively. The peaks at 2.37–3.93 and 43.46–55.78 ppm are due to the methylene protons and carbons, respectively. The NMR spectra of



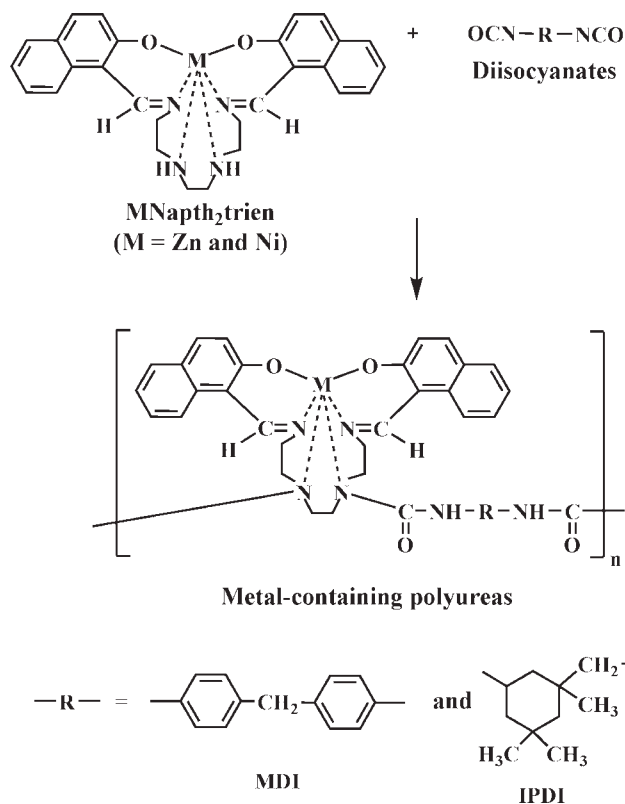
**Scheme 1** Synthesis of naphtrien metal complexes (MNaph<sub>2</sub>trien), where the metals are zinc and nickel.

NiNaph<sub>2</sub>trien could not be obtained because the complex is 6-coordinated and therefore paramagnetic. Only 4-coordinated nickel complex with square planar geometry is diamagnetic and give NMR signals. 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 ZnNaph<sub>2</sub>trien and NiNaph<sub>2</sub>trien are within the calculated values.

TGA thermograms of ZnNaph<sub>2</sub>trien and NiNaph<sub>2</sub>trien show their IDTs at 298 and 280°C, respectively. Considering the weight of residue of metal complexes at 600°C, ZnNaph<sub>2</sub>trien is more thermally stable than NiNaph<sub>2</sub>trien with char yields



**Figure 1** <sup>1</sup>H-NMR spectrum of ZnNaph<sub>2</sub>trien.



**Scheme 2** Synthesis of metal-containing polyureas from MNaph<sub>2</sub>trien and diisocyanates.

of 55% and 37%, respectively. When compared with the Schiff-base metal complexes previously synthesized<sup>16</sup> using salicylaldehyde and its derivatives instead of 2-hydroxy-1-naphthaldehyde, it is found that both ZnNaph<sub>2</sub>trien and NiNaph<sub>2</sub>trien show higher char yield at 600°C because naphthaldehyde-based metal complexes contain more aromatic rings than salicylaldehyde-based metal complexes.

### Synthesis and characterization of metal-containing polyureas from metal complexes and diisocyanates

Metal-containing polyureas were synthesized from the reaction between MNaph<sub>2</sub>trien and diisocyanates (Scheme 2) at the mole ratio of MNaph<sub>2</sub>trien : diisocyanate = 1 : 1 with dibutyltin dilaurate as a catalyst. The polymerization was carried out in CH<sub>2</sub>Cl<sub>2</sub> as the progress of polymerization could be followed by IR spectroscopy and the polyurea can be easily separated from the reaction mixture. The polymerization mechanism is the amine groups in MNaph<sub>2</sub>trien undergo reactions with isocyanate groups to give urea linkages.

The progress of polymerization was investigated by heating an equimolar mixture of metal complex and diisocyanate in CH<sub>2</sub>Cl<sub>2</sub> at reflux under nitrogen atmosphere and samples of reaction mixture were taken from the reaction for analysis. The IR sample

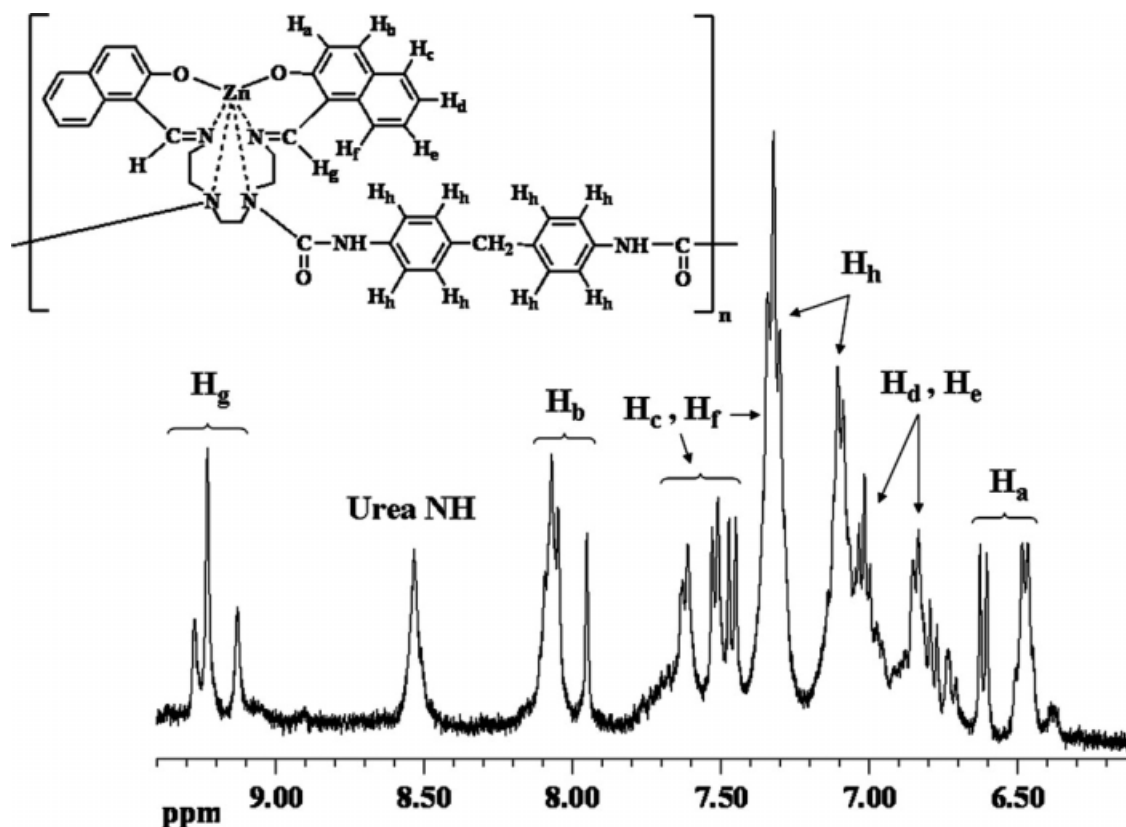


Figure 2  $^1\text{H-NMR}$  spectrum of  $\text{ZnNaph}_2\text{trien-MDI}$ .

was prepared by casting the reaction mixture in  $\text{CH}_2\text{Cl}_2$  onto the NaCl disk and the solvent was then removed by evaporation. The reaction progress could be observed by the disappearance of a strong NCO absorption and the appearance of a new urea  $\text{C}=\text{O}$  absorption band. As an example, IR spectra of a reaction mixture of  $\text{ZnNaph}_2\text{trien}$  with MDI at different reaction times show a new carbonyl stretching vibration of NCON group at  $1703\text{ cm}^{-1}$ , which could be clearly observed after 3 h. The completeness of polymerization was supported by the absence of the NCO peak at  $2270\text{ cm}^{-1}$  after heating for 4 h. IR study also shows that the reaction of  $\text{ZnNaph}_2\text{trien}$  with MDI is faster than IPDI and  $\text{ZnNaph}_2\text{trien}$  shows the same reactivity in polymerization reaction as  $\text{NiNaph}_2\text{trien}$ .

The solubility of zinc- and nickel-containing polyureas was tested in various polar and nonpolar solvents. All polymers, except  $\text{ZnNaph}_2\text{trien-MDI}$ , are soluble in DMF and DMSO and insoluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ , THF, and  $\text{CH}_3\text{OH}$ .  $\text{ZnNaph}_2\text{trien-MDI}$  is partially soluble in both DMF and DMSO.

All zinc- and nickel-containing polyureas show similar IR spectra. The important characteristic absorption bands are observed at  $3360\text{--}3400\text{ cm}^{-1}$  (N—H stretching) and  $1616\text{--}1623\text{ cm}^{-1}$  ( $\text{C}=\text{N}$  stretching). The carbonyl of urea appears in the range  $1692\text{--}1703\text{ cm}^{-1}$ , which is different from the

typical urea  $\text{C}=\text{O}$  group normally appears around  $1660\text{ cm}^{-1}$ . As discussed earlier,<sup>16</sup> the IR absorption of urea group in metal-containing polyureas is similar to that of amide group. This might be because one of urea nitrogen lone pair electron does not delocalize into the carbonyl part because of its coordination with metal atom.

$^1\text{H-NMR}$  spectrum of  $\text{ZnNaph}_2\text{trien-IPDI}$  shows signals at  $0.65\text{--}3.94\text{ ppm}$ , which are assigned to the aliphatic parts of  $\text{ZnNaph}_2\text{trien}$  and IPDI. The signals in this region are difficult to be observed because of the large peaks of  $\text{H}_2\text{O}$  and DMSO. The urea NHs are observed at  $4.37\text{--}5.98\text{ ppm}$ . The  $\text{CH}=\text{N}$  peaks are observed as multiplets at  $9.08\text{--}9.31\text{ ppm}$ . The aromatic peaks of  $\text{ZnNaph}_2\text{trien}$  are found in  $\text{ZnNaph}_2\text{trien-IPDI}$  at  $6.59\text{--}8.16\text{ ppm}$ , which are close to the region of aromatic protons observed in the  $\text{ZnNaph}_2\text{trien}$  complex at  $6.62\text{--}8.06\text{ ppm}$ . However, all  $^1\text{H-NMR}$  signals of  $\text{ZnNaph}_2\text{trien}$  in  $\text{ZnNaph}_2\text{trien-IPDI}$  appear as multiplets and there are more peaks than those observed in the  $\text{ZnNaph}_2\text{trien}$  complex. This might be due to the rigid structure of the polymer which causes these protons to be nonequivalent.

For  $\text{ZnNaph}_2\text{trien-MDI}$ , the  $^1\text{H-NMR}$  spectrum (Fig. 2) shows  $\text{—CH}=\text{N—}$  signals as multiplets at  $9.09\text{--}9.28\text{ ppm}$ . The urea NHs are observed at  $8.49\text{--}8.58$  and  $4.82\text{--}4.87\text{ ppm}$ . The aromatic protons of

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

Polymers	Wt % <sup>a</sup>	Yield (%)	$\eta_{inh}$ (dL g <sup>-1</sup> )	$T_g$ (°C)	IDT (°C)	Weight of residue at 600°C (%)	Solubility in DMSO <sup>b</sup>
ZnNaph <sub>2</sub> trien-MDI	67.4	85	–	–	280	48	+-
ZnNaph <sub>2</sub> trien-IPDI	69.9	65	0.145	–	226	19	++
NiNaph <sub>2</sub> trien-MDI	67.1	82	0.113	149 <sup>c</sup>	284	34	++
NiNaph <sub>2</sub> trien-IPDI	69.7	53	0.169	–	286	6	++
ZnNaph <sub>2</sub> trien-MDI-PMDA (1: 2 : 0.5)	45.9	77	0.188	117 <sup>c</sup>	270	58	++
ZnNaph <sub>2</sub> trien-MDI-PMDA (1: 2 : 1)	41.9	72	0.736	–	232	58	+
ZnNaph <sub>2</sub> trien-MDI-BTDA (1: 2 : 0.5)	43.9	92	0.260	151 <sup>c</sup>	254	44	++
ZnNaph <sub>2</sub> trien-MDI-BTDA (1: 2 : 1)	38.6	89	0.355	–	209	58	+
NiNaph <sub>2</sub> trien-MDI-PMDA (1: 2 : 0.5)	45.6	87	0.228	–	234	54	++
NiNaph <sub>2</sub> trien-MDI-PMDA (1: 2 : 1)	41.6	86	0.663	115 <sup>d</sup>	222	54	+
NiNaph <sub>2</sub> trien-MDI-BTDA (1: 2 : 0.5)	43.6	68	0.299	–	243	56	++
NiNaph <sub>2</sub> trien-MDI-BTDA (1: 2 : 1)	38.3	80	0.349	89 <sup>d</sup>	207	60	++
ZnNaph <sub>2</sub> trien-IPDI-PMDA (1: 2 : 0.5)	48.3	89	0.181	–	224	26	++
ZnNaph <sub>2</sub> trien-IPDI-PMDA (1: 2 : 1)	43.9	90	0.527	–	217	37	+
ZnNaph <sub>2</sub> trien-IPDI-BTDA (1: 2 : 0.5)	46.2	66	0.274	–	246	34	++
ZnNaph <sub>2</sub> trien-IPDI-BTDA (1: 2 : 1)	40.3	54	0.307	–	207	35	+
NiNaph <sub>2</sub> trien-IPDI-PMDA (1: 2 : 0.5)	48.0	52	0.210	–	229	36	++
NiNaph <sub>2</sub> trien-IPDI-PMDA (1: 2 : 1)	43.6	89	0.687	110 <sup>d</sup>	245	43	++
NiNaph <sub>2</sub> trien-IPDI-BTDA (1: 2 : 0.5)	45.8	88	0.289	–	240	33	++
NiNaph <sub>2</sub> trien-IPDI-BTDA (1: 2 : 1)	40.0	84	0.322	–	235	46	++

<sup>a</sup> Percent by weight of MNaph<sub>2</sub>trien in the polymer.

<sup>b</sup> ++ = Soluble at room temperature; + = soluble on heating; +- = partial soluble on heating; – = insoluble.

<sup>c</sup> Determined by DSC.

<sup>d</sup> Determined by DMTA.

MDI and ZnNaph<sub>2</sub>trien are observed at 6.42–8.19 ppm. The peaks at 2.38–4.16 ppm are assigned to the methylene protons of ZnNaph<sub>2</sub>trien and MDI.

The chemical structure of metal-containing polyureas was confirmed by elemental analysis. For all polymers, the elemental analysis data shows that the experimentally determined percentage values of carbon, hydrogen, and nitrogen are within the calculated values. The inherent viscosity all metal-containing polyureas was measured at 40°C in DMSO (Table I). It was found that both MDI- and IPDI-based polymers have low viscosities. The viscosity of ZnNaph<sub>2</sub>trien-MDI could not be obtained because the polymer is not completely soluble in DMSO.

TGA thermograms of zinc- and nickel-containing polyureas are shown in Figure 3. Thermal stability of the polymers is evaluated by the IDT value and weight of residue at different temperatures. For this work, IDT is identified as the temperature where 5 wt % losses of the polymers occurs. ZnNaph<sub>2</sub>trien-IPDI shows the lowest IDT whereas the other polymers show higher IDTs in the range 280–284°C. For all polymers, there is not much different in the initial weight percent loss occurs in the temperature range 200–300°C, whereas an appreciable difference in weight percent loss in the range 400–700°C could be observed. Considering the weight percent losses of polymers at 600°C, the MDI-based polymers are more thermally stable than the polymers based on IPDI. Zinc-containing polymers show better thermal

stability than nickel-containing polymers. Among all polymers, ZnNaph<sub>2</sub>trien-MDI is the most thermally stable polymers with IDT of 270°C and char yield of 48% at 600°C.

All the XRD patterns of zinc- and nickel-containing polyureas show broad peaks. This indicates that these polymers are amorphous in nature, which is supported by the solubility test of polymers (Table I) that they are soluble in DMF and DMSO.

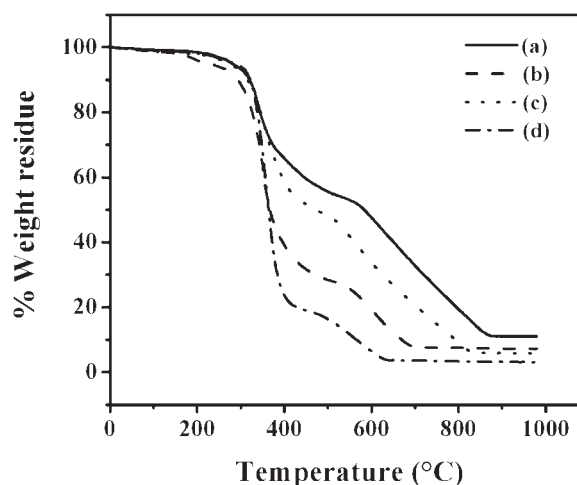
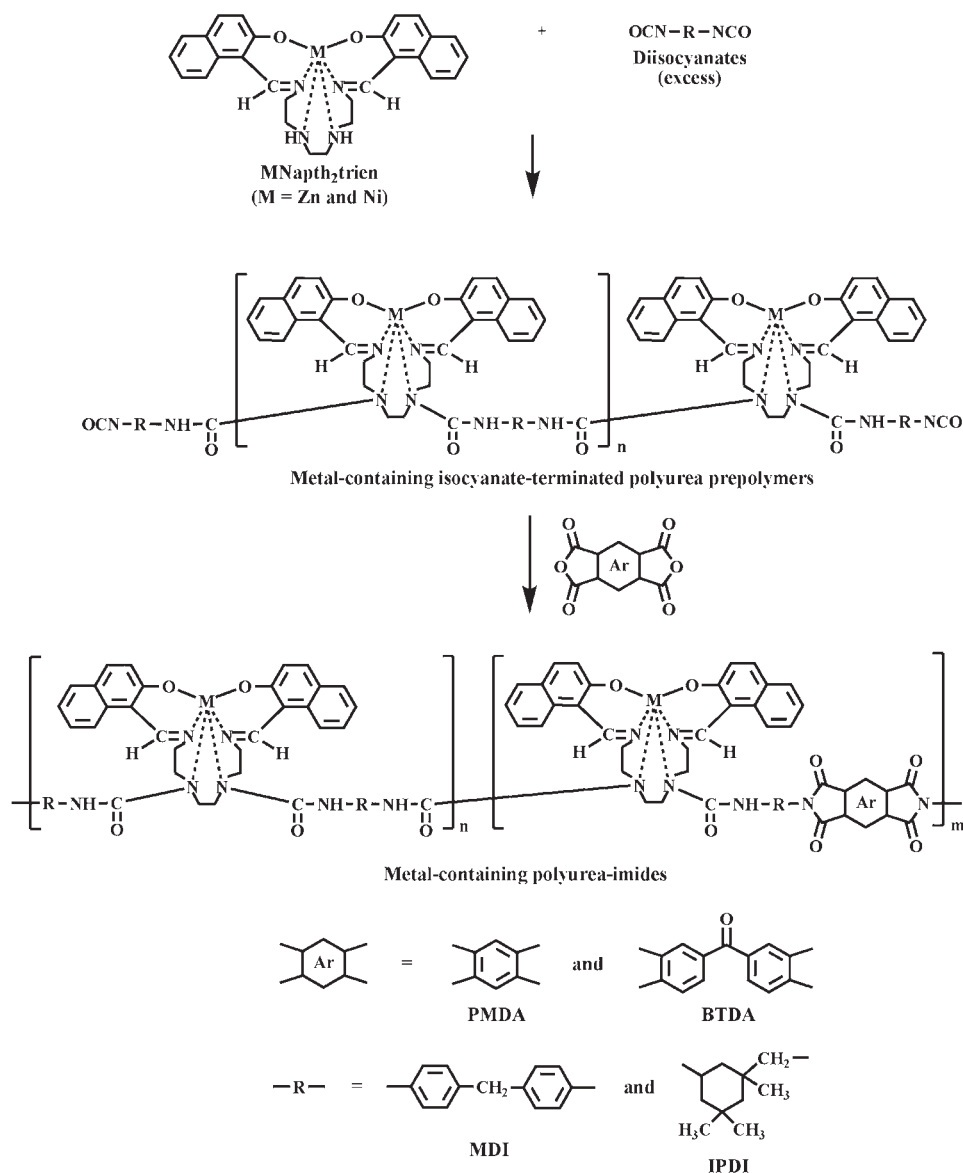


Figure 3 TGA thermograms of (a) ZnNaph<sub>2</sub>trien-MDI, (b) ZnNaph<sub>2</sub>trien-IPDI, (c) NiNaph<sub>2</sub>trien-MDI, and (d) NiNaph<sub>2</sub>trien-IPDI.





**Scheme 3** Synthesis of metal-containing poly(urea-imide)s from MNaph<sub>2</sub>trien, diisocyanates, and dianhydrides.

### Synthesis of metal-containing poly(urea-imide)s from the reaction between MNaph<sub>2</sub>trien, diisocyanates, and dianhydrides

One of the known methods frequently used for introduction of imide group into the polyurethane backbone is the reaction of isocyanate-terminated PU prepolymer with acid anhydride. By using this synthetic methodology, metal-containing poly(urea-imide)s were synthesized from MNaph<sub>2</sub>trien, MDI or IPDI, and dianhydrides as shown in Scheme 3. The polymerization was done in DMSO using dibutyltin dilaurate as a catalyst. Metal complexes first underwent the reaction with excess diisocyanates to give isocyanate-terminated polyurea prepolymers, which was then reacted with dianhydrides to yield metal-containing poly(urea-imide)s. By addition of dianhydrides during the polymerization, there are

additional imide linkages in the polyurea structure and it is expected that the polymers should have improved thermal stability. The reactions between MNaph<sub>2</sub>trien, diisocyanate, and dianhydride at two mole ratios, 1 : 2 : 0.5 and 1 : 2 : 1, were carried out to study the effect of starting material compositions on the polymer properties. The polymerization reaction of MDI-based polymers was faster than that of IPDI-based polymers. When PMDA was used, the reaction was faster than that of BTDA.

### Characterization of metal-containing poly(urea-imide)s

All metal-containing poly(urea-imide)s have similar IR spectra. The important characteristic absorption bands are 3350–3482 cm<sup>-1</sup> (N–H stretching) and the

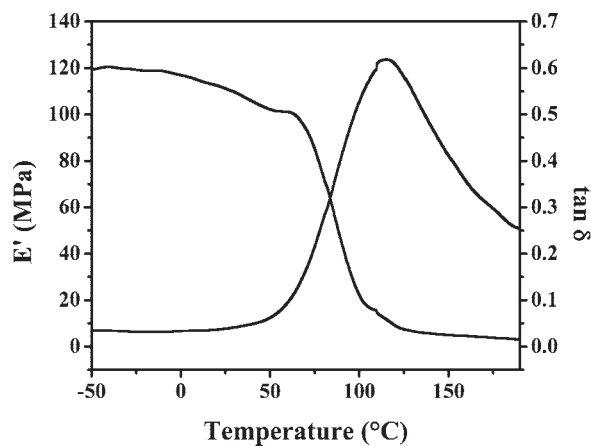


two imide carbonyl bands are observed at 1766–1775 and 1713–1722  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra of poly(urea-imide)s based on  $\text{ZnNaph}_2\text{trien-IPDI}$  show signals at 0.55–4.19 ppm, which are assigned to the aliphatic parts of  $\text{ZnNaph}_2\text{trien}$  and IPDI. The urea NHs are observed at 5.38–5.99 ppm. The  $\text{CH=N}$  peaks are observed at 9.01–9.60 ppm. The aromatic peaks of  $\text{ZnNaph}_2\text{trien}$  and dianhydrides are found at 6.64–8.36 ppm. For the poly(urea-imide)s based on  $\text{ZnNaph}_2\text{trien-MDI}$ , their  $^1\text{H-NMR}$  spectra show  $-\text{CH=N}-$  signals at 9.51–9.64 ppm. The urea NHs are observed at 8.30–8.64 and 4.67–4.94 ppm. The aromatic protons of  $\text{ZnNaph}_2\text{trien}$ , MDI, and dianhydrides are observed at 6.50–8.30 ppm. The peaks at 2.28–4.06 ppm are assigned to the methylene protons of  $\text{ZnNaph}_2\text{trien}$  and MDI. All  $^1\text{H-NMR}$  signals appear as multiplets.

Solubility test shows that metal-containing poly(urea-imide)s are soluble in DMF and DMSO, and insoluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ , THF, and  $\text{CH}_3\text{OH}$ . Nickel-containing polymers show better solubility than zinc-containing polymers. For most metal-containing poly(urea-imide)s, increase of dianhydride content in the polymers results in less solubility in DMF and DMSO. This is supported by XRD results because zinc- and nickel-containing poly(urea-imide)s show broad XRD peaks, and therefore the polymers are amorphous.

Inherent viscosity of the poly(urea-imide)s (Table I) is found to be in the range between 0.181 and 0.736 dL/g for zinc-containing polymers and 0.210–0.687 dL/g for nickel-containing polymers. The viscosity of poly(urea-imide)s is higher than that of polyureas. Poly(urea-imide)s obtained from  $\text{MNaph}_2\text{trien}$  : diisocyanate : dianhydride at the mole ratio of 1 : 2 : 1 show higher viscosities than those obtained at the mole ratio of 1 : 2 : 0.5.

Glass transition temperature ( $T_g$ ) of the polymers was first determined by DSC.  $T_g$ s could be obtained for  $\text{NiNaph}_2\text{trien-MDI}$ ,  $\text{ZnNaph}_2\text{trien-MDI-PMDA}$  (1 : 2 : 0.5), and  $\text{ZnNaph}_2\text{trien-MDI-BTDA}$  (1 : 2 : 0.5).  $T_g$ s of all other polymers could not be clearly observed. Therefore, their  $T_g$ s were determined from the maximum point of  $\tan \delta$  peak in DMTA thermograms. DMTA samples were prepared by solution-cast and using NMP as a solvent. Because the solubility of metal-containing polyureas and zinc-containing poly(urea-imide)s in NMP are not good, brittle materials were obtained and their DMTA samples could not be prepared. Nickel-containing poly(urea-imide)s prepared at the mole ratio of  $\text{MNaph}_2\text{trien}$  : diisocyanate : dianhydride = 1 : 2 : 0.5 are also brittle polymers. Only nickel-containing poly(urea-imide)s prepared at the mole ratio of  $\text{MNaph}_2\text{trien}$  : diisocyanate : dianhydride = 1 : 2 : 1 could be cast from NMP solution into DMTA samples.  $T_g$ s of  $\text{NiNaph}_2\text{trien-MDI-PMDA}$  (1 : 2 : 1),



**Figure 4** DMTA thermogram of  $\text{NiNaph}_2\text{trien-MDI-PMDA}$ .

$\text{NiNaph}_2\text{trien-MDI-BTDA}$  (1 : 2 : 1), and  $\text{NiNaph}_2\text{trien-IPDI-PMDA}$  (1 : 2 : 1) were observed at 115°C, 89°C, and 110°C, respectively. PMDA-based polymers are harder material than BTDA-based polymers.  $\text{NiNaph}_2\text{trien-IPDI-BTDA}$  is brittle material and its DMTA sample could not be obtained.  $T_g$ s of nickel-containing poly(urea-imide)s are lower than that of their corresponding polyurea.  $\text{NiNaph}_2\text{trien-MDI-PMDA}$  show slightly higher  $T_g$  than  $\text{NiNaph}_2\text{trien-IPDI-PMDA}$ . Figure 4 shows DMTA thermogram of  $\text{NiNaph}_2\text{trien-MDI-PMDA}$  (1 : 2 : 1).

TGA results (Table I) show that the IDTs of zinc- and nickel-containing poly(urea-imide)s are in the range 207–270°C and 207–245°C, respectively, which are lower than those of the metal-containing polyureas synthesized without PMDA and BTDA. This is because the  $\text{MNaph}_2\text{trien}$  contents in polyureas are higher than those in poly(urea-imide)s. Metal-containing polyureas contain  $\text{MNaph}_2\text{trien}$  in the range 67.1–69.7 wt %, whereas the  $\text{MNaph}_2\text{trien}$  amount presents in metal-containing poly(urea-imide)s is in the range 38.3–48.3 wt %. Most poly(urea-imide)s show the decrease in IDTs when the weight percent of  $\text{MNaph}_2\text{trien}$  in the polymers is decreased.

All metal-containing poly(urea-imide)s have higher char yields at 600°C than the metal-containing polyureas synthesized without PMDA and BTDA, namely,  $\text{ZnNaph}_2\text{trien-MDI}$ ,  $\text{NiNaph}_2\text{trien-MDI}$ ,  $\text{ZnNaph}_2\text{trien-IPDI}$ , and  $\text{NiNaph}_2\text{trien-IPDI}$ . This is due to the introduction of imide groups into the polymer backbone. When comparing with their corresponding metal-containing polyureas, addition of PMDA and BTDA in the synthesis of nickel-containing poly(urea-imide)s results in better improvement in char yields than in the case of zinc-containing poly(urea-imide)s.

For most of MDI-based poly(urea-imide)s, TGA results of  $\text{ZnNaph}_2\text{trien-MDI-PMDA}$ ,  $\text{NiNaph}_2\text{trien-MDI-PMDA}$ , and  $\text{NiNaph}_2\text{trien-MDI-BTDA}$

show that the variable amount of MNaph<sub>2</sub>trien in zinc- and nickel-containing poly(urea-imide)s does not affect their char yields at 600°C. Except for ZnNaph<sub>2</sub>trien-MDI-BTDA (1 : 2 : 0.5), which has less char yield than ZnNaph<sub>2</sub>trien-MDI-BTDA (1 : 2 : 1). TGA results of most IPDI-based poly(urea-imide)s, namely, ZnNaph<sub>2</sub>trien-IPDI-PMDA, NiNaph<sub>2</sub>trien-IPDI-PMDA, and NiNaph<sub>2</sub>trien-IPDI-BTDA show that their char yields at 600°C increase with increasing amount of PMDA and BTDA in the copolymers. Except for ZnNaph<sub>2</sub>trien-IPDI-BTDA, which the polymers obtained from different amount of BTDA have the same char yield.

Nickel-containing poly(urea-imide)s are hard materials. They could be cast from NMP solution into DMTA samples. The samples for hardness test could be also prepared by solution-cast, whereas the film samples cannot be prepared. Therefore, mechanical property of the polymers investigated was hardness on a Shore D scale. NiNaph<sub>2</sub>trien-MDI-PMDA (1 : 2 : 1) and NiNaph<sub>2</sub>trien-IPDI-PMDA (1 : 2 : 1) show high hardness at 92 and 94, respectively, whereas NiNaph<sub>2</sub>trien-IPDI-BTDA (1 : 2 : 1) has low hardness at 34.

## CONCLUSIONS

Metal-containing polyureas and poly(urea-imide)s containing MNaph<sub>2</sub>trien (M = Zn and Ni) in the polymer chain were synthesized. All polymers are soluble in DMF and DMSO. Nickel-containing polymers show better solubility than zinc-containing polymers. IDTs of the polymers increase as the amount of MNaph<sub>2</sub>trien in the polymer composition is increased. Metal-containing poly(urea-imide)s have higher char yield than their related metal-containing polyureas. Zinc-containing polymers are more thermally stable than nickel-containing polymers. Among all poly(urea-imide)s, ZnNaph<sub>2</sub>trien-MDI-PMDA (1 : 2 : 0.5) is the most thermally stable polymer with better solubility in organic solvents than

ZnNaph<sub>2</sub>trien-MDI. However, zinc-containing polymers are brittle materials. Nickel-containing poly(urea-imide)s based on PMDA are thermally stable polymers.  $T_g$ , IDT, and char yield at 600°C of NiNaph<sub>2</sub>trien-MDI-PMDA (1 : 2 : 1) are 115°C, 222°C, and 54%, respectively. NiNaph<sub>2</sub>trien-IPDI-PMDA (1 : 2 : 1) has  $T_g$ , IDT, and char yield at 600°C of 110°C, 245°C, and 43%, respectively. Both NiNaph<sub>2</sub>trien-MDI-PMDA (1 : 2 : 1) and NiNaph<sub>2</sub>trien-IPDI-PMDA (1 : 2 : 1) are hard materials with Shore D hardness of 92 and 94, respectively.

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