CHAPTER III

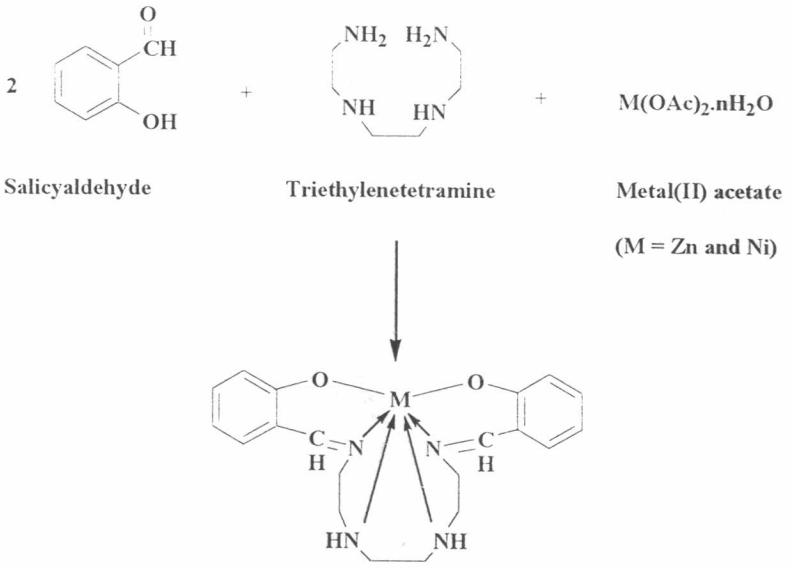
RESULTS AND DISCUSSION

It was previously found in our research group that hexadentate Schiff base metal complexes showed birefringence with an uncharacteristic texture upon heating.[16] This result suggested that the metal complexes were liquid crystals.

The purpose of this research was to synthesize metal-containing liquid crystalline polyurethane-urea elastomers. Hexadentate Schiff base metal complexes were used as a chain-extender in the preparation of liquid crystalline polyurethane-urea elastomers. It was expected that the obtained polymers would show liquid crystalline properties. From the result obtained from DSC thermogram, the polymers did not have endotherm peak which is the property of liquid crystalline materials. Since the obtained metal-containing polyurethane-ureas showed good thermal stability, therefore we emphasized the study on thermal properties of the polymers.

3.1 Synthesis of hexadentate Schiff base metal complex ($MSal_2trien$)

Hexadentate Schiff base metal complex was synthesized following the synthetic route described in the literature.[15] The spectroscopic data of $MSal_2trien$ agree with the value reported.



Scheme 3.1 Synthesis of the hexadentate Schiff base metal complexes ($MSal_2trien$)

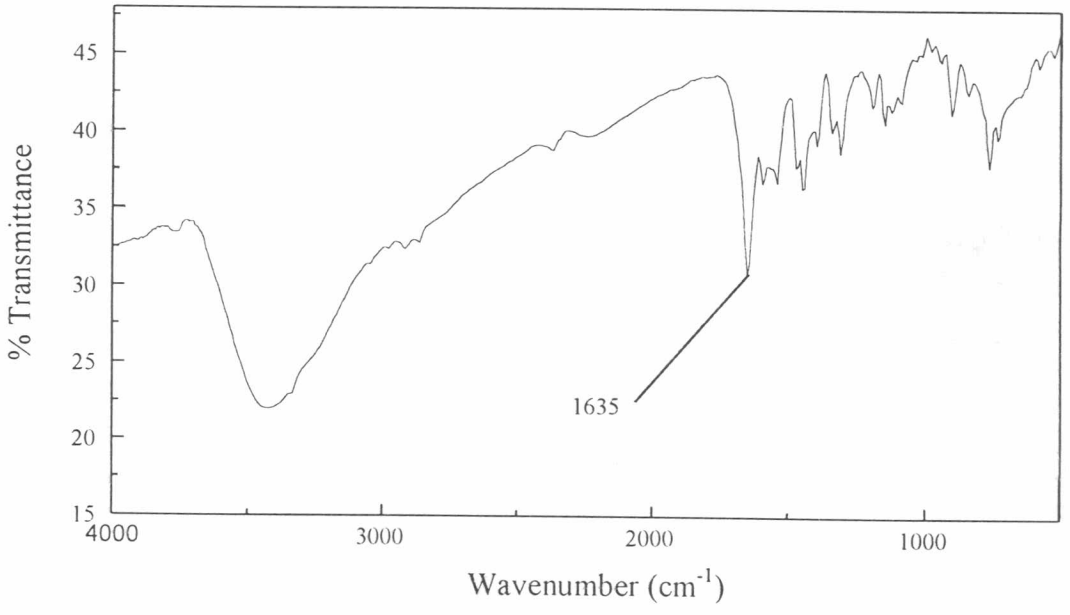


Figure 3.1 FTIR spectrum of hexadentate Schiff base zinc complex ($ZnSal_2trien$)

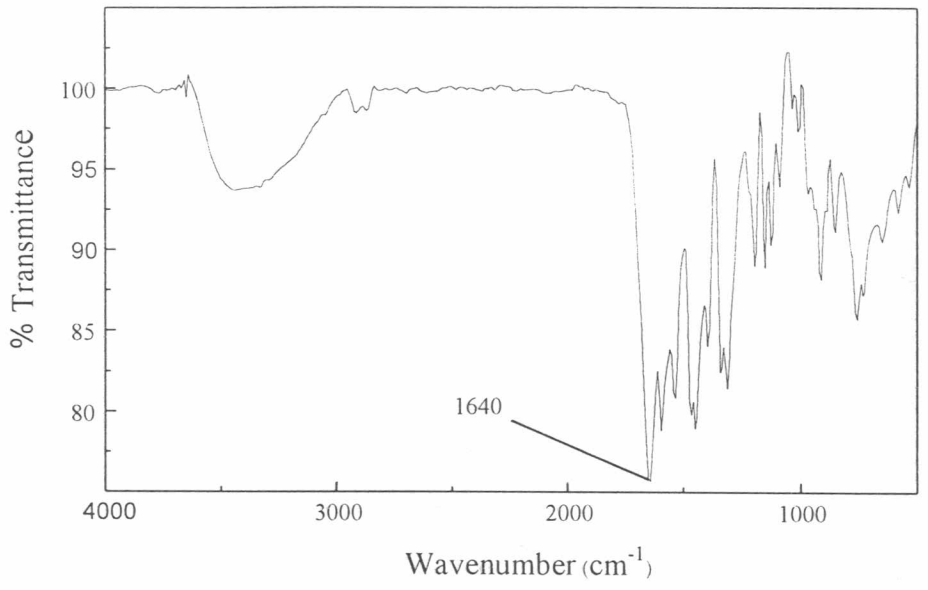


Figure 3.2 FTIR spectrum of hexadentate Schiff base nickel complex ($NiSal_2trien$)

3.2 Synthesis of polyurethane-ureas

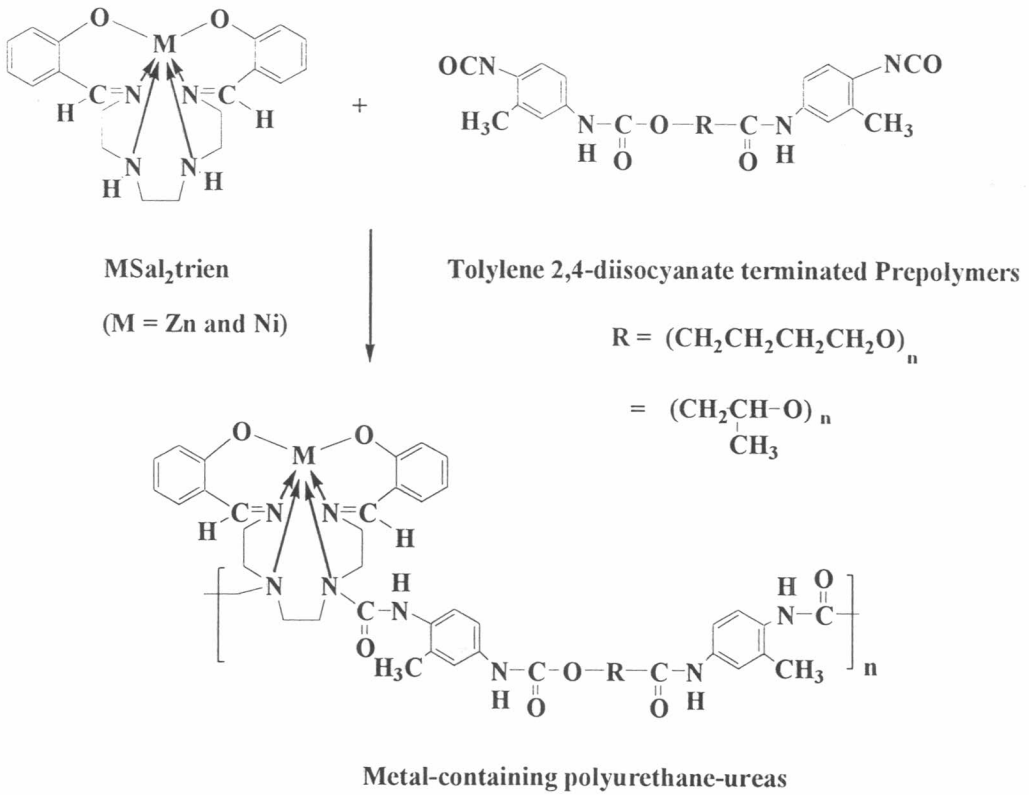
3.2.1 Synthesis of polyurethane-ureas from $MSal_2trien$ and prepolymers

Polyurethane-ureas were synthesized from the reaction between $MSal_2trien$ and prepolymers. The prepolymers used were PB900, PB1600, PP1000 and PP2300. These prepolymers are aromatic diisocyanate terminated prepolymers which different polyol part. The reaction times for polymer synthesis was reduced using dibutyltin diraulate as a catalyst. The reaction of metal complex with prepolymer for polyurethane-ureas synthesis was done at the mole ratio of prepolymer : $MSal_2trien$ = 1 : 1. Each isocyanate at the end of prepolymer chain reacted with a nitrogen atom in $MSal_2trien$.

The obtained polyurethane-ureas with $ZnSal_2trien$ were yellow powder except for PP2300-Zn-20. Because PP2300-Zn-20 was synthesized from high molecular weight prepolymer, therefore PP2300-Zn-20 was obtained as an elastomeric material. However, the obtained polyurethane-ureas with $NiSal_2trien$ were different. Viscous elastomers were obtained in PB900-Ni-30, PB1600-Ni-20, PP1000-Ni-30 and PP2300-Ni-20. The yield of polyurethane-ureas obtained from $ZnSal_2trien$ were in the

range of 50-70 %. The yield of polyurethane-ureas obtained from $NiSal_2trien$ were in the range of 90-98 %.

The reaction of metal complexes with prepolymers for polyurethane-ureas synthesis is shown in Scheme 3.2.



Scheme 3.2 Synthesis of polyurethane-ureas from metal complex with different prepolymers

The progress of reaction was investigated by IR spectroscopy. The reaction progress could be observed by the disappearance of the strong NCO absorption in prepolymer and the appearance of new –NCON- absorption band from reaction of $ZnSal_2trien$ with NCO. The progress of the reaction of $ZnSal_2trien$ with PB900 and PP1000 are shown in Figure 3.3 and 3.4, respectively. The progress in reaction of $NiSal_2trien$ with PB900 and PP1000 are shown in Figure 3.5 and 3.6, respectively.

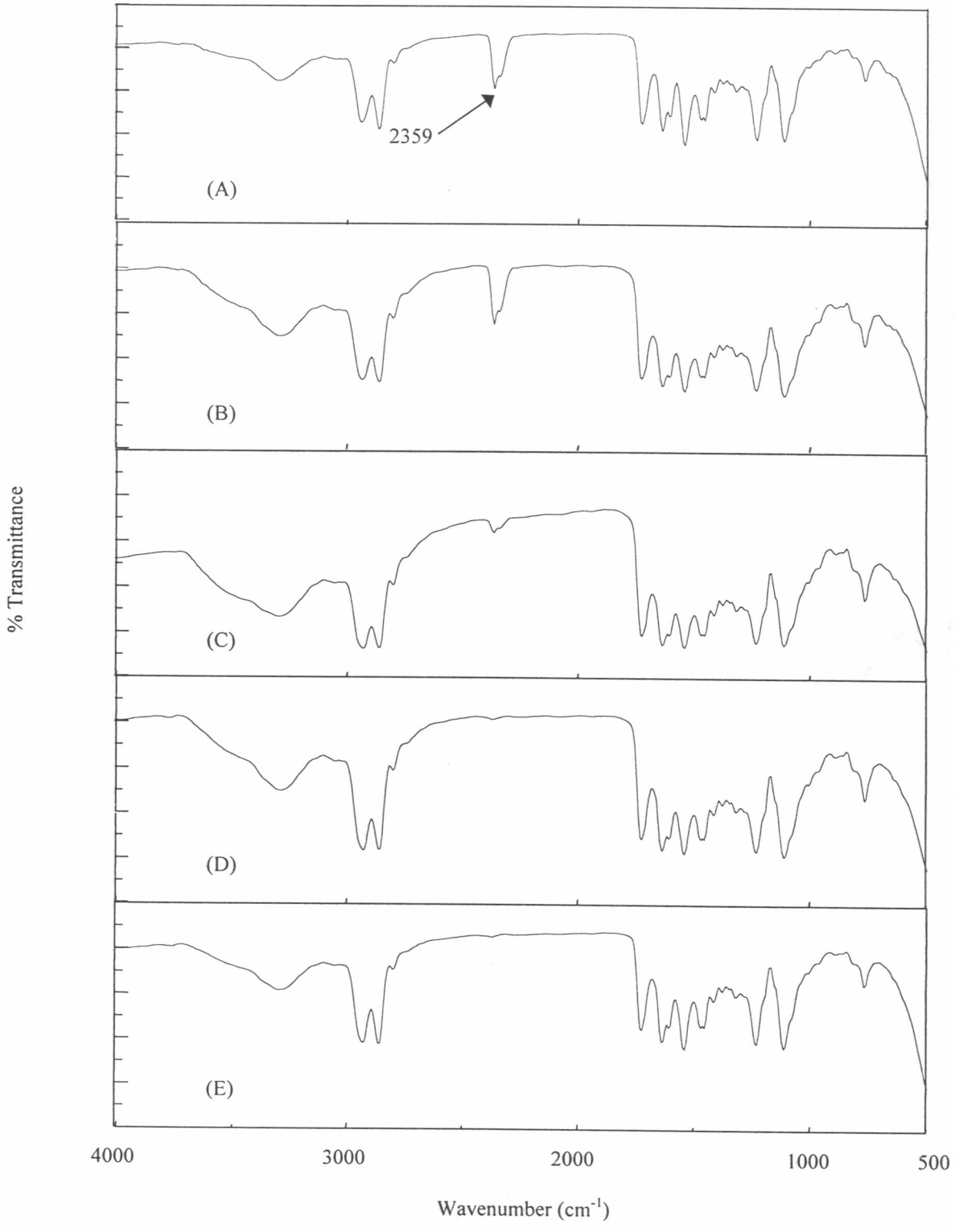


Figure 3.3 IR spectra of the reaction mixture of $ZnSal_2trien$ with PB900 at different times (A) 0 h (B) 2 h (C) 4 h (D) 6 h (E) 8 h

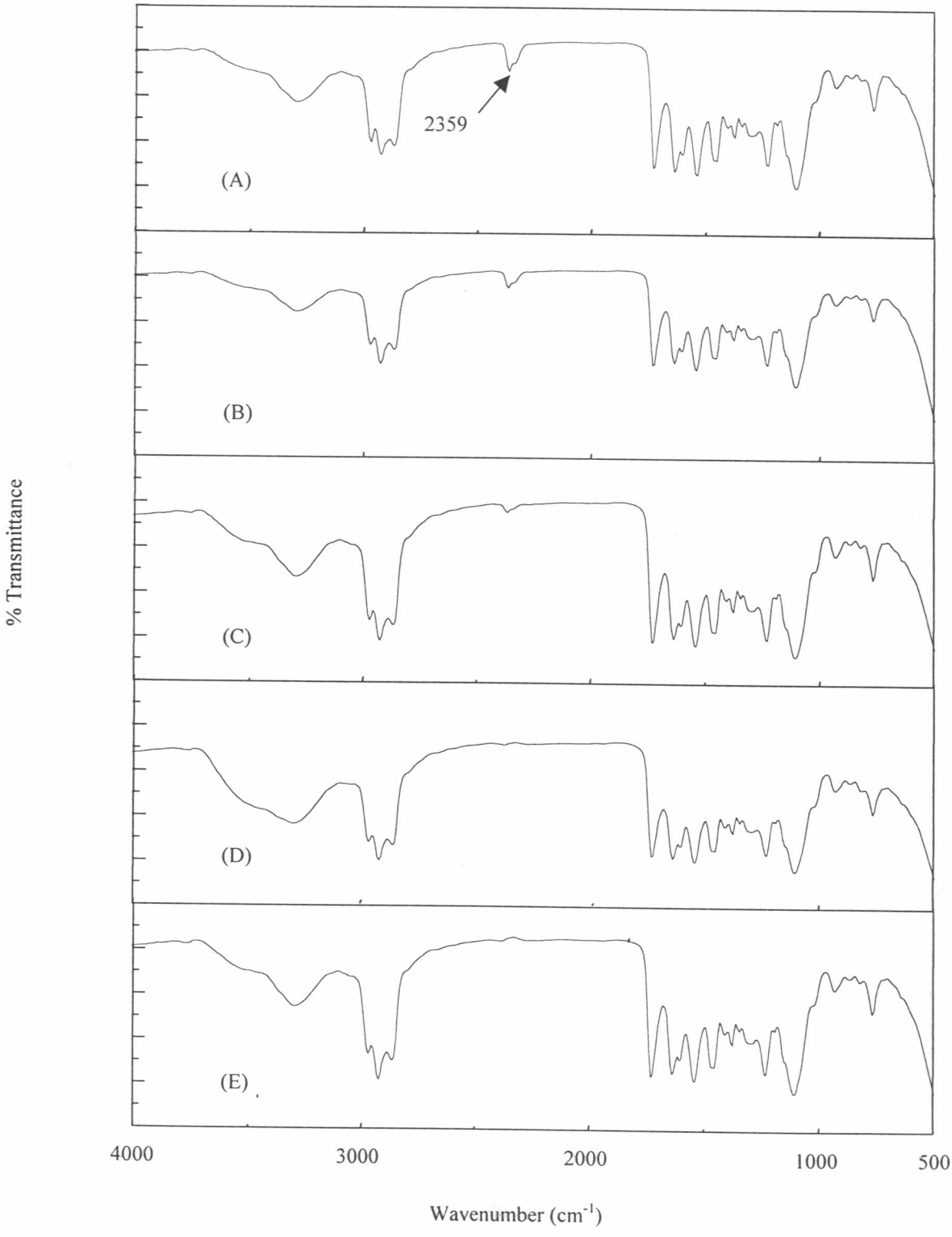


Figure 3.4 IR spectra of the reaction mixture of $ZnSal_2trien$ with PP1000 at different times (A) 0 h (B) 2 h (C) 4 h (D) 6 h (E) 8 h

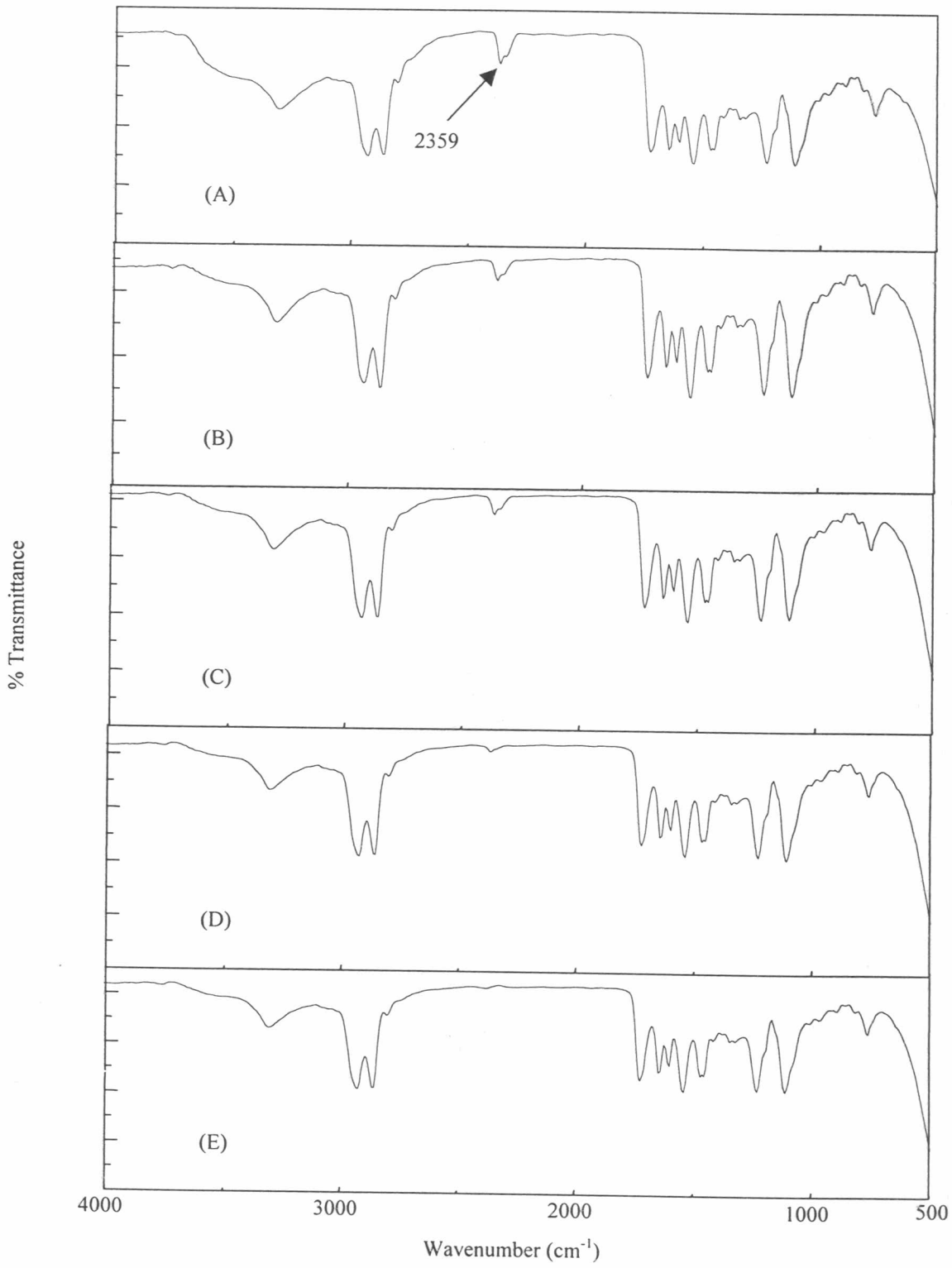


Figure 3.5 IR spectra of the reaction mixture of $NiSal_2trien$ with PB900 at different times (A) 0 h (B) 2 h (C) 4 h (D) 6 h (E) 8 h

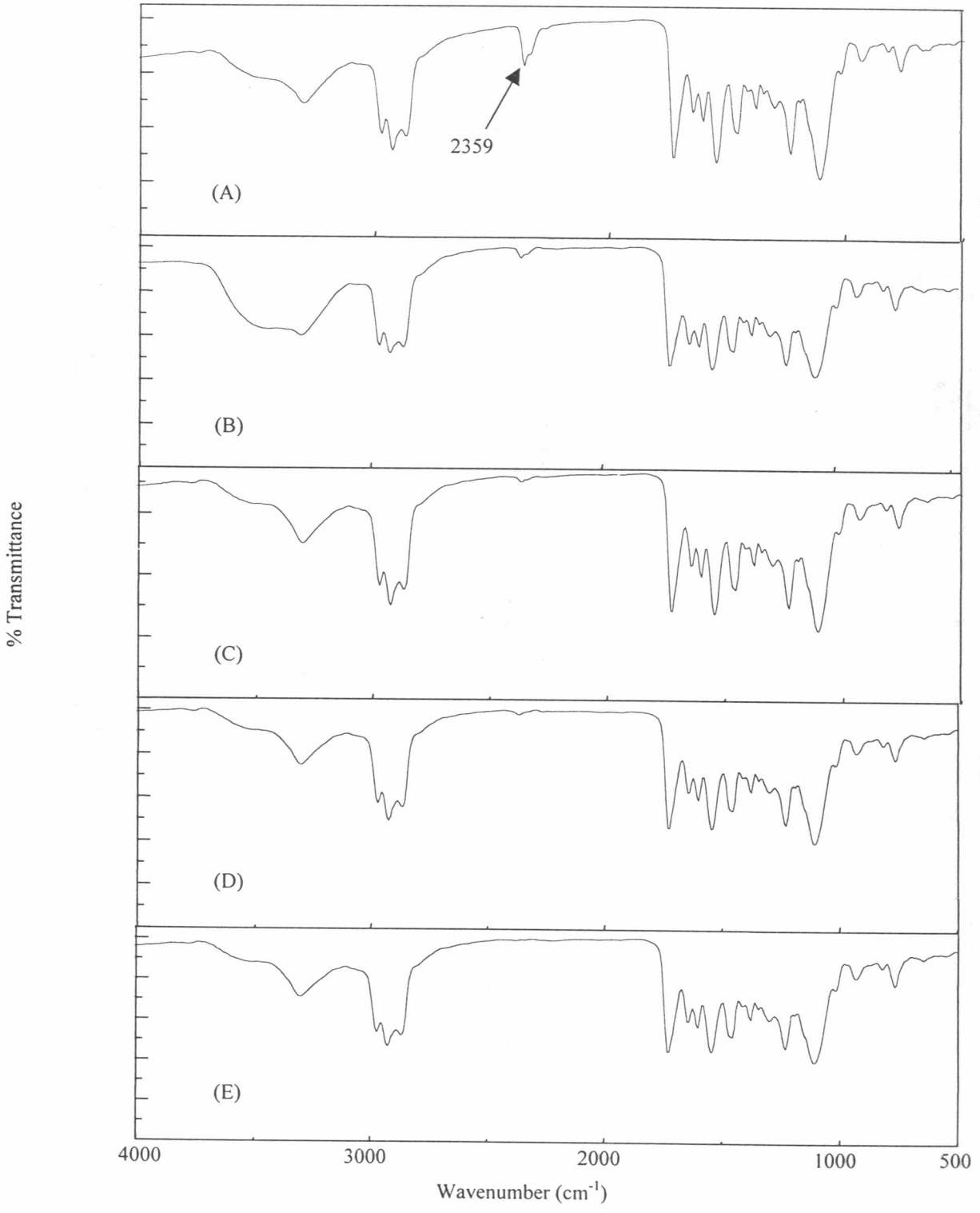


Figure 3.6 IR spectra of the reaction mixture of $NiSal_2trien$ with PP1000 at different times (A) 0 h (B) 2 h (C) 4 h (D) 6 h (E) 8 h

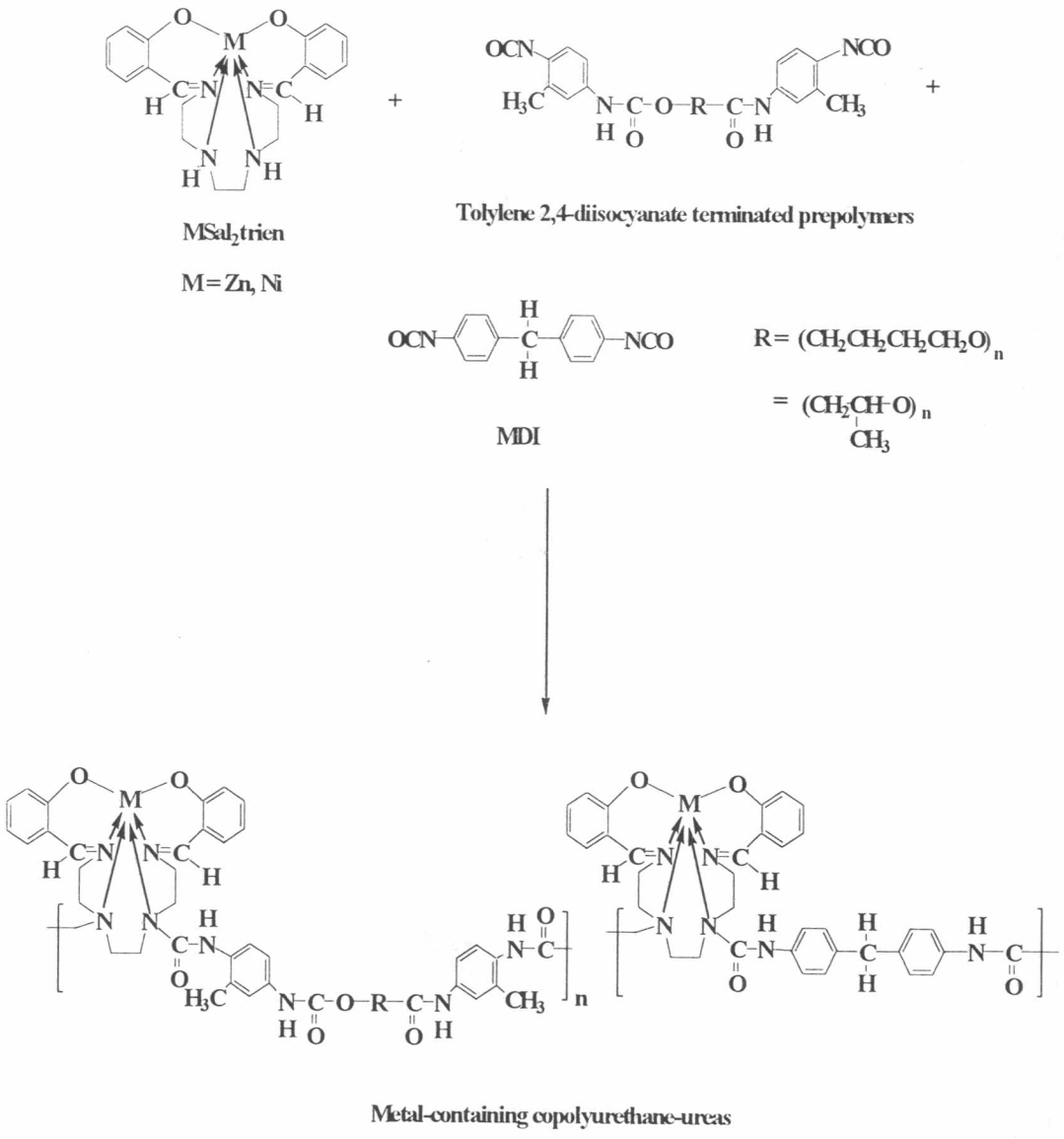
The progress of the reaction of $MSal_2trien$ with prepolymer was followed by IR spectra in both zinc and nickel complexes. The completeness of reaction was confirmed by the absence of the characteristic NCO peak absorption band at around 2359 cm^{-1} and the presence of the new carbonyl (C=O) stretching of –NCON- group observed at around 1710 cm^{-1}. However, the peak of urea (-NCON-) group and urethane (-NCOON-) group occurred almost at the same position around 1700-1730 cm^{-1}. Therefore, it was difficult to identify the urea linkage peak in polyurethane-ureas. The completeness of reaction was confirmed by the lack of –NCO peak at 2359 cm^{-1}, which was observed at the reaction time of 8 hours. The absorption band at 1635 cm^{-1} and 1640 cm^{-1} are imine (C=N) stretching presenting in $ZnSal_2trien$ and $NiSal_2trien$, respectively. These results confirmed the presence of $MSal_2trien$ in polyurethane-ureas.

3.2.2 Synthesis of copolyurethane-ureas from $MSal_2trien$, prepolymers and MDI

The copolyurethane-ureas were synthesized from the reaction between $MSal_2trien$ and prepolymers in the present of MDI. MDI was used as other chain-extender to yield co-polymers with different wt % of metal complex in the polymer chain. The reaction times for polymer synthesis were also reduced using dibutyltin diraulate as a catalyst. The reaction of metal complexes with prepolymers and MDI for copolyurethane-ureas synthesis was done at different mole ratios of prepolymer : $MSal_2trien$: MDI as shown in the experimental part.

The obtained copolyurethane-ureas with $ZnSal_2trien$ were yellow powder. The obtained copolyurethane-ureas with $NiSal_2trien$ were different. PB900-Ni-MDI-50, PP1000-Ni-MDI-50, PB1600-Ni-MDI-50 and PP2300-Ni-MDI-50 were light-green powder. Both of PB1600-Ni-MDI-30 and PP2300-Ni-MDI-30 were light-green elastomers.

The mechanism found in copolyurethane synthesized by metal complexes with MDI was different from polyurethane-ureas. Nitrogen atom in metal complex could react with both NCO group of prepolymer and NCO group of MDI. Therefore, the order of repeating unit founded in polyurethane-ureas was random. The reaction of metal complexes with prepolymers and MDI for copolyurethane-ureas synthesis is shown in Scheme 3.3.



Scheme 3.3 Synthesis of metal-containing copolyurethane-ureas

3.3 Characterization of polymers

3.3.1 Infrared spectra

3.3.1.1 Infrared spectra of metal-containing polyurethane-ureas

PB900, PB1600, PP1000 and PP2300 showed characteristic NCO stretching band at 2275 cm^{-1}. When prepolymers were polymerized with both $ZnSal_2trien$ and $NiSal_2trien$, an imine (C=N) stretching band from $MSal_2trien$ occurred at 1635 cm^{-1}. The carbonyl band (C=O) due to the formation of a urethane linkage was observed at 1726 cm^{-1} and the NCO peak of diisocyanate at 2359 cm^{-1} disappeared after the polymerization was completed. Because metal complexes were used as a chain extender, then reaction of metal complexes with prepolymers underwent a reaction to form urea linkage (-NCON-). This urea linkage (-NCON-) was observed at 1726 cm^{-1}. From the spectra shown in Figures 3.3 – 3.6, the urea linkage (-NCON-) peak was not clearly observed because peak of urethane linkage (-NCOO-) in the polymer overlapped with the urea linkage peak. The IR data of polyurethane-ureas with $MSal_2trien$ in their structures were shown in Table 3.1.

Table 3.1 IR data of polyurethane-ureas containing $MSal_2trien$ in the main chain

Polymers	Wavenumber (cm^{-1})						
	NH_2	NCO	C=O	C=N	Phenyl ring		
PB900-Zn-30	3440-3310	2359	1720	1635	1600	1536	763
PB1600-Zn-20	3440-3310	2359	1720	1635	1600	1536	758
PP1000-Zn-30	3440-3311	2359	1729	1635	1600	1536	763
PP2300-Zn-20	3440-3312	2359	1724	1630	1600	1536	763
PB900-Ni-30	3440-3314	2359	1720	1640	1600	1536	758
PB1600-Ni-20	3440-3315	2359	1720	1640	1600	1536	756
PP1000-Ni-30	3440-3316	2359	1720	1635	1600	1536	758
PP2300-Ni-20	3440-3317	2359	1724	1635	1600	1536	758

3.3.1.2 Infrared spectra of metal-containing copolyurethane-ureas

MDI was used as another diisocyanate in the synthesis of copolyurethane-ureas with different wt % of $MSal_2trien$ in the polymer chain. In the polymerization reaction, $MSal_2trien$ reacted with both prepolymers and MDI to form copolyurethane-ureas. IR spectrum of copolyurethane-ureas showed absorption peaks similar to those of polyurethane-ureas. At the 50 wt % of metal complex in copolyurethane-ureas, carbonyl (C=O) stretching band at 1720 cm^{-1} overlapped with imine (C=N) stretching at 1635 cm^{-1} and resulted in a broad peak. This result was also found in PB900-Zn-MDI-50, PP1000-Zn-MDI-50, PB1600-Zn-MDI-50, PP2300-Zn-MDI-50 and PP2300-Ni-MDI-50 (Figures A.1-A.5).

3.3.2 ^1H NMR

3.3.2.1 ^1H NMR spectrum of metal-containing polyurethane-ureas

^1H NMR spectrum of PB900-Zn-30 showed a signal at δ 8.6-8.4 ppm. (Figure 3.7). For the N-H protons of urethanes (-NHCOO-) and ureas (-NHCONH-) groups which are shifted to downfield due to inter and intramolecular hydrogen bonding between the N-H group with carbonyl (C=O) of the polyurethane. This result was also found in case of PP1000-Zn-30, PB1600-Zn-20 and PP2300-Zn-20 (Figures A.6-A.8). However, ^1H NMR spectra of starting prepolymers (Figures A.9-A.10) were absence of this signal. The peaks due to (H-C=N) at δ 8.0 – 8.2 ppm appear in the spectrum of PP2300-Zn-20 which indicated the presence of $MSal_2trien$ in the polymer (Figure A.8).

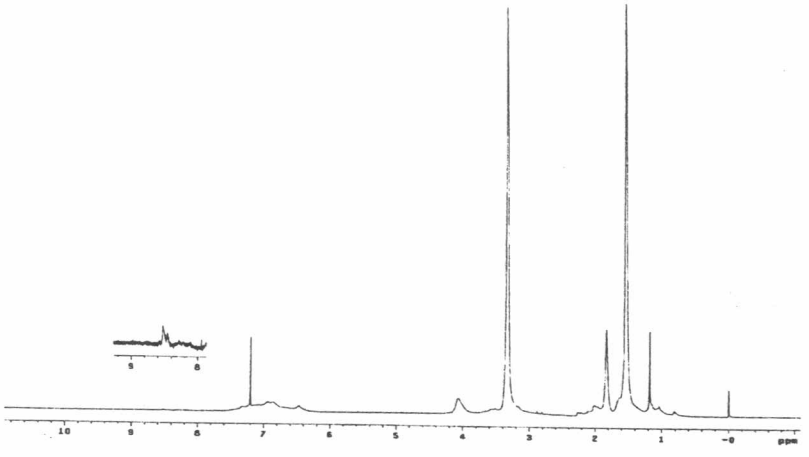
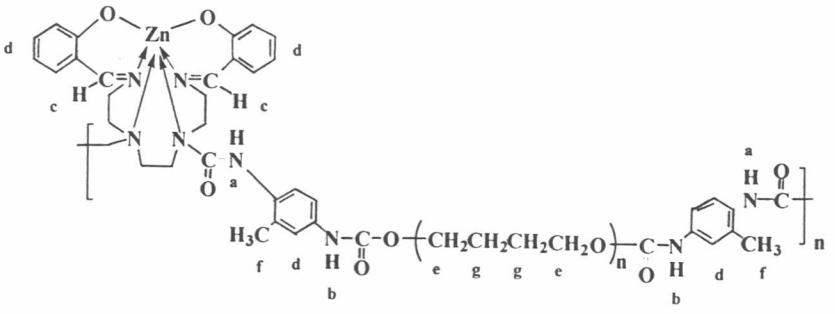


Figure 3.7 ^{1}H NMR of PB900-Zn-30

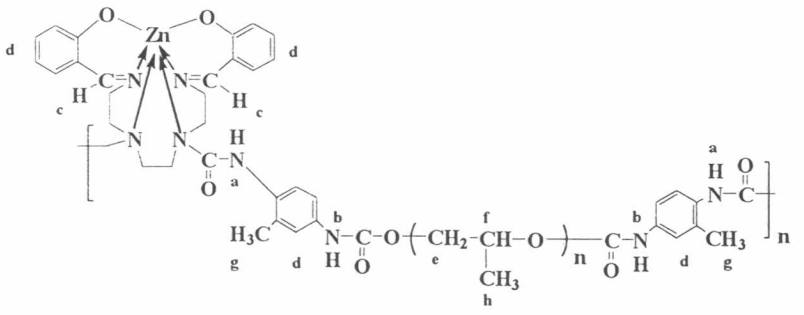
The chemical shifts of PB900-Zn-30 and PB1600-Zn-20 are shown in Table 3.2 and the chemical shifts of PP1000-Zn-30 and PP2300-Zn-20 are shown in Table 3.3.

Table 3.2 Chemical shift of PB900-Zn-30 and PB1600-Zn-20



Polymers	Chemical Shift (ppm)					
	a , b	c	d	e	f	g
PB900-Zn-30	8.6 , 8.4	-	7.3 – 6.8	4.1 - 3.1	2.2 - 1.8	1.6
PB1600-Zn-20	8.6 , 8.4	-	7.5 – 6.5	4.2 - 3.2	2.4 - 1.8	1.7

Table 3.3 Chemical shift of PP1000-Zn-30 and PP2300-Zn-20



Polymers	Chemical Shift (ppm)						
	a , b	c	d	e	f	g	h
PP1000-Zn-30	8.6 , 8.4	-	7.3 - 6.5	3.7 - 3.5	3.5 - 3.3	2.2 - 1.8	1.3 - 1.1
PP2300-Zn-20	8.6 , 8.4	8.2 - 8	7.4 - 6.4	3.7 - 3.5	3.5 - 3.3	2.2 - 1.8	1.3 - 1.1

3.3.3 Elemental analysis

Elemental analysis of metal-containing polyurethane-ureas was studied. Analytical data of the polymers is given in Table 3.4. The experimentally determined percentage of carbon, hydrogen and nitrogen were within the calculated range.

Elemental analysis of metal-containing copolyurethane-ureas was not investigated. This was due to random repeating unit in the copolymers and therefore the absolute repeating unit could not be determined.

Table 3.4 Analytical data of metal-containing polyurethane-ureas

Polymers	Repeating unit	Analytical data found (calcd) (%)		
		C	H	N
$ZnSal_2$trien Series				
PB900-Zn-30	$C_{66}H_{94}N_8O_{14}Zn$	61.50 (61.51)	7.35 (7.38)	8.69 (8.37)
PB1600-Zn-20	$C_{106}H_{174}N_8O_{24}Zn$	63.34 (63.33)	8.73 (8.64)	5.57 (5.53)
PP1000-Zn-30	$C_{71}H_{104}N_8O_{18}Zn$	59.93 (59.93)	7.37 (7.39)	7.87 (7.88)
PP2300-Zn-20	$C_{137}H_{236}N_8O_{40}Zn$	60.93 (60.94)	8.81 (8.82)	4.15 (3.93)
$NiSal_2$trien Series				
PB900-Ni-30	$C_{66}H_{94}N_8O_{14}Ni{\cdot}3CH_3OH$	60.13 (60.14)	7.75 (9.21)	8.13 (8.07)
PB1600-Ni-30	$C_{106}H_{174}N_8O_{24}Ni{\cdot}3CH_3OH$	62.36 (62.57)	8.93 (8.96)	5.34 (5.39)
PP1000-Ni-30	$C_{71}H_{104}N_8O_{18}Ni{\cdot}3CH_3OH$	58.77 (58.60)	7.73 (7.84)	7.41 (7.28)
PP2300-Ni-20	$C_{137}H_{236}N_8O_{40}Ni{\cdot}3CH_3OH$	60.26 (60.28)	8.96 (9.07)	4.02 (4.02)

3.3.4 Solubility

3.3.4.1 Solubility of metal-containing polyurethane-ureas

The solubility of the metal-containing polyurethane-ureas was tested in various polar and non-polar solvents. Solubility test shows that these metal-containing polyurethane-ureas were insoluble in water, toluene, diethyl ether, hexane and methanol. They were soluble in polar solvent such as CH_2Cl_2, $CHCl_3$, DMF and DMSO. The solubility increased as wt % of metal complex in the polymers increased. The solubility test of metal-containing polyurethane-ureas is shown in Table 3.5.

The data from Table 3.5 showed that both of $ZnSal_2$trien-based polyurethane-ureas and $NiSal_2$trien-based polyurethane-ureas were soluble in chlorinated solvent such as CH_2Cl_2 and $CHCl_3$. The polyurethane-ureas were soluble in DMF, THF and slightly soluble in DMSO. It was not soluble in H_2O, CH_3OH. Polyurethane-ureas were also not soluble in nonpolar solvent, for instance, toluene, diethyl ether and hexane.

Table 3.5 Solubility of metal-containing polyurethane-ureas

Polymers	Solvents									
	Hexane	Toluene	Diethyl ether	$CHCl_3$	THF	CH_2Cl_2	CH_3OH	DMF	DMSO	H_2O
$ZnSal_2$trienseries										
PB900-Zn-30	-	-	-	++	++	++	-	++	++	-
PB1600-Zn-20	-	-	-	++	+	++	-	+	+	-
PP1000-Zn-30	-	-	-	++	++	++	-	++	+	-
PP2300-Zn-20	-	-	-	++	++	++	-	++	+	-
$NiSal_2$trien series										
PB900-Ni-30	-	-	-	++	++	++	-	++	+	-
PB1600-Ni-20	-	-	-	++	++	++	-	++	+	-
PP1000-Ni-30	-	-	-	++	++	++	-	++	+	-
PP2300-Ni-20	-	-	-	++	++	++	-	++	+	-

-, Insoluble; +, partial soluble; ++, soluble

3.3.4.2 Solubility of metal-containing copolyurethane-ureas

The solubility of the metal-containing copolyurethane-ureas was tested in various polar and non-polar solvents. The copolyurethane-ureas were soluble in some kinds of solvent similar to polyurethane-ureas. But at the higher wt % metal complex in polymer, some copolyurethane-ureas could not be soluble in DMSO, for example, PB1600-Ni-MDI-30, PB1600-Ni-MDI-50, PP2300-Ni-MDI-30 and PP2300-Ni-MDI-50. Within the same series of $MSal_2$trien, the solubility of copolyurethane-ureas was less than that of polyurethane-ureas. This result was due to wt % of metal complex in copolyurethane-ureas was higher than that in polyurethanes-ureas. The solubility of $NiSal_2$trien-based copolyurethane-ureas was less than that of $ZnSal_2$trien-based copolyurethane-ureas. The solubility of metal-containing copolyurethane-ureas is shown in Table 3.6.

Table 3.6 Solubility of metal-containing copolyurethane-ureas

Polymers	Solvents									
	Hexane	Toluene	Diethyl ether	$CHCl_3$	THF	CH_2Cl_2	CH_3OH	DMF	DMSO	H_2O
$ZnSal_2trien$ series										
PB900-Zn-MDI-50	-	-	-	+	+	++	-	+	+	-
PB1600-Zn-MDI-30	-	-	-	+	+	++	-	++	+	-
PB1600-Zn-MDI-50	-	-	-	-	+	++	-	+	+	-
PP1000-Zn-MDI-50	-	-	-	+	+	++	-	+	+	-
PP2300-Zn-MDI-30	-	-	-	+	+	++	-	+	+	-
PP2300-Zn-MDI-50	-	-	-	+	+	++	-	+	+	-
$NiSal_2trien$ series										
PB900-Ni-MDI-50	-	-	-	+	+	+	-	+	+	-
PB1600-Ni-MDI-30	-	-	-	+	-	+	-	+	-	-
PB1600-Ni-MDI-50	-	-	-	+	+	+	-	+	-	-
PP1000-Ni-MDI-50	-	-	-	+	+	+	-	+	+	-
PP2300-Ni-MDI-30	-	-	-	+	+	+	-	+	-	-
PP2300-Ni-MDI-50	-	-	-	+	+	+	-	+	-	-

-, Insoluble; +, partial soluble; ++, soluble

3.4.5 Inherent viscosity

3.4.5.1 Inherent viscosity of metal-containing polyurethane-ureas and copolyurethane-ureas

The inherent viscosity of all polyurethane-ureas was measured at 40°C in DMSO. The viscosity data of metal-containing polyurethane-ureas and copolyurethane-ureas are shown in Table 3.7 and 3.8, respectively.

Table 3.7 Inherent viscosity of metal-containing polyurethane-ureas

Polymers	ηinh (g/dL)	Polymers	ηinh (g/dL)
PB900-Zn-30	0.0910	PB900-Ni-30	0.1832
PB1600-Zn-20	0.1842	PB1600-Ni-20	0.2606
PP1000-Zn-30	0.0968	PP1000-Ni-30	0.1411
PP2300-Zn-20	0.2814	PP2300-Ni-20	0.3677

Table 3.8 Inherent viscosity of metal-containing copolyurethane-ureas

Polymers	ηinh (g/dL)	Polymers	ηinh (g/dL)
PB900-Zn-MDI-50	0.1441	PB900-Ni-MDI-50	0.1963
PB1600-Zn-MDI-30	0.2482	PB1600-Ni-MDI-30	0.3213
PB1600-Zn-MDI-50	0.4939	PB1600-Ni-MDI-50	0.4156
PP1000-Zn-MDI-50	0.2008	PP1000-Ni-MDI-50	0.3028
PP2300-Zn-MDI-30	0.3223	PP2300-Ni-MDI-30	0.3997
PP2300-Zn-MDI-50	0.5141	PP2300-Ni-MDI-50	0.4613

The data showed that wt % of metal complex in the polymer increased, the inherent viscosity also increased. Moreover, if the molecular weight of prepolymer increased, the inherent viscosity of metal-containing polyurethane-ureas would also increase. These results were not the same as the previous work reported by Qiu[9], which the metal complexes in the polymer chain dissociated and this caused the polymers to have low viscosity. This cause metal in polyurethane-ureas and copolyurethane-ureas did not dissociate.

At the same % metal complex, the inherent viscosity of propylene glycol prepolymer-based polyurethane was higher than that of 1,4-butanediol prepolymer-based polyurethanes in both case of Zn and Ni series. The higher inherent viscosity was due to the propylene glycol prepolymer-based polyurethanes had a steric effect more than 1,4-butanediol prepolymer-based polyurethanes. The $NiSal_2trien$-based polyurethanes showed higher inherent viscosity more than $ZnSal_2trien$-based polyurethanes.

3.4.6 Thermal analysis

3.4.6.1 Thermal analysis of metal-containing polyurethane-ureas

The thermal stability of polyurethane-ureas was investigated by TGA. The % weight loss data are shown in Table 3.9.

Table 3.9 TGA data of metal-containing polyurethane-ureas

Polymers	IDT	% weight loss at different temperatures					
		300	400	500	600	700	800
$ZnSal_2$trien series							
PB900-Zn-30	237	6	36	70	80	91	95
PB1600-Zn-20	255	3	27	78	87	96	96
PP1000-Zn-30	227	15	65	72	86	94	94
PP-2300-Zn-20	207	7	67	84	93	95	95
$NiSal_2$trien series							
PB900-Ni-30	187	19	38	69	79	88	91
PB1600-Ni-20	215	13	33	76	88	92	92
PP1000-Ni-30	163	21	58	74	85	91	91
PP-2300-Ni-20	157	10	67	85	94	94	94

When molecular weight of the prepolymer was increased, the % weights loss at high temperature of $ZnSal_2$trien-based polyurethane-ureas also increased. In contrast, the % weight loss of $NiSal_2$trien decreased when molecular weight of prepolymer increased. The weights loss of $ZnSal_2$trien-based polyurethane-ureas was less than that of $NiSal_2$trien-based polyurethane-ureas at the same wt % of metal complex in the polymers.

3.4.6.2 Thermal analysis of metal-containing copolyurethane-ureas

The thermal stability of copolyurethane-ureas was investigated by TGA. The % weight loss data are shown in Table 3.10.

Table 3.10 TGA data of metal-containing copolyurethane-ureas

Polymers	IDT	% weight loss at different temperatures					
		300	400	500	600	700	800
$ZnSal_2$trien series							
PB900-Zn-MDI-50	255	7	42	59	68	82	91
PB1600-Zn-MDI-30	256	3	28	72	81	91	94
PB1600-Zn-MDI-50	265	6	40	55	64	75	85
PP1000-Zn-MDI-50	229	12	48	55	65	78	90
PP-2300-Zn-MDI-30	222	7	56	68	81	93	93
PP-2300-Zn-MDI-50	240	6	47	55	65	77	88
$NiSal_2$trien series							
PB900-Ni-MDI-50	229	8	40	65	78	89	95
PB1600-Ni-MDI-30	257	5	32	75	81	90	96
PB1600-Ni-MDI-50	257	6	35	65	70	81	93
PP1000-Ni-MDI-50	233	10	46	63	69	82	94
PP-2300-Ni-MDI-30	223	6	60	69	80	90	96
PP-2300-Ni-MDI-50	247	5	46	56	64	75	86

The thermal stability of copolyurethane-ureas was similar to that of polyurethane-ureas. The data showed that the wt % of metal complex in polymer was increased, the % weight loss of polymer decreased. This result was observed at high temperature in both series of $ZnSal_2$trien-based copolyurethane-ureas and $NiSal_2$trien-based copolyurethane-ureas. In comparison to metal-containing polyurethane-ureas, metal-containing copolyurethane-ureas showed less % weight loss. This was because the copolyurethane-ureas contained higher wt % of metal complex in the polymer chain. The aromatic rings in MDI might also help to stabilize the polymer at high temperature.

3.4.7 Flame retardancy

3.4.7.1 Flame retardancy of metal-containing polyurethane-ureas

Flame retardancy property of metal-containing polyurethane-ureas was investigated by limiting oxygen index (LOI). The values are shown in Table 3.11.

Table 3.11 LOI data of metal-containing polyurethane-ureas

Polymers	LOI	Polymers	LOI
PB900-Zn-30	24	PB900-Ni-30	24
PB1600-Zn-20	25	PB1600-Ni-20	26
PP1000-Zn-30	28	PP1000-Ni-30	25
PP2300-Zn-20	29	PP2300-Ni-20	29

It was found that LOI of metal-containing polyurethane-ureas was low. It was observed that the LOI of $ZnSal_2$trien-based polyurethane-ureas was equal to those of $NiSal_2$trien-based polyurethane-ureas. The LOI value increased with increasing in molecular weight of the prepolymer in both of $ZnSal_2$trien-based polyurethane-ureas and $NiSal_2$trien-based polyurethane-ureas.

3.4.7.2 Flame retardancy of metal-containing copolyurethane-ureas

Flame retardancy property of metal-containing copolyurethane-ureas was also investigated by limiting oxygen index (LOI). The values are shown in Table 3.12.

Table 3.12 LOI data of metal-containing copolyurethane-ureas

Polymers	LOI	Polymers	LOI
PB900-Zn-MDI-50	29	PB900-Ni-MDI-50	29
PB1600-Zn-MDI-30	27	PB1600-Ni-MDI-30	30
PB1600-Zn-MDI-50	32	PB1600-Ni-MDI-50	32
PP1000-Zn-MDI-50	29	PP1000-Ni-MDI-50	31
PP-2300-Zn-MDI-30	31	PP-2300-Ni-MDI-30	30
PP-2300-Zn-MDI-50	31	PP-2300-Ni-MDI-50	34

It was found that when wt % metal complex in the polymer was increased, the LOI data of metal-containing copolyurethane-ureas also increased. When compared to polyurethane-ureas, the LOI of metal-containing copolyurethane-ureas was higher than those of polyurethane-ureas. This was because the copolyurethane-ureas contained higher wt % of metal complex in the polymer chain. The aromatic rings in MDI might also help to stabilize the polymer at high temperature.

In comparison to the previous work reported by Nanjundan,[12] which described the synthesis of metal-containing polyurethane-ureas from divaleny metal salts of mono(hydroxybutyl) hexolate, the obtained polymers showed LOI values in the range between 27 to 36.