

CHAPTER III

RESULTS AND DISCUSSION

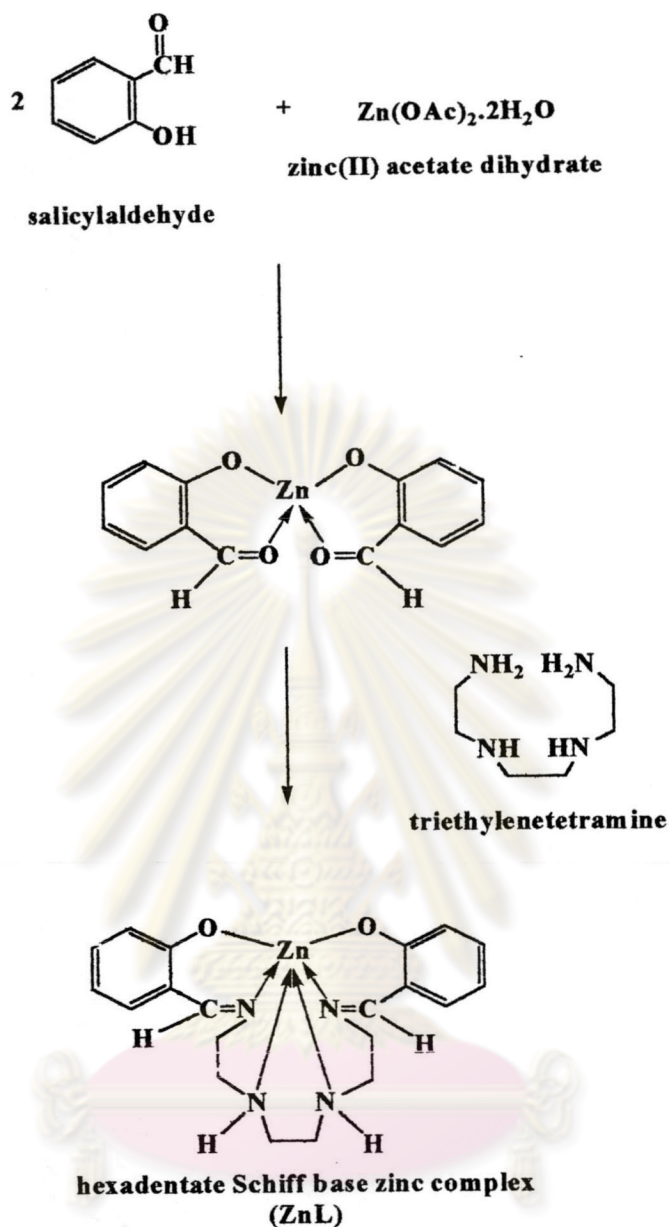
There were rare examples of the synthesis of metal-containing liquid crystalline polymers. As described in the introduction part, the work by Serrano was about the synthesis of metal-containing liquid crystalline polyesters using Schiff base metal complexes as the mesogenic part. An example of metal-containing liquid crystalline polyurethanes was done by Chang.⁹ They synthesized main-chain liquid-crystalline polyurethanes with a high aspect ratio mesogenic diol as a chain extender. The general problem of incorporating metal into polymers is the nonhomogeneous and phase separation.

The purpose of this research is to find the suitable polyols for polyurethane starting material, the suitable reaction conditions and to prepare polymers in the form of powder and film to gain the preliminary results for further studies. The polyols studied in this system are PCL diol, PCL triol and PP glycol. The isocyanate used in the work is HDI since it has the most possibility to exhibit liquid crystalline property due to its flexibility although the mechanical property of the resulting polymer is not good due to the very low T_g of the resulting polyurethanes.

The formulation for polyurethane preparation was chosen to obtain the polymer samples which will lead to the study of the polyurethane mechanical properties in more details in the future. Therefore, the appropriate polyurethane formulation should be homogeneous mixture with low viscosity.

3.1 Synthesis of the hexadentate Schiff base zinc complex (ZnL)

Hexadentate Schiff base zinc complex (ZnL) was synthesized following the synthetic route described in the literature.¹⁹ The spectroscopic data of ZnL agreed with the values reported.



Scheme 3.1 Synthesis of the hexadentate Schiff base zinc complex

In previous work, Batiya²¹ synthesized hexadentate Schiff base zinc complex (ZnL). The DSC thermogram of ZnL is shown in Figure 3.1. The peak appearing at 140°C might be associate with crystal-crystal transition since the POM observation did not reveal any crystal-mesophase-transition as confirmed by the POM. Upon heating of ZnL on the hot stage of POM to 210°C, ZnL started to melt and underwent a transition from solid to birefringence viscous liquid with an uncharacteristic texture. ZnL texture had a grainy appearance with yellow zones on a dark background (Figure 3.2).

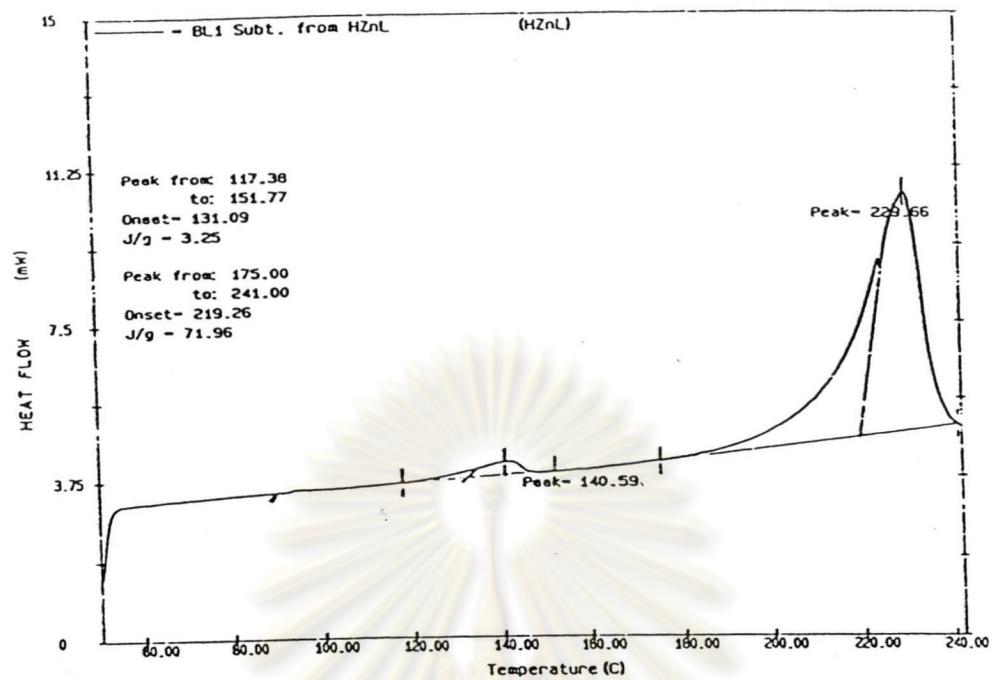
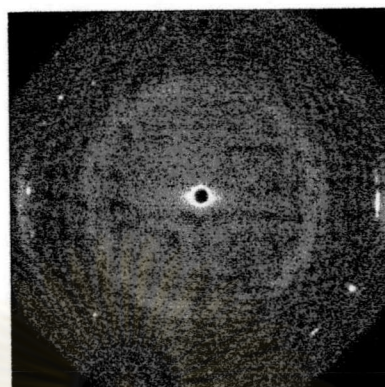


Figure 3.1 DSC thermogram of ZnL

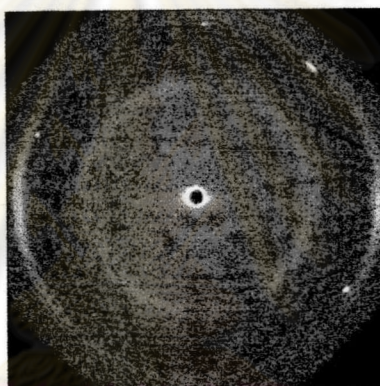


Figure 3.2 LC Morphology of ZnL observed by POM at 213°C on heating

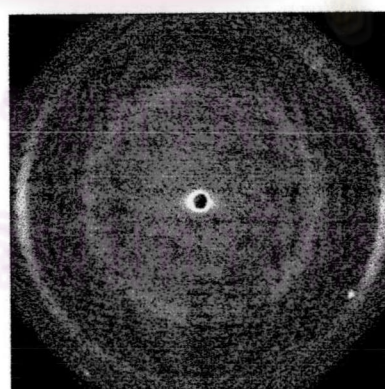
In this research, the liquid crystalline phases of ZnL were further studied using SAXS. Figures 3.3 and 3.4 show the X-ray diffraction of ZnL recorded at different temperatures.



(a)



(b)



(c)

Figure 3.3 X-ray diffractogram of ZnL at (a) room temperature, (b) 210°C and (c) 220°C

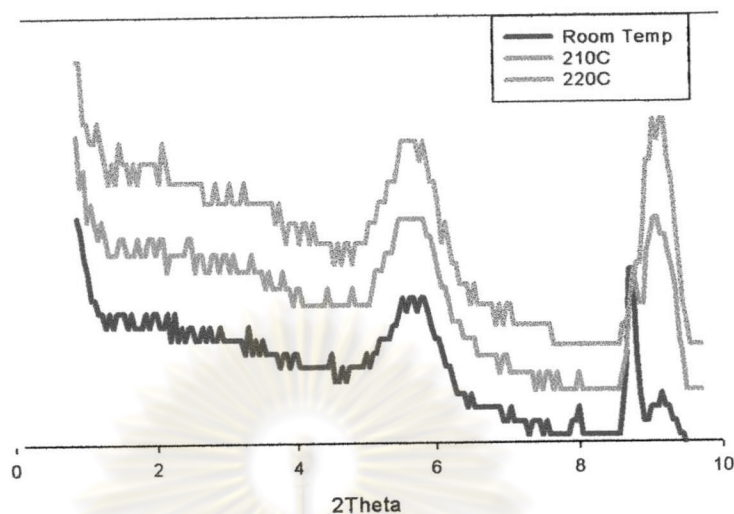


Figure 3.4 X-ray diffractogram of ZnL

The peaks at $d = 11.2, 10.2$ and 9.7 \AA were observed at room temperature. When ZnL was heated to 210°C , where the mesophase started to form, the peak at 11.2 \AA disappeared. The intensity of the peak at 9.7 \AA was stronger than that of 10.2 \AA . At 220°C , the peak which was characterized by an equatorial halo at 9.7 \AA was present and the peak at 10.2 \AA appeared as a shoulder. This diffraction pattern is an indicative of an ordered structure which might be due to the arrangement of ZnL molecules.

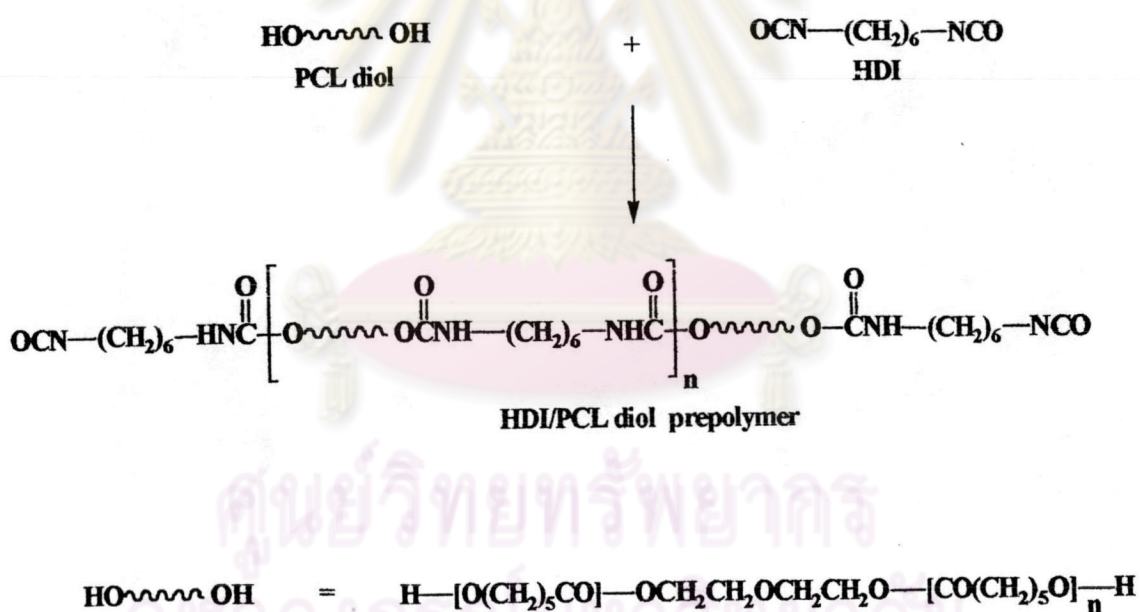
3.2 Synthesis of Polyurethanes

Prepolymer method was used in the synthesis of polyurethane elastomers. Polyurethanes were synthesized from the reaction between ZnL and prepolymers obtained from HDI and different polyols. The polyols employed in this study were PCL diol, PCL triol and PP glycol. The polyurethane elastomer was synthesized by a two-step process. In the first step, an NCO-terminated prepolymer was prepared by the polyaddition reaction of polyol and excess amount of HDI, which was chain-extended in the next step with ZnL to yield the polyurethane elastomer.

The structural confirmation of the polyurethane was restricted to FTIR spectroscopy because the polymers could not be characterized by NMR spectroscopy on account of poor solubility in deuterated solvents.

3.2.1 Synthesis and spectroscopic characterization of PCL diol polyurethane from the reaction between ZnL, HDI and PCL diol

Prepolymer for PCL diol polyurethane was synthesized from the reaction between HDI and PCL diol as shown in Scheme 3.2. The mole ratio of HDI:PCL diol was 1:1. The molecular weight of PCL diol employed in this study was 530. The reaction was done by heating a mixture of HDI and PCL diol under nitrogen atmosphere and the amount of NCO was determined by titration. Table 3.1 showed the amount of isocyanate in the prepolymer at different times.

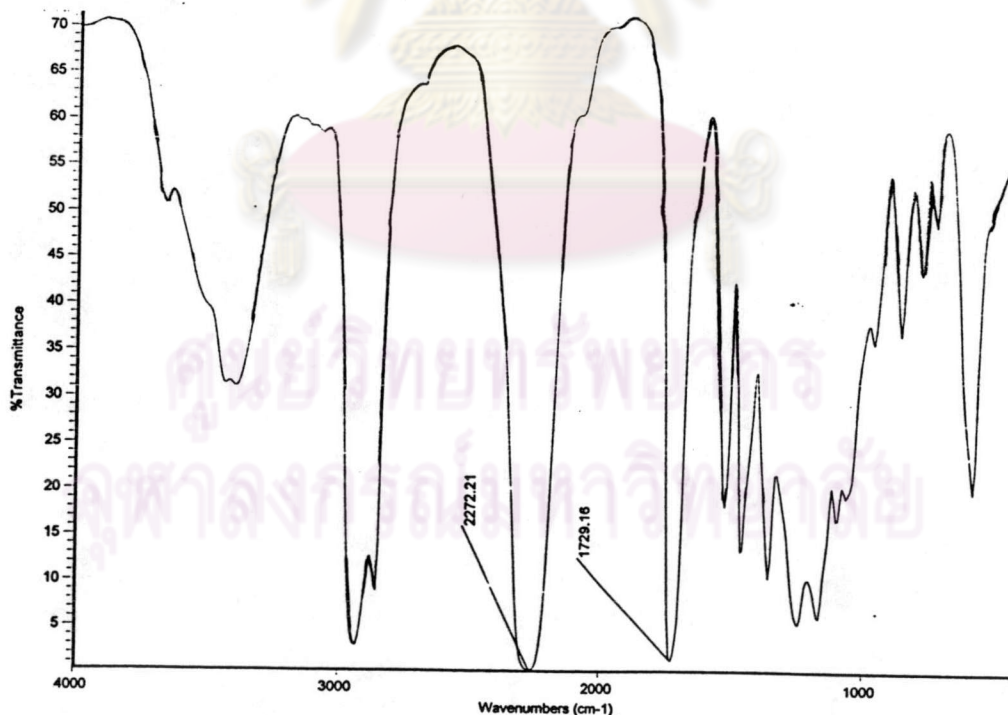


Scheme 3.2 Synthesis of HDI / PCL diol prepolymers from HDI and PCL diol

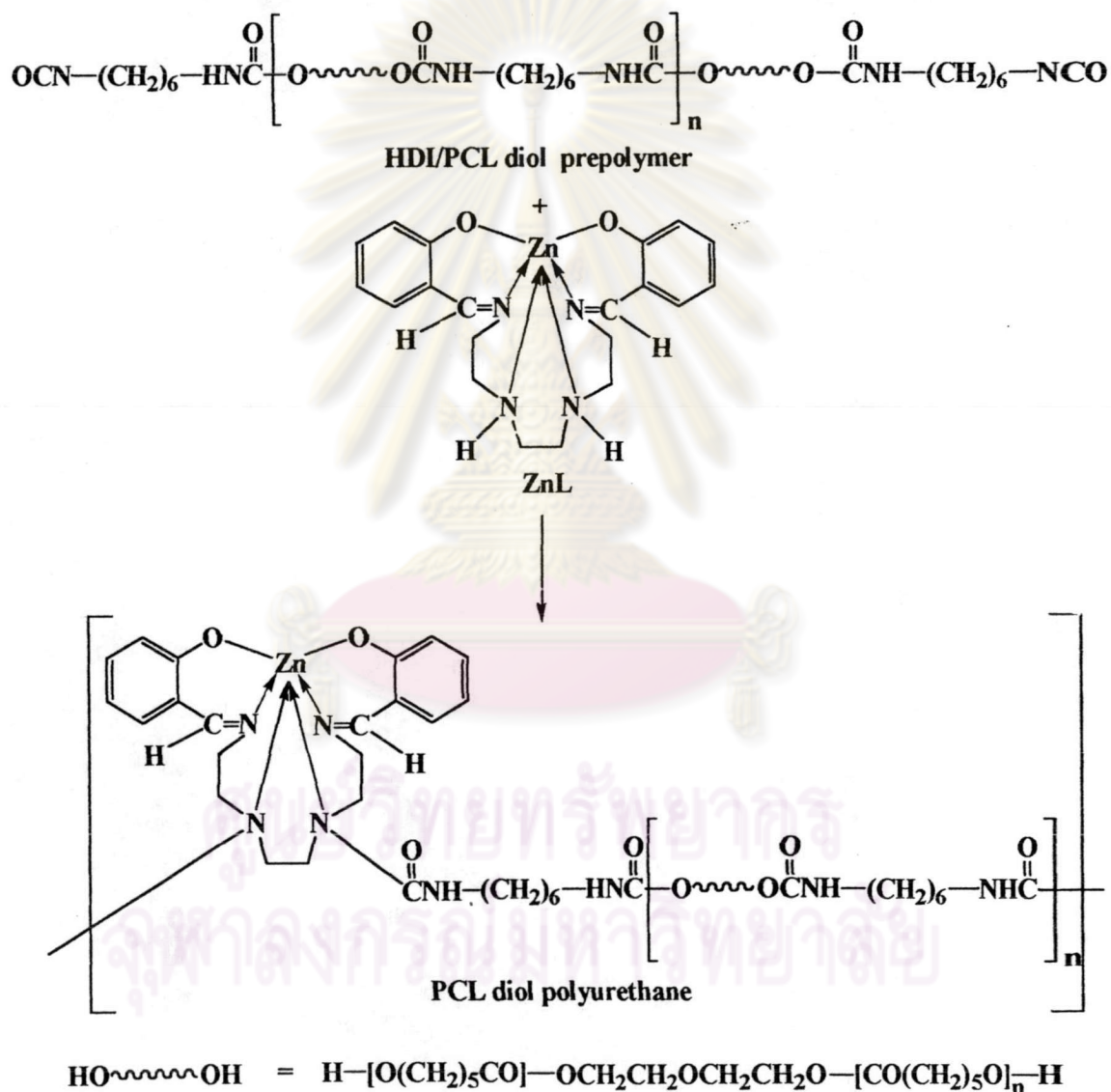
Table 3.1 Amount of isocyanate in HDI / PCL diol prepolymer at different times

Time(min)	% NCO
90	56
120	35
150	22
180	17
300	13
480	11

The prepolymer structure was investigated by IR spectroscopy. The IR spectrum of HDI/PCL diol prepolymers showed strong absorption of NCO stretching at 2272 cm^{-1} and C=O stretching of the ester and urethane group (-OCONH-) at 1729 cm^{-1} . A representative IR spectrum of HDI / PCL diol prepolymers is shown in Figure 3.5.

**Figure 3.5** IR spectrum of HDI / PCL diol prepolymer at the 17% NCO group

The next step was the reaction between HDI / PCL diol prepolymer and ZnL as shown in Scheme 3.3. The mole ratio of ZnL : NCO groups in prepolymer was kept at 1:1 to avoid crosslinking in the polymer. HDI / PCL diol prepolymers with different NCO contents were used to prepare the polyurethane. It was found that suitable prepolymer for the preparation of polyurethane was the one with 17% NCO and therefore, the content of ZnL in polyurethane was 9% wt (ZnL : % NCO groups = 1:1 by mole). The polyurethane with 17% NCO was flexible enough for DMA. Where as the polyurethane with 35% NCO was too brittle, to be characterized by DMA.

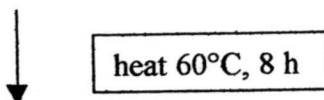


Scheme 3.3 Synthesis of PCL diol polyurethanes from the reaction between HDI / PCL diol prepolymer and ZnL

PCL diol polyurethanes were prepared using two methods as follows:

Method 1

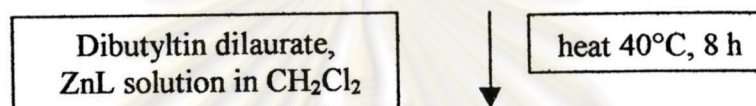
HDI/PCL diol prepolymer + ZnL solution in CH_2Cl_2



PCL diol polyurethane-1

Method 2

HDI/PCL diol prepolymer solution in CH_2Cl_2



PCL diol polyurethane-2

In method 1, dibutyltin dilaurate was not used as a catalyst since the catalyst would remain in the prepolymer. When ZnL was added to the prepolymer, removal of the solvent and air bubble was difficult since the polymerization occurred at this step. This method yielded polyurethane sample which was suitable for characterization with DMA.

In method 2, when ZnL was added to the prepolymer solution, the resulting mixture was more homogeneous than that observed when using the method 1.

Both PCL diol polyurethanes-1 and-2 showed similar IR absorptions. The obtained polyurethanes were yellow. The IR spectra showed the following characteristic absorption bands: 3366 cm^{-1} (NH stretching), 2935 and 2865 cm^{-1} (aliphatic CH stretching), 1729 cm^{-1} (carbonyl of urethane and urea), 1536 cm^{-1} (NH bending) and 1251 cm^{-1} (CO stretching). A representative IR spectrum of PCL diol polyurethane is shown in Figure 3.6. Since dichloromethane was not used during the preparation of polyurethane-1, ZnL did not mix very well with the prepolymer due to the high viscosity of the mixture. This resulted in the nonhomogeneous polymer sample. When dichloromethane was used during polymer preparation in polyurethane-2 along with dibutyltin dilaurate as a catalyst, more homogeneous polymer was obtained.

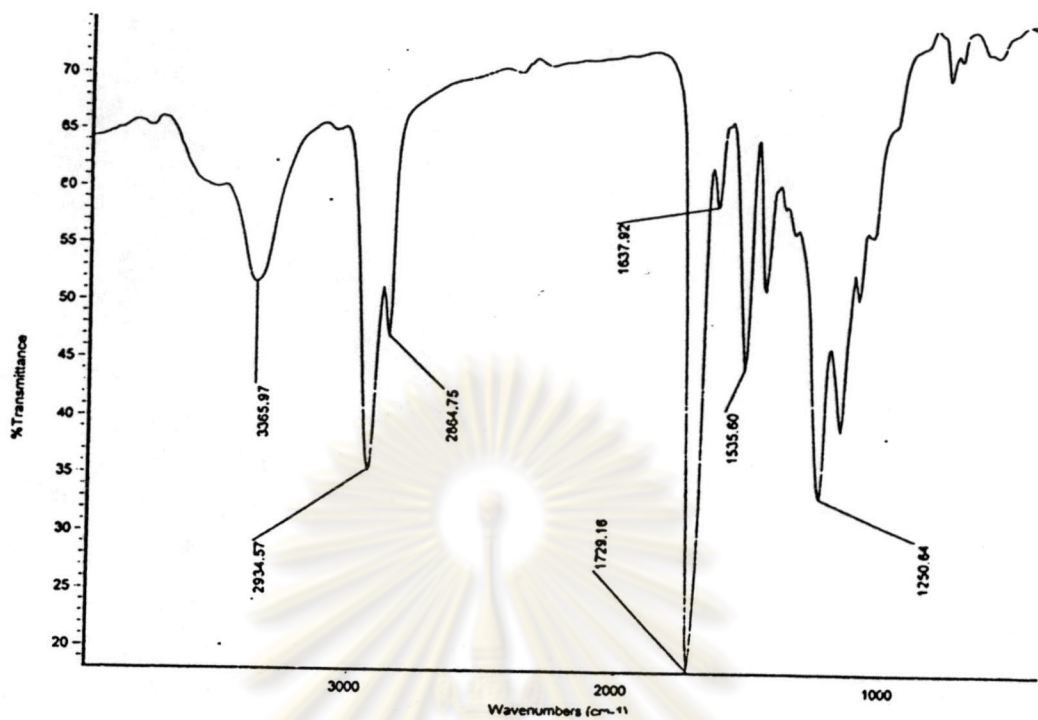


Figure 3.6 IR spectrum of PCL diol polyurethane from the reaction between HDI / PCL diol prepolymer and ZnL

Dynamic mechanical analysis of PCL diol polyurethane-1 showed a T_g at -29°C as shown in Figure 3.7 which was typical for polyurethane elastomers.

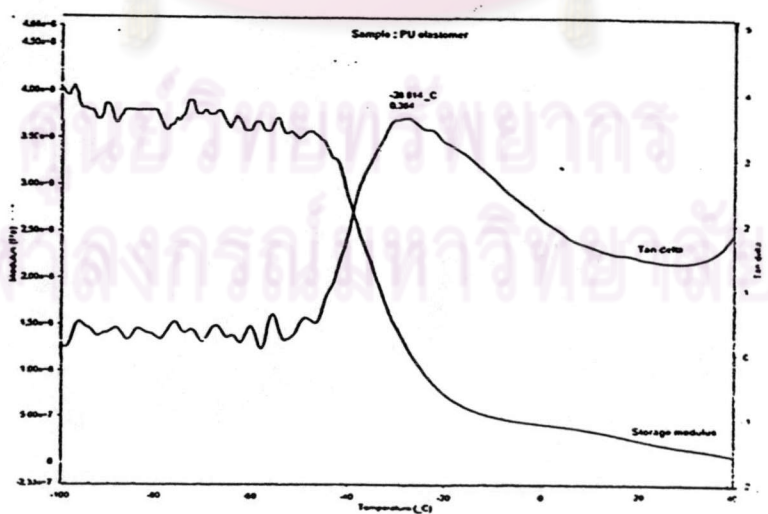


Figure 3.7 Dynamic mechanical analysis

The morphology of PCL diol polyurethans-1 and-2 was studied using SEM with electron probe microanalyzer as shown in Figures 3.8 and 3.9. Figures 3.10 and 3.11 show composition of the elements in PCL diol polyurethanes-1 and-2 which were obtained by using characteristic X-ray lines.



Figure 3.8 Morphology of PCL diol polyurethane-1 observed by SEM



Figure 3.9 Morphology of PCL diol polyurethane-2 observed by SEM

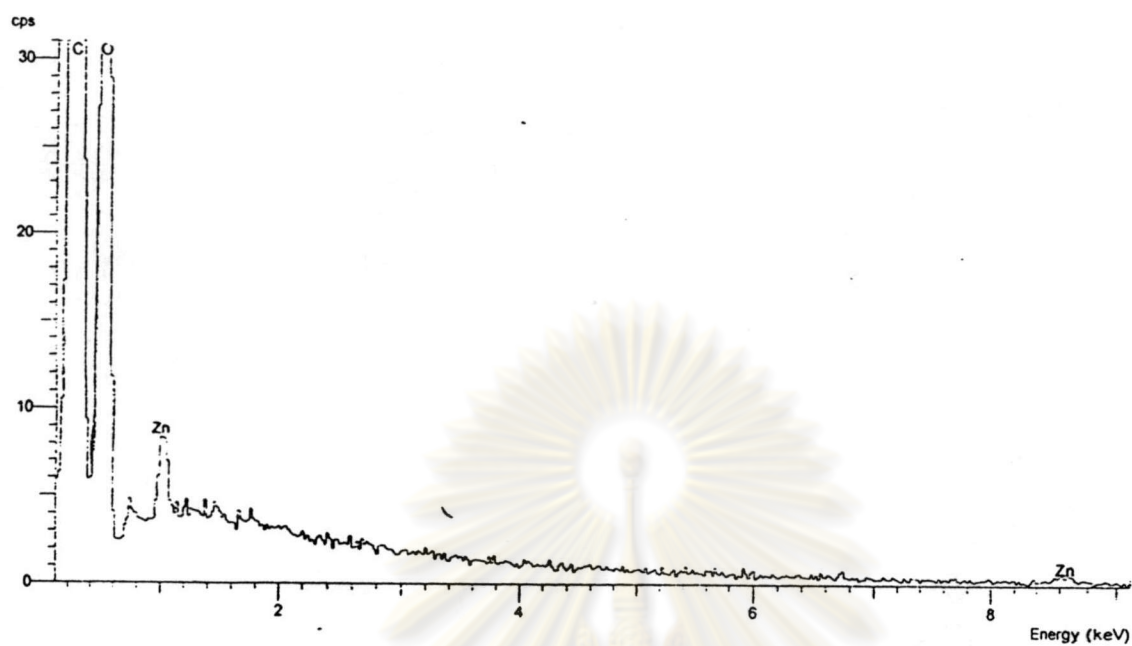


Figure 3.10 Composition of elements in PCL diol polyurethane-1

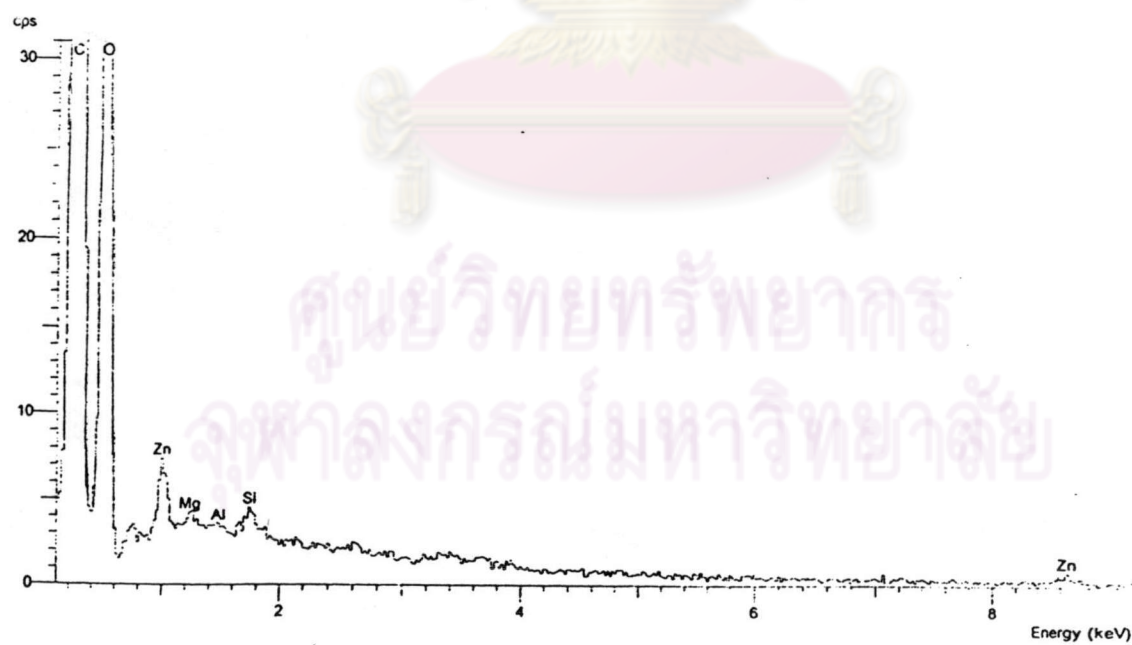
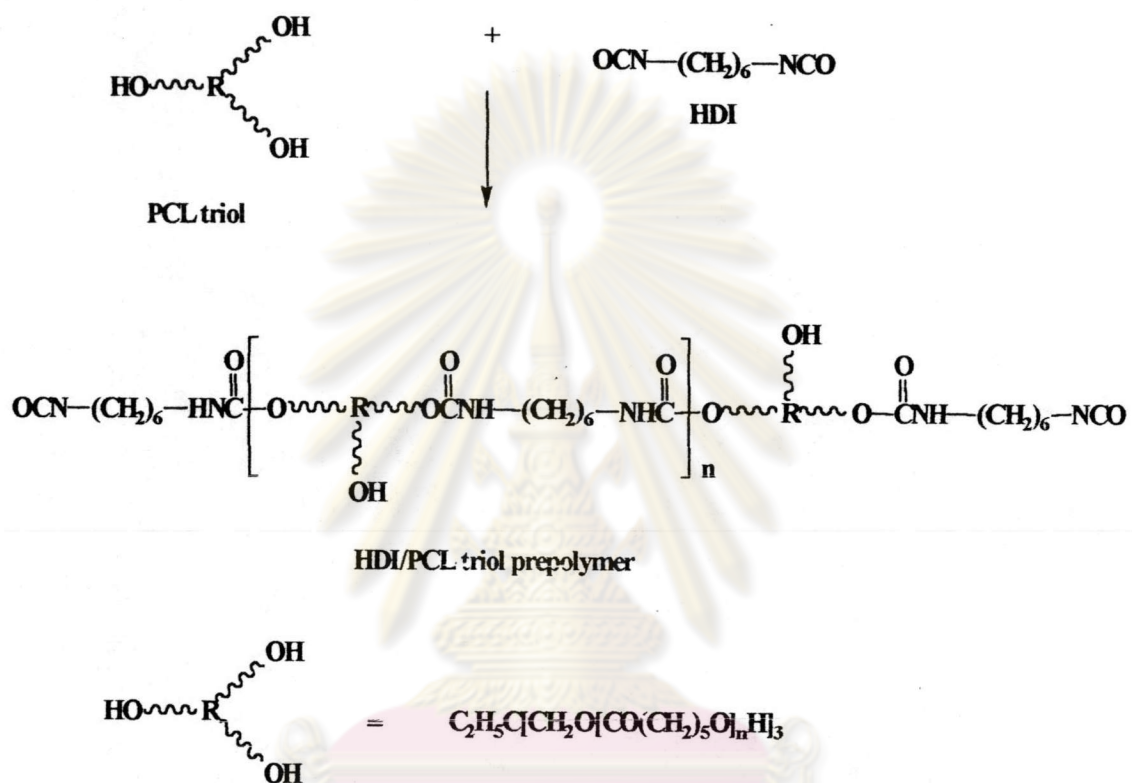


Figure 3.11 Composition of elements in PCL diol polyurethane-2

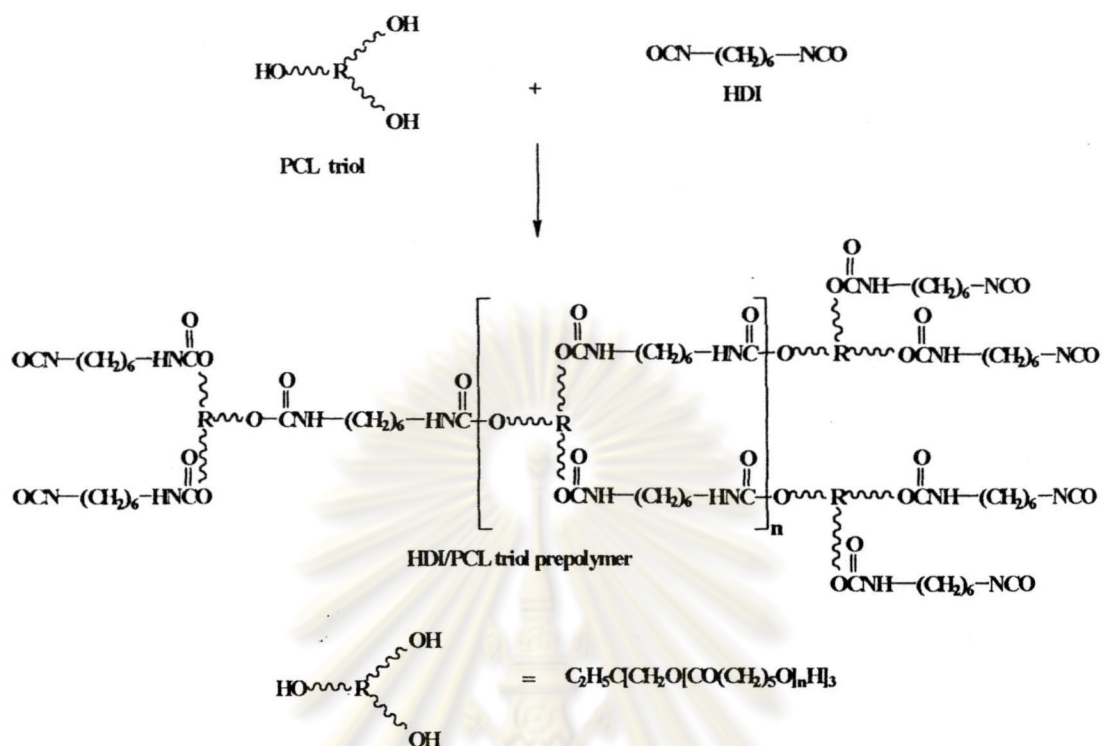
3.2.2 Synthesis and spectroscopic characterization of PCL triol polyurethane from the reaction between ZnL, HDI and PCL triol

Prepolymer for PCL triol polyurethane was synthesized by the reaction between HDI and PCL triol as shown in Schemes 3.4 and 3.5.



Scheme 3.4 Synthesis of HDI / PCL triol prepolymers from HDI : PCL triol (1:1)

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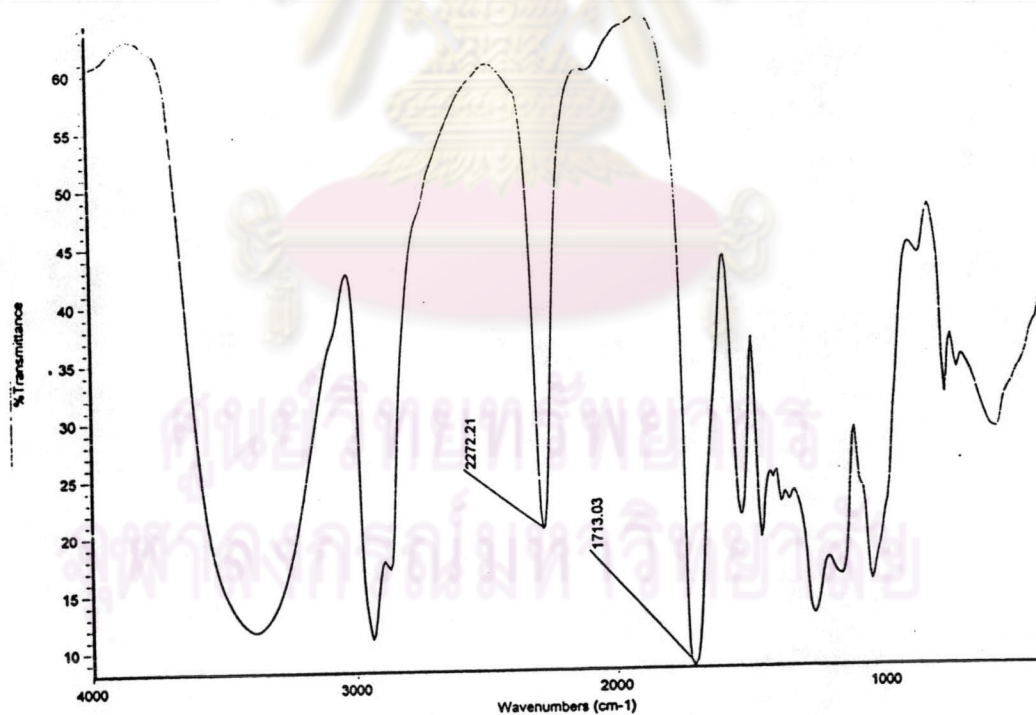
Scheme 3.5 Synthesis of HDI / PCL triol prepolymer from HDI : PCL triol (1.5:1)

The mole ratios of HDI : PCL triol employed were 1:1 and 1.5:1 to study the effect of different mole ratios of the starting materials in the resulting polyurethanes. The molecular weight of PCL triol employed in this study was 300. The reaction was done by following the same method as HDI / PCL diol prepolymer and the amount of NCO at different reaction times was determined by titration as shown in Table 3.2. The reaction of PCL triol was faster than PCL diol.

Table 3.2 Amount of isocyanate in HDI / PCL triol prepolymer at different times

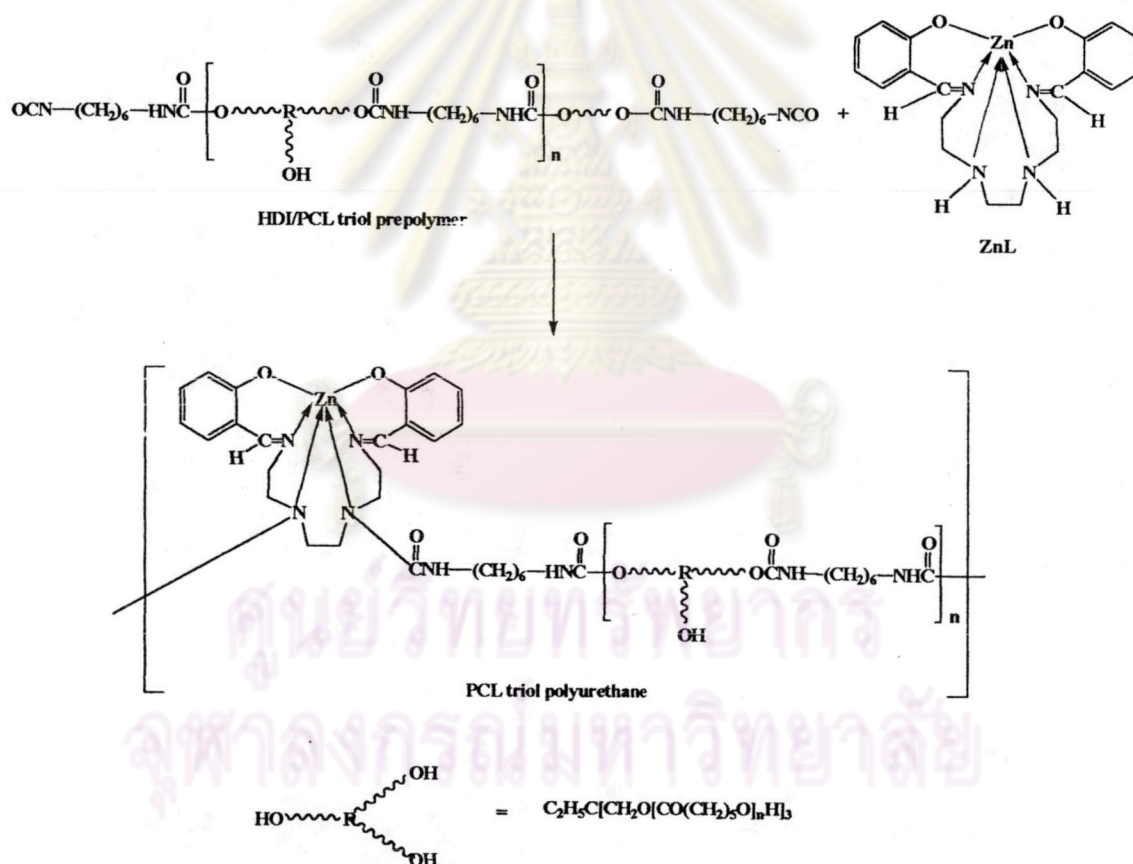
Time (min)	% NCO	
	HDI : PCL = 1:1	HDI : PCL = 1.5:1
90	34	28
120	13	18
150	11	13
180	8	12
300	7	8
480	6	7

IR spectrum of HDI / PCL triol prepolymers showed strong NCO absorption at 2272 cm^{-1} . An absorption at 1713 cm^{-1} was assigned as C=O stretching of the ester group in PCL triol and the urethane group (-OCONH-). A representative IR spectrum of HDI / PCL triol prepolymer is shown in Figure 3.12.

**Figure 3.12** IR spectrum of HDI / PCL triol prepolymer at the 13% NCO group

In the polymerization step by the reaction between HDI / PCL triol prepolymer and ZnL to yield polyurethane elastomer, the mole ratio of ZnL:NCO groups in prepolymer was kept at 1:1 as shown in Scheme 3.6. It was found that only the prepolymer obtained from HDI: PCL triol at the mole ratio of 1:1 can be used to prepare the polyurethane elastomers. The appropriate NCO content in the prepolymer for the preparation of polyurethane was 13%. Therefore, the content of ZnL in polyurethane was 10% wt (ZnL : % NCO groups = 1:1 by mole). The prepolymers with NCO contents less than 13% had high viscosity and it was difficult to mix with ZnL to obtain homogeneous mixture.

Another prepolymer obtained from HDI : PCL triol at the mole ratio of 1.5:1 could not be used since the mixture became highly viscous and could not be mixed effectively with ZnL.



Scheme 3.6 Synthesis of PCL triol polyurethanes from the reaction between HDI / triol prepolymer and ZnL

PCL triol polyurethanes were prepared using two methods as follows:

Method 1

HDI/PCL triol prepolymer + ZnL solution in CH_2Cl_2



heat 60°C, 8 h

PCL triol polyurethane-1

Method 2

HDI/PCL triol prepolymer solution in CH_2Cl_2

Dibutyltin dilaurate,
ZnL solution in CH_2Cl_2



heat 40°C, 8 h

PCL triol polyurethane-2

In method 1, dibutyltin dilaurate was not used as a catalyst since the catalyst would remain in the prepolymer and therefore the reaction with ZnL was fast. When ZnL was added to the prepolymer, removal of the solvent and air bubble was difficult.

In the method 2, When ZnL was added to the prepolymer solution, a homogeneous mixture was obtained. After the solvent was evaporated, phase separation of the polymer occurred like a wax in the solution.

Both PCL triol polyurethanes-1 and -2 showed similar IR absorptions. The polyurethanes were obtained as yellow elastomers. The IR spectra showed the following characteristic absorption bands: 3390-3360 cm^{-1} (NH stretching), 2934 and 2862 cm^{-1} (aliphatic CH stretching), 1713 cm^{-1} (carbonyl of urethane and urea), 1536 cm^{-1} (NH bending) and 1259 cm^{-1} (C-O stretching). A representative IR spectrum of PCL triol polyurethane is shown in Figure 3.13.

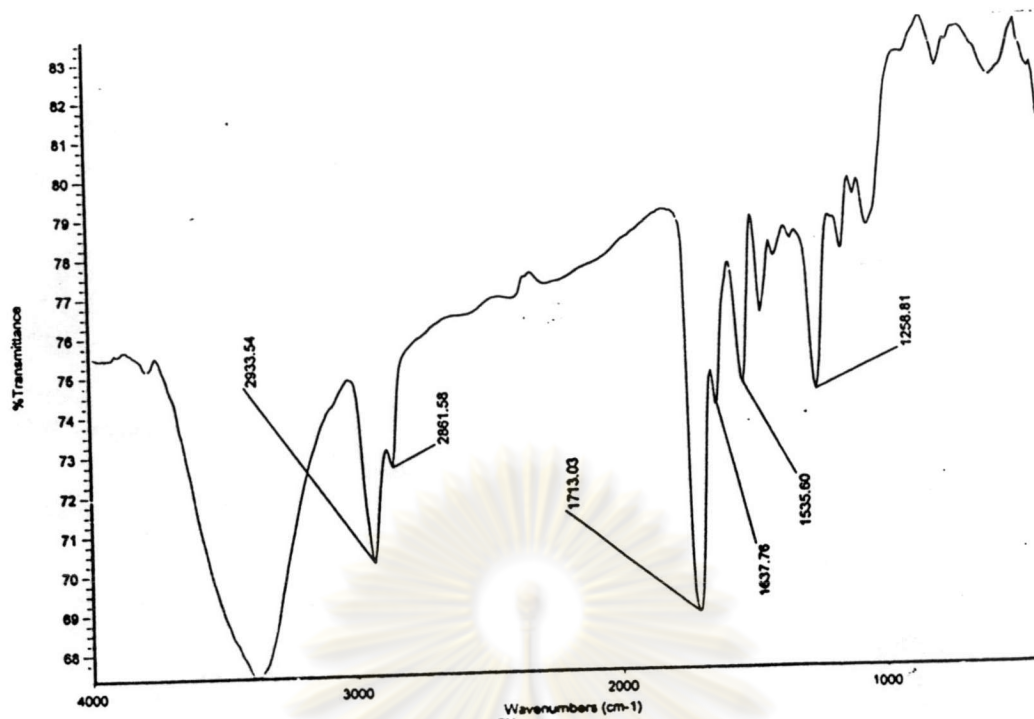


Figure 3.13 IR spectrum of PCL triol polyurethane from the reaction between HDI / PCL triol prepolymer and ZnL

The morphology of PCL triol polyurethanes-1 and -2 was studied using SEM with electron probe microanalyzer as shown in Figures 3.14 and 3.15. The elemental distribution of PCL triol polyurethanes-1 and -2 are shown in Figures 3.16 and 3.17.

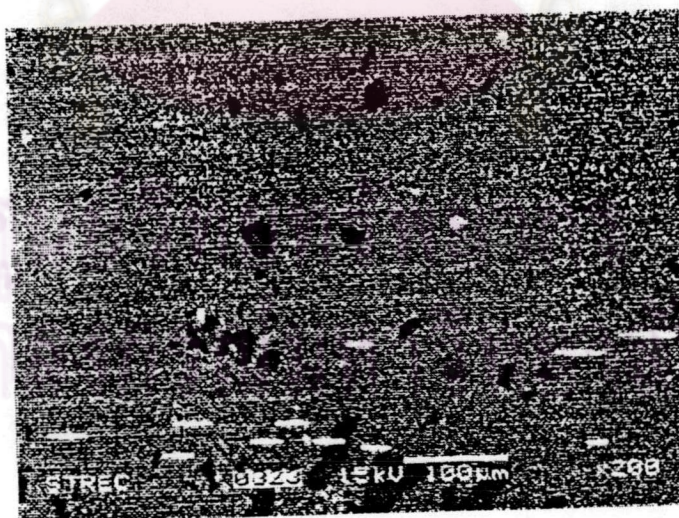


Figure 3.14 Morphology of PCL triol polyurethane-1 observed by SEM



Figure 3.15 Morphology of PCL triol polyurethane-2 observed by SEM

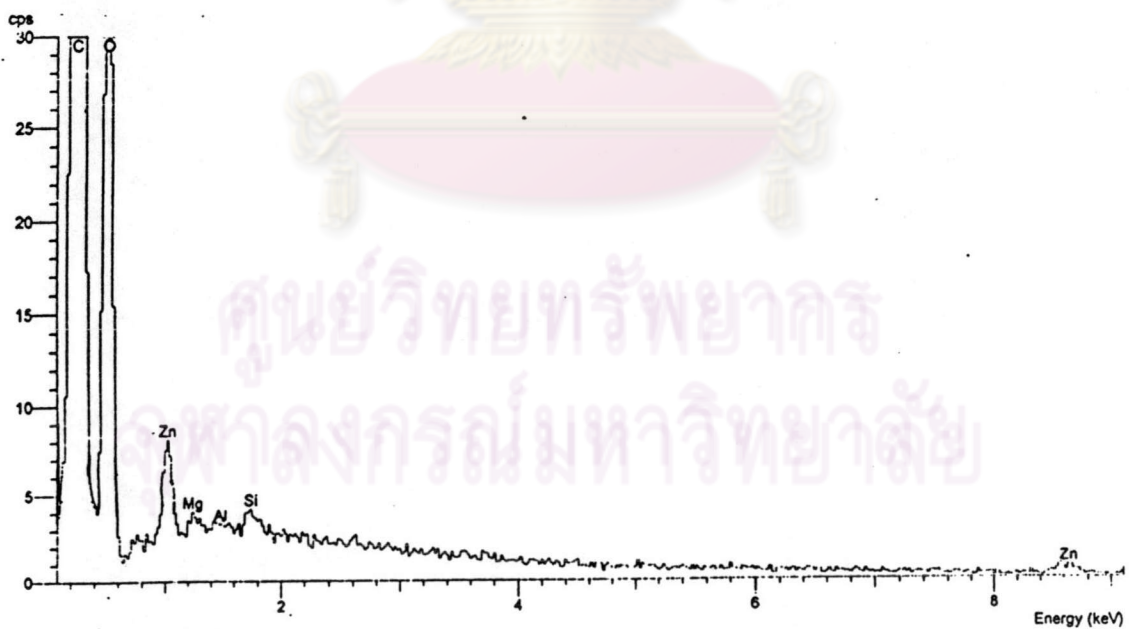


Figure 3.16 Composition of element in PCL triol polyurethane-1

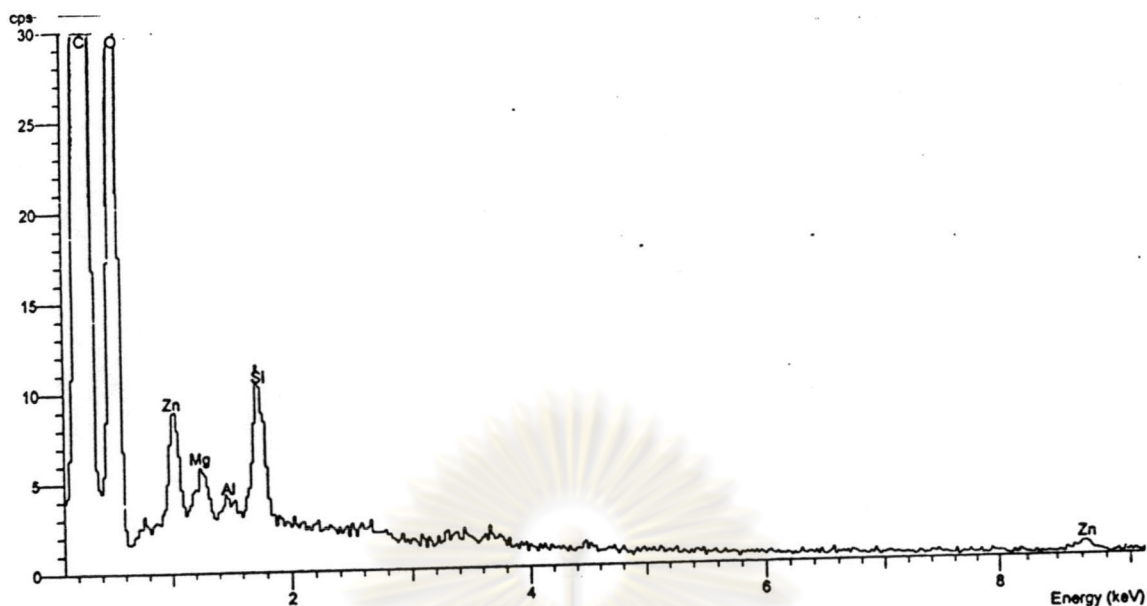
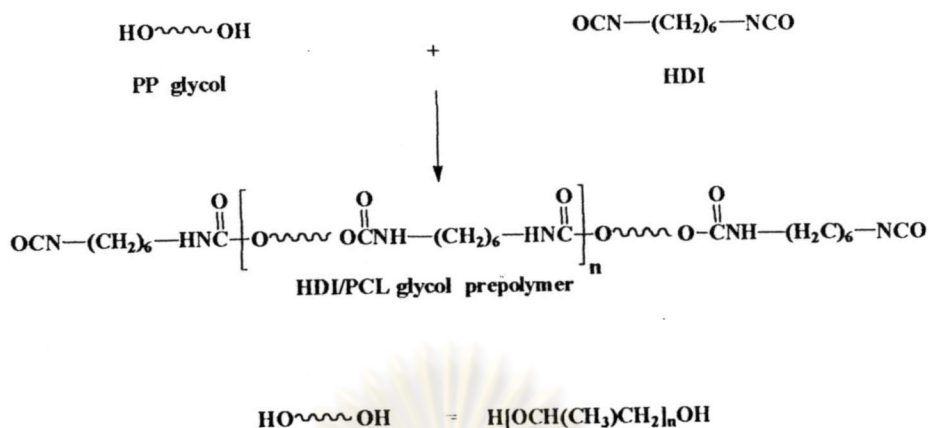


Figure 3.17 Composition of element in PCL triol polyurethane-2

3.2.3 Synthesis and spectroscopic characterization of PP glycol polyurethane from the reaction between ZnL, HDI and PP glycol

It was of interest to use PP glycol since it has low viscosity and therefore it was easy to obtain good polyurethane sample. The molecular weight of PP glycol employed in this study was 1000. Prepolymer for PP glycol polyurethane was synthesized by the reaction between HDI and PP glycol as shown in Scheme 3.7. The reaction was done by following the same method as HDI / PCL diol prepolymer and the amount of NCO at different times was determined by titration as shown in Table 3.3.

It was found that suitable prepolymer for the preparation of polyurethane was the one with 55% NCO and therefore, the content of ZnL in polyurethane was 16% wt (ZnL : % NCO groups = 1:1 by mole).



Scheme 3.7 Synthesis of HDI / PP glycol prepolymer from HDI and PP glycol

Table 3.3 Amount of isocyanate in HDI / PP glycol prepolymer at different times

Time(min)	% NCO
90	68
120	55
150	54
180	54
300	54
480	54

IR spectrum of HDI / PP glycol prepolymers showed strong NCO absorption at 2272 cm^{-1} . An absorption at 1713 cm^{-1} was assigned as C=O stretching of the ester group in PP glycol and the urethane group (-OCONH-). A representative IR spectrum of HDI / PCL triol prepolymers is shown in Figure 3.18.

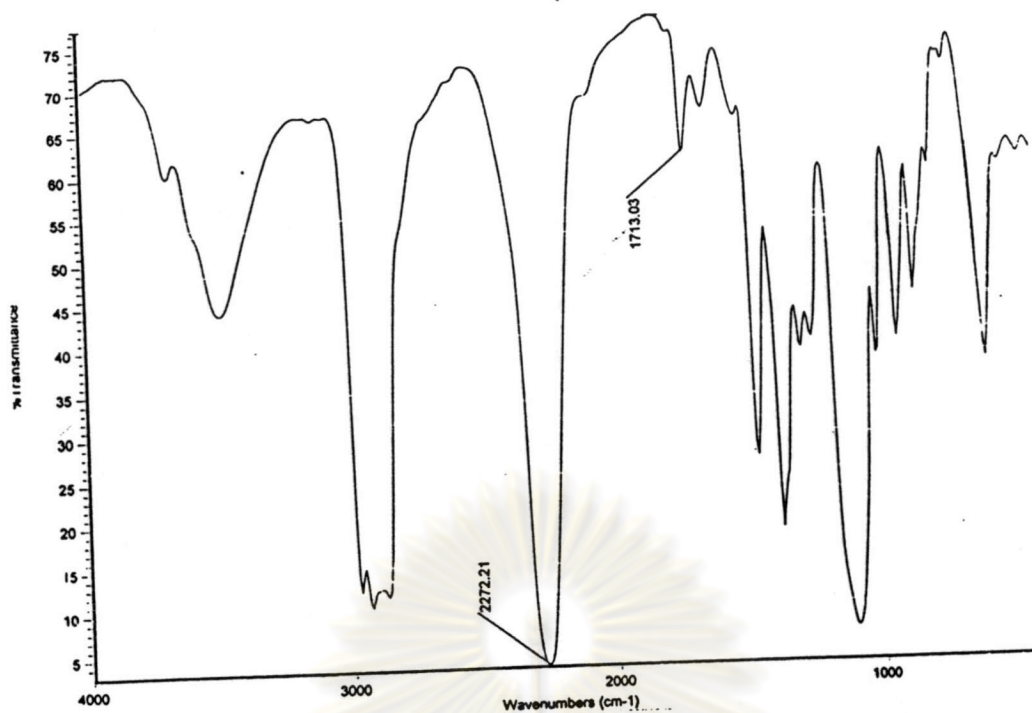
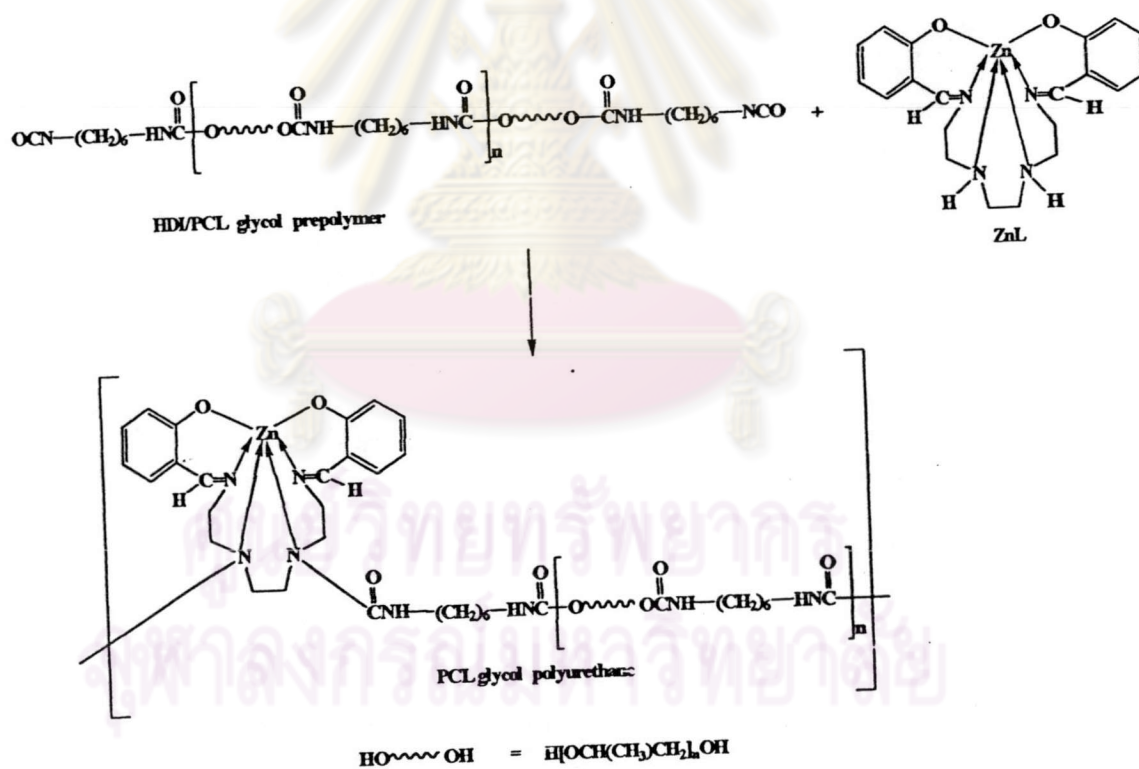


Figure 3.18 IR spectrum of HDI / PP glycol prepolymer at the 55% NCO group

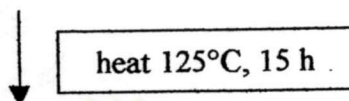


Scheme 3.8 Synthesis of PP glycol polyurethane from the reaction between HDI / PP glycol prepolymer and ZnL

PP glycol polyurethanes were prepared from the reaction between HDI / PP glycol prepolymer as shown in Scheme 3.8 by using two methods as follows:

Method 1

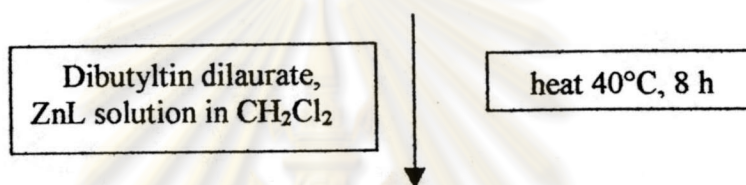
HDI / PP glycol prepolymer + ZnL solution in CH_2Cl_2



PP glycol polyurethane-1

Method 2

HDI / PP glycol prepolymer solution in CH_2Cl_2



PP glycol polyurethane-2

In method 1, dibutyltin dilaurate was not used as a catalyst. The polymerization reaction was slow. The prepolymer mix very well with ZnL due to the low viscosity of the mixture. When ZnL was added to the prepolymer, the polymerization was completed by heated at 125°C for 15 hours.

In method 2, when ZnL was added to the prepolymer solution, the reactions prefer to be completed at low temperature. The reaction went to completion by heated at 40°C for 8 hours.

Both PP glycol polyurethanes-1 and -2 showed similar IR absorptions. The obtained polyurethanes were yellow. The IR spectra showed the following characteristic absorption bands: 3500-3350 cm^{-1} (NH stretching), 2923 and 2870 cm^{-1} (aliphatic CH stretching), 1713 cm^{-1} (carbonyl of urethane and urea), 1541 cm^{-1} (NH bending) and 1251 cm^{-1} (CO stretching). A representative IR spectrum of PP glycol polyurethane is shown in Figure 3.19.

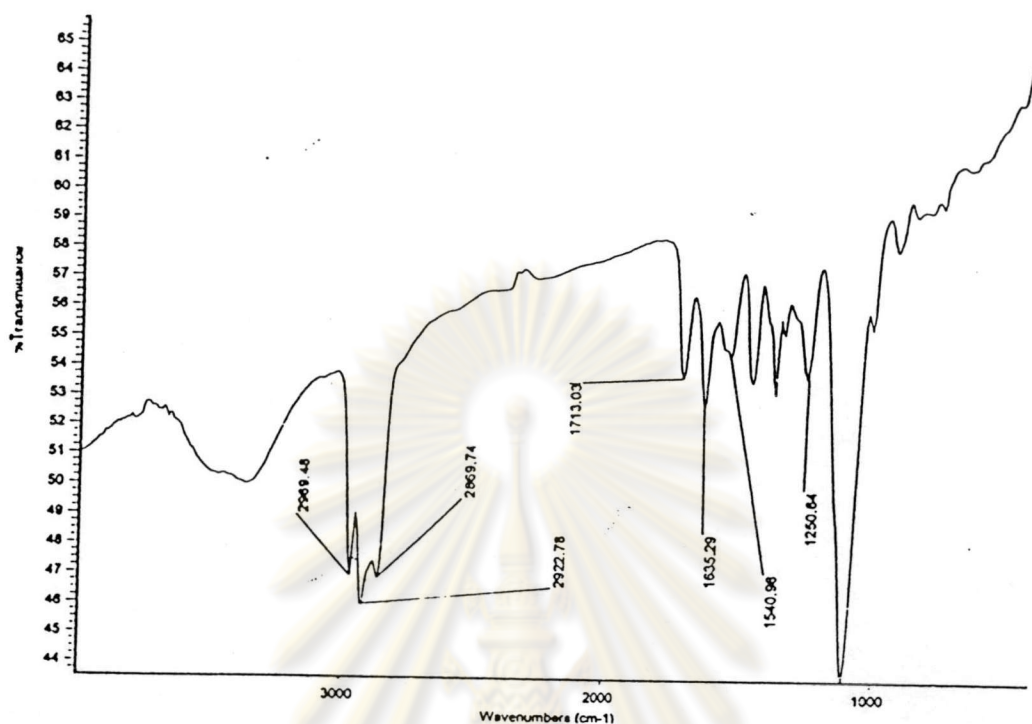


Figure 3.19 IR spectrum of PP glycol polyurethane from the reaction between HDI / PP glycol prepolymer and ZnL

3.3 Liquid Crystalline Property of Polyurethanes

Liquid crystalline property of polyurethane synthesized was determined by DSC measurement at a heating rate of 10°C/min and were observed under a polarizing optical microscope. It was found that significant melting and isotropic transition could not be observed in the DSC thermograms. However, they were observed visually under the polarizing optical microscope.

Polyurethanes were prepared as thin film. It was found that the polyurethane prepared from different methods gave different liquid crystalline properties. Polymerization of prepolymer with ZnL in method 1 was done by heating the polymer in an oven at 60°C without using solvent. While polymerization in method 2 was done in refluxing dichloromethane at 40°C.

3.3.1 PCL diol polyurethane

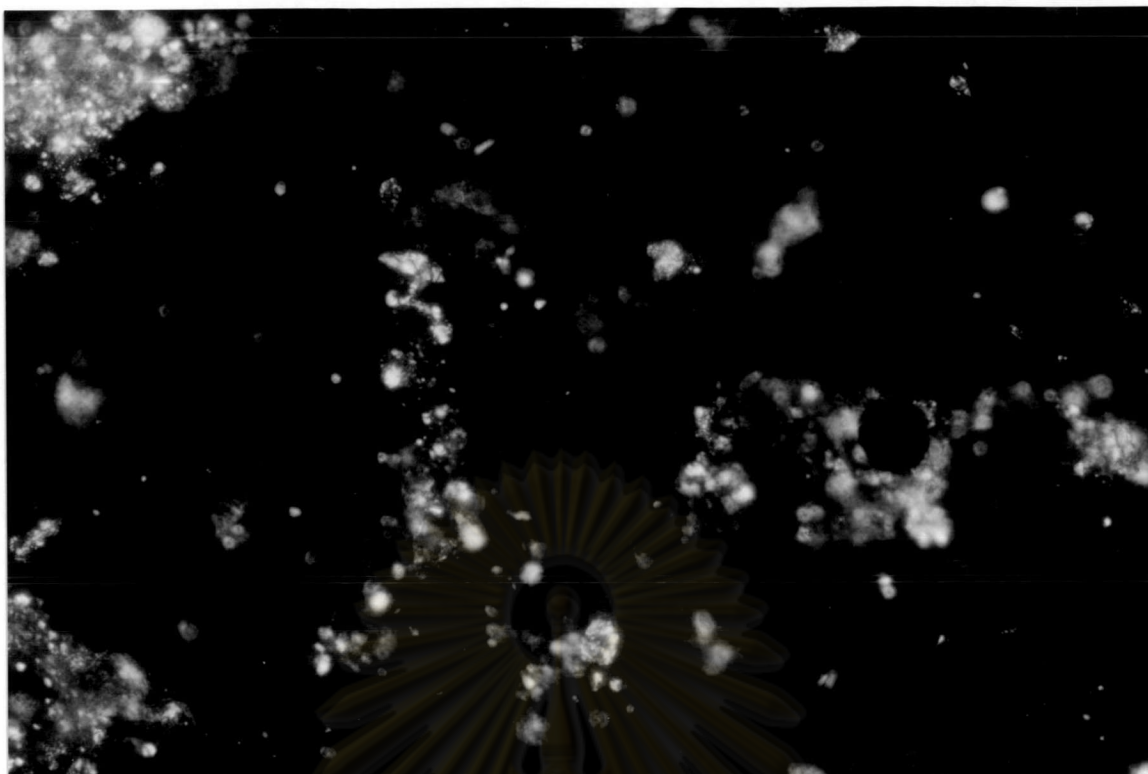
When examined under POM, the polymers were only slightly birefringent presumably because of the presence of a low degree of mesomorphic order formed during preparation of the samples or the percent by weight of ZnL in the polymer was low.

Both PCL diol polyurethanes prepared from methods 1 and 2 exhibited weak birefringence from room temperature to 75°C followed by melting to isotropic phase as shown in Figures 3.20 and 3.21. After quenching from molten stage to room temperature, the PCL diol polyurethane-1 did not show mesomorphism. In the case of the PCL diol polyurethane-2, the mesophase reappeared after leaving the polymer at room temperature for 2 hours.



(a)

Figure 3.20 Polarizing optical micrographs of PCL diol polyurethane-1: (a) at room temperature (b) at 69°C on heating



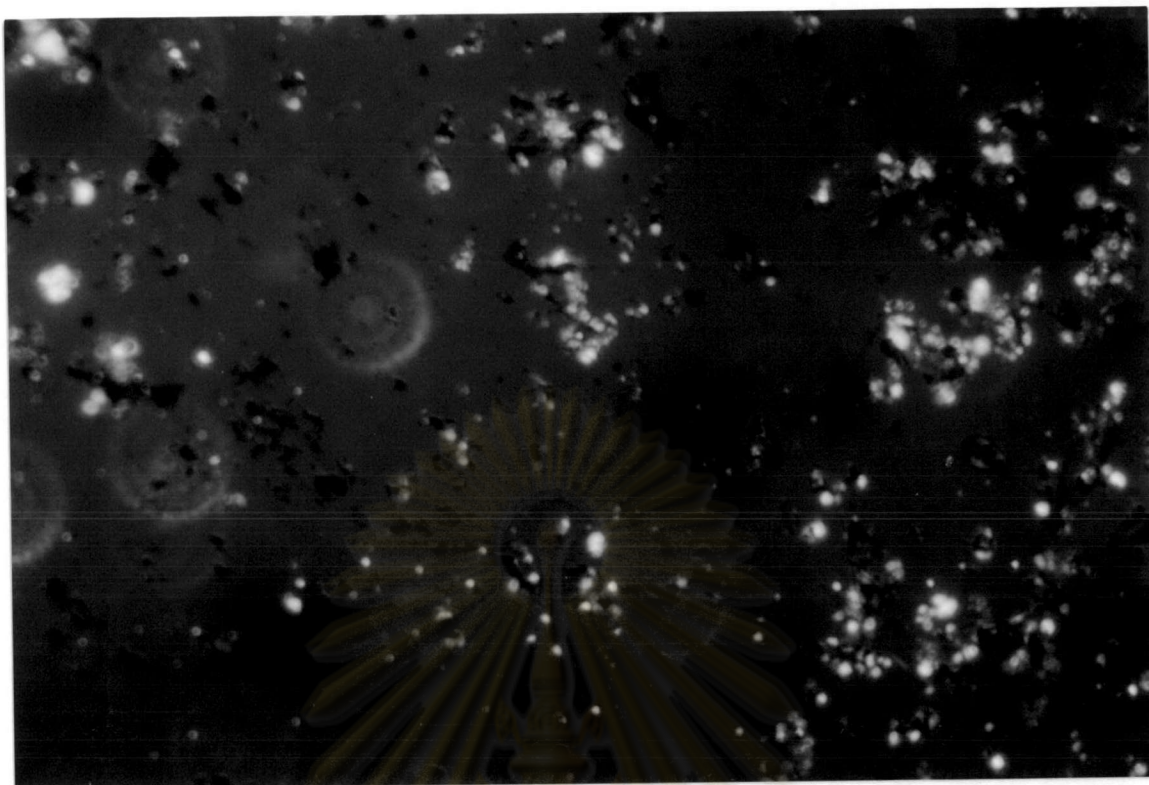
(b)

Figure 3.20 (con't) Polarizing optical micrographs of PCL diol polyurethane-1: (a) at room temperature (b) at 69°C on heating



(a)

Figure 3.21 Polarizing optical micrographs of PCL diol polyurethane-2: (a) at room temperature (b) quenched from isotropic phase to room temperature



(b)

Figure 3.21 (con't) Polarizing optical micrographs of PCL diol polyurethane-2: (a) at room temperature (b) quenched from isotropic phase to room temperature

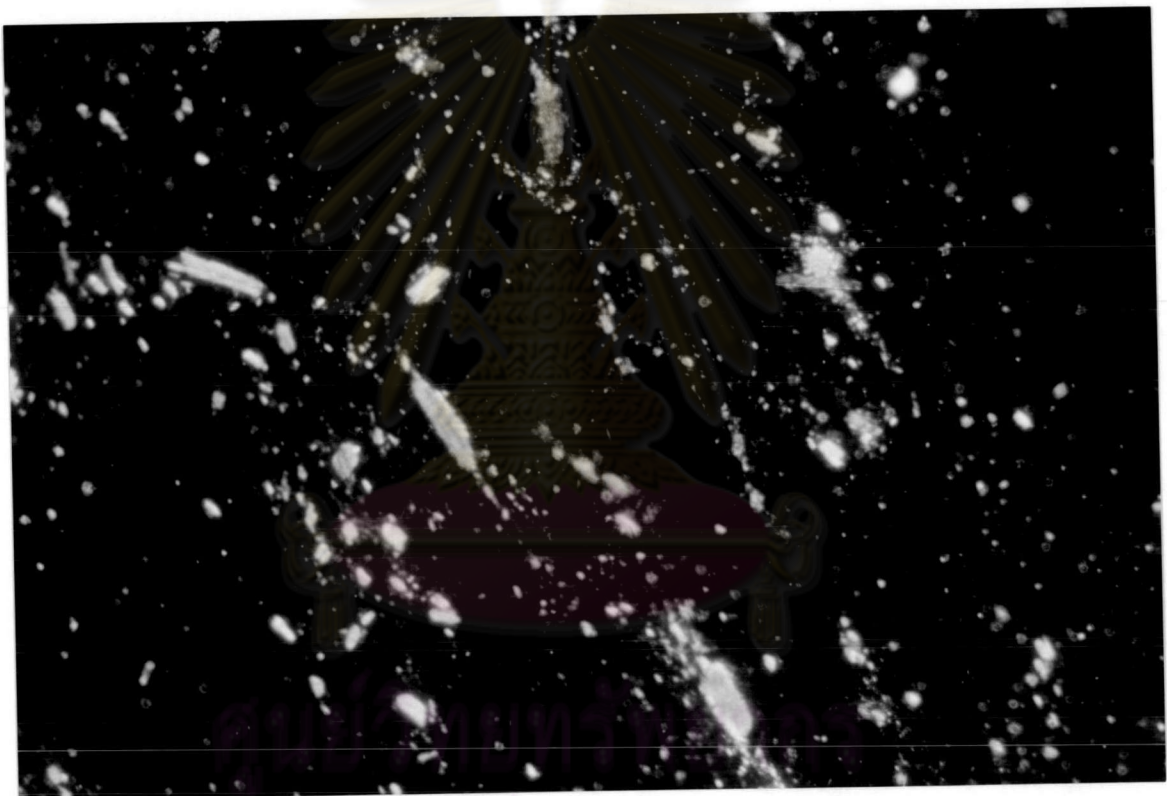
3.3.2 PCL triol polyurethane

Both PCL triol polyurethanes-1 and-2 were elastomeric solid at room temperature and exhibit similar phenomena when observed by optical microscope under polarized light as shown in Figures 3.22 and 3.23. Both PCL triol polyurethanes exhibited birefringence at room temperature. Upon heating, the polymer underwent a transition from the rubbery solid to a birefringence viscous fluid, which exhibits an uncharacteristic texture. The birefringence of PCL triol polyurethane-1 was observed from room temperature up to 215 °C. The birefringence of PCL triol polyurethane-2 was observed from room temperature up to 127 °C. Clearing to isotropic stage was detected by a sudden increase in viscosity (fluidity) and the complete extinction under polarized light. When the polymer was quenched from the isotropic phase to room temperature, as evidence in the POM pattern, the birefringence reappeared on cooling

and this pattern could be preserved at room temperature. In the case of the PCL triol polyurethanes-2, the mesophase reappeared after leaving the polymer at room temperature for 2 hours.

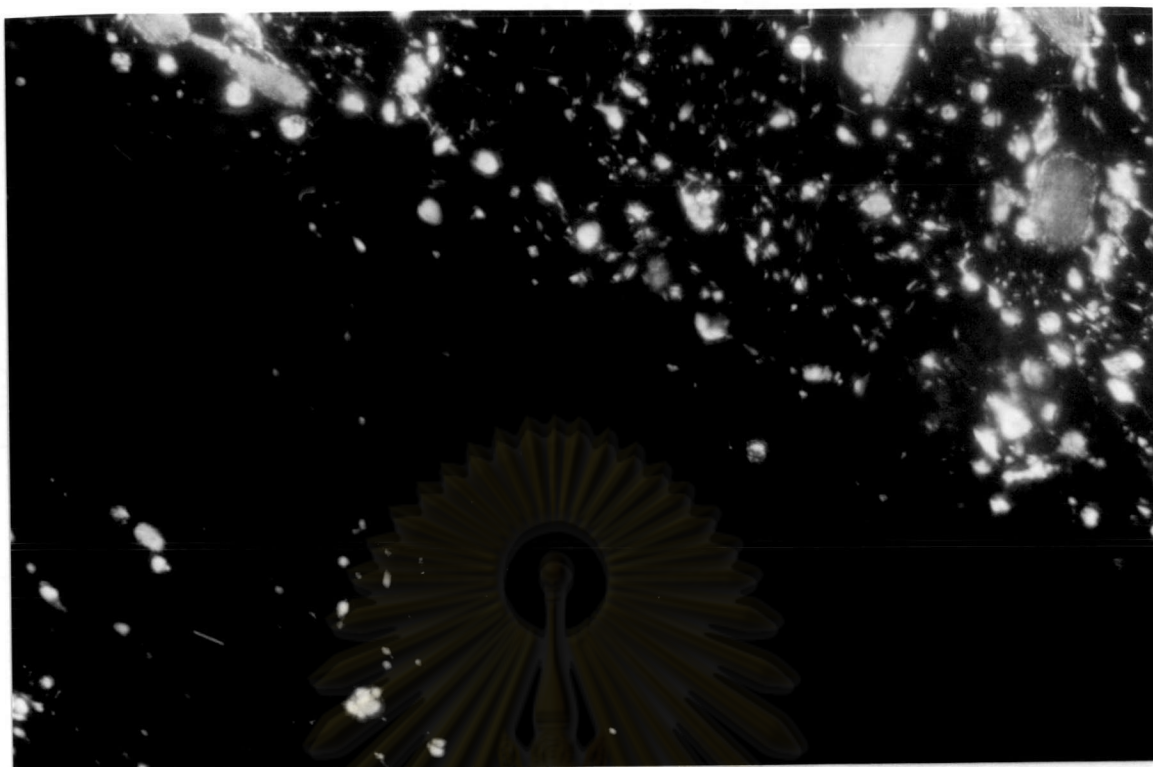
It was observed that PCL triol polyurethane-1 showed stronger birefringence than PCL triol polyurethane-2.

No liquid crystalline was found during the cooling cycles under the polarizing microscope observations. This might be because the time was not long enough for the mesophase to aligned again.



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(a)

Figure 3.22 Polarizing optical micrographs of PCL triol polyurethane-1: (a) at room temperature (b) at 159°C on heating (c) quenched from molten stage to room temperature

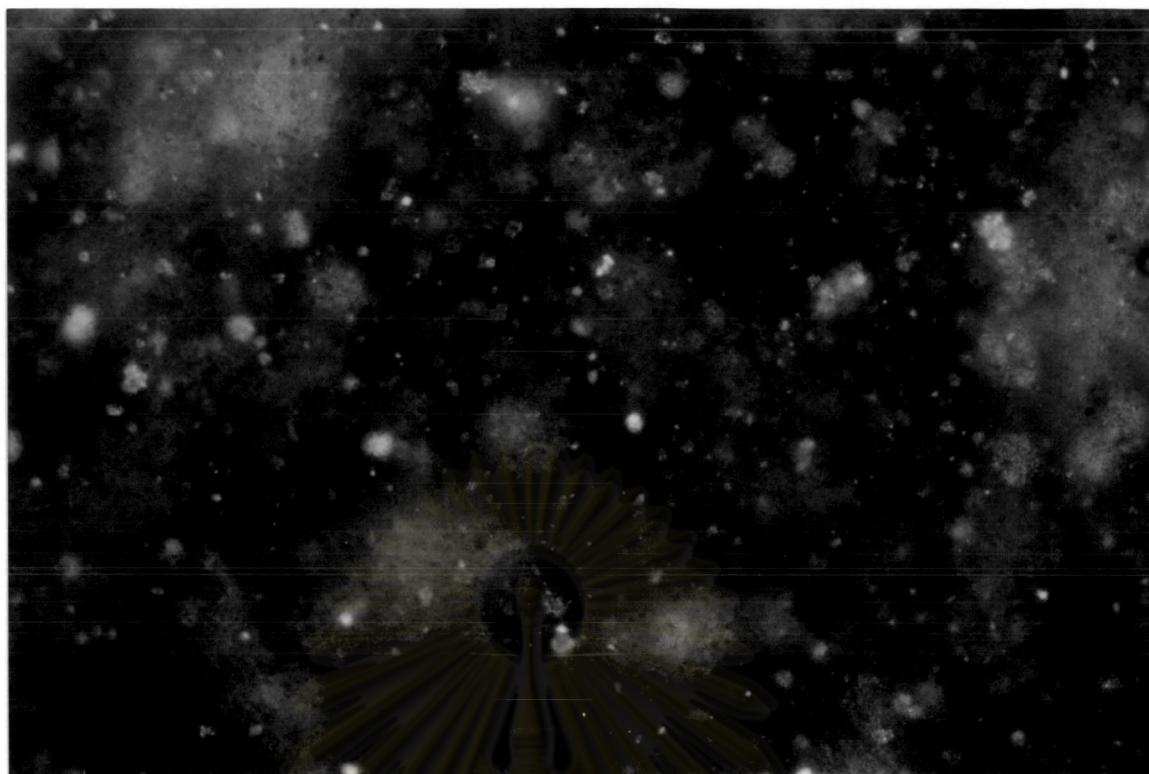


(b)

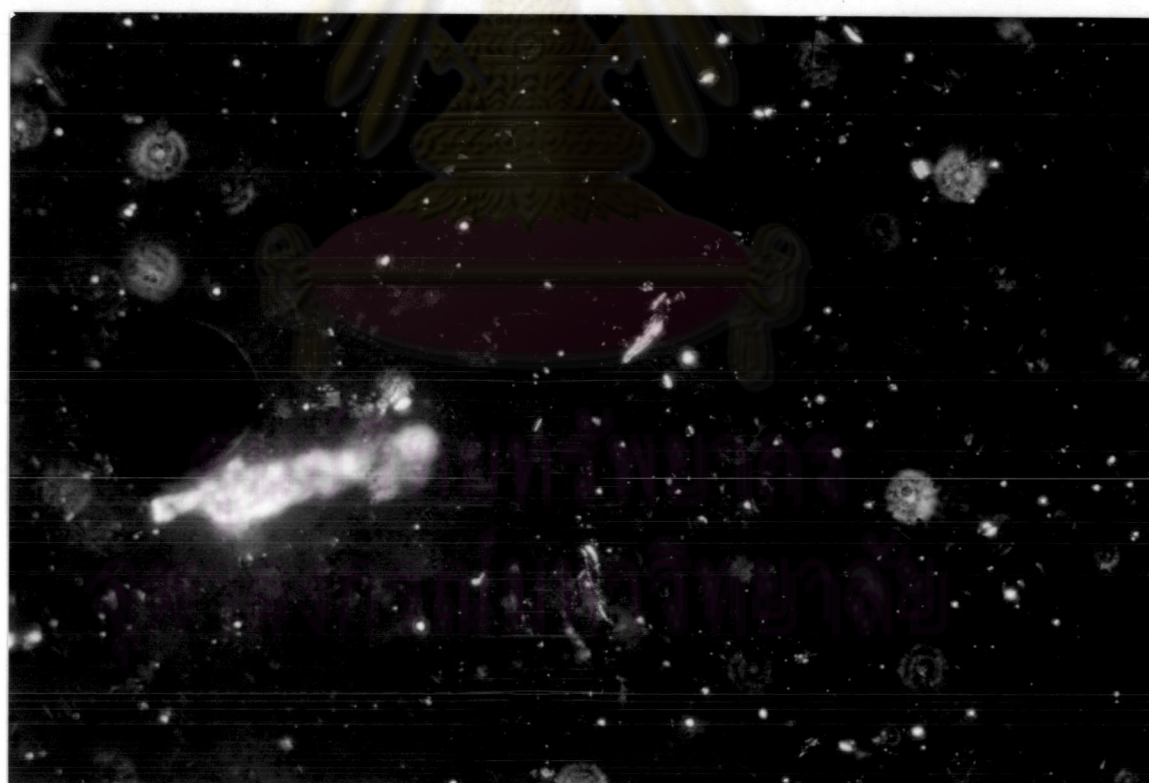


(c)

Figure 3.22 (con't) Polarizing optical micrographs of PCL triol polyurethane-1: (a) at room temperature (b) at 159°C on heating (c) quenched from molten stage to room temperature



(a)

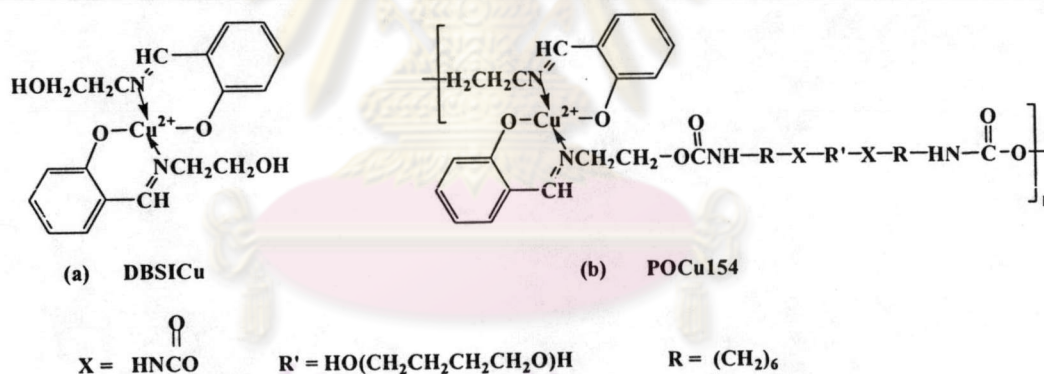


(b)

Figure 3.23 Polarizing optical micrographs of PCL triol polyurethane-2: (a) at room temperature (b) quenched from molten stage to room temperature

Similar example of metal-containing liquid crystalline polyurethane elastomer was the work done by Yang.²⁰ For DBSICu, a perfect needle crystal structure was found at room temperature without any thermal treatment. Upon heating this diol to 140°C, the needle crystal began to melt and a band structure appeared under POM. This band structure reappeared on cooling the sample from the isotropic phase at 160°C. On further cooling to either the low temperature or room temperature, this well-formed band structure could be preserved.

In the case of POCu154, shearing the polymer in the liquid crystalline phase produced a well-formed band structure, which also can be quenched at room temperature.



Scheme 3.9 Structures of (a) DBSICu and (b) POCu154

3.3.3 PP glycol polyurethane

When observed by optical microscope under polarized light, PP glycol polyurethane-1 did not exhibit mesomorphism at room temperature as shown in Figure 3.24. PP glycol polyurethane-2 exhibit weak birefringence as shown in Figure 3.25. Upon heating, the polymer underwent a transition from the rubbery solid to a viscous fluid without birefringence.

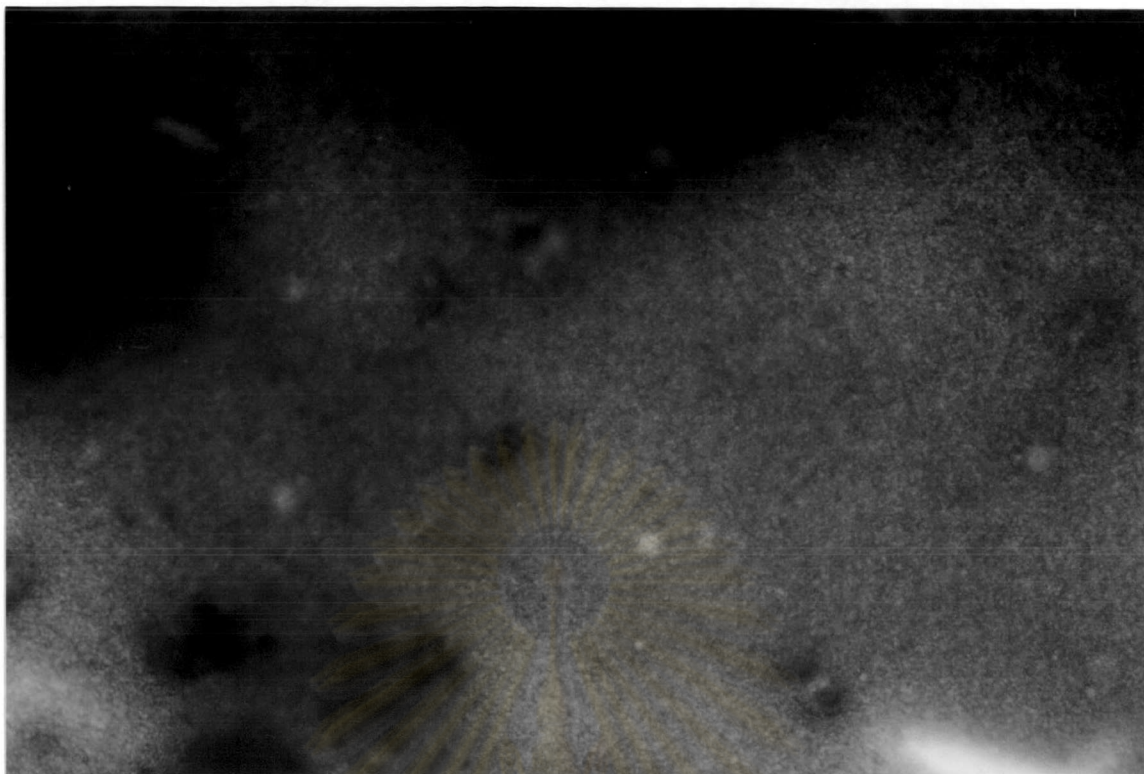


Figure 3.24 Polarizing optical micrographs of PP glycol polyurethane-1 at room temperature

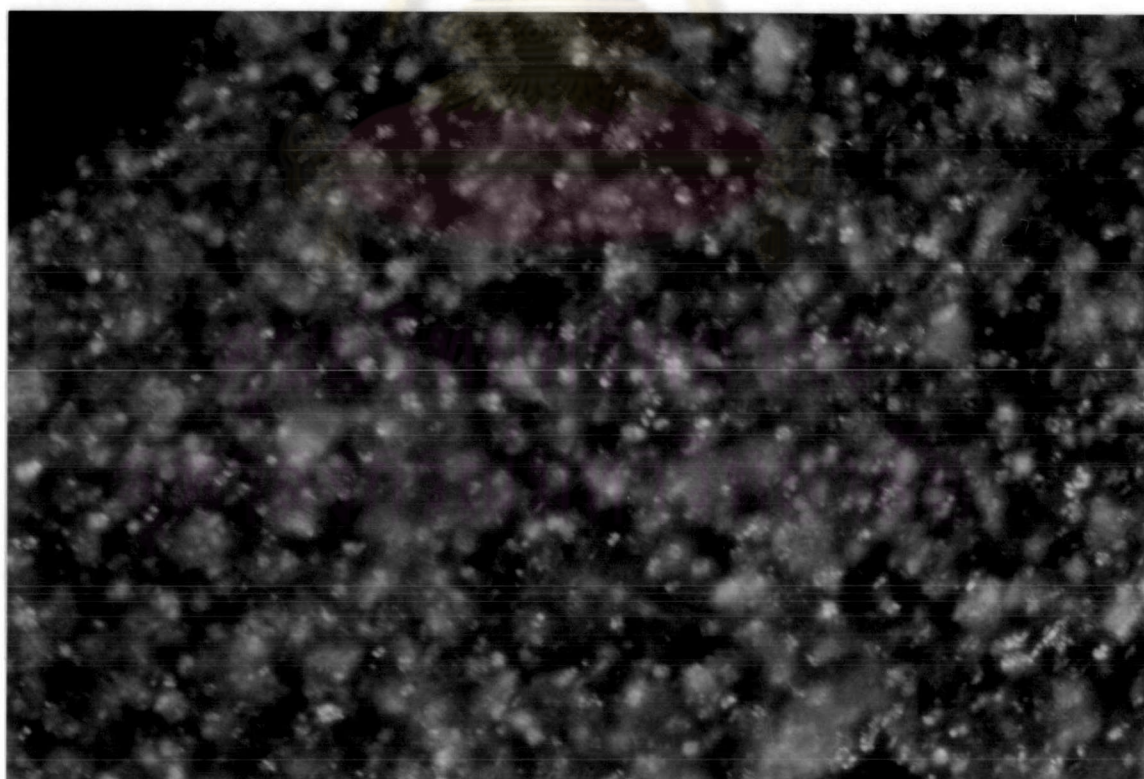


Figure 3.25 Polarizing optical micrographs of PP glycol polyurethane-2 at room temperature