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# SYNTHESIS OF POLYUREAS AND POLYURETHANES CONTAINING HETEROCYCLES

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for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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งานวิจัยนี้เป็นการสังเคราะห์เฮเทอโรไซคลิกพอลิยูเรีย พอลิยูรีเทน และ พอลิยูรีเทน-ยูเรีย ซึ่งทำได้โดยใช้สารประกอบเฮเทอโรไซคลิกที่มีหมู่ฟังก์ชันเป็นไดเอมีนและไดออลมาทำปฏิกิริยาพอลิเมอไรเซชันกับสารประกอบไดไอโซไซยาเนตที่อัตราส่วน 1 : 1 เฮเทอโรไซเคิลที่ใช้ คือ โพรฟลาวิน (PF) นิวฟุชซิน (NF) และ บรอมฟีนอลบลู (BPB) สารประกอบไดไอโซไซยาเนตที่ใช้ คือ ไอโซฟอโรนไดไอโซไซยาเนต (IPI), 4,4′-เมทิลีนบิสฟีนิลไอโซไซยาเนต (MDI), โทลิลลีน 2,4-ไดไอโซไซยาเนต เทอมิเนเตด พอลิ 1,4-บิวเทนไดออล พรีพอลิเมอร์ และ โทลิลลีน 2,4-ไดไอโซไซยาเนต เทอมิเนเตด โพลีโพรพิลลีน ไกลคอล พรีพอลิเมอร์ การศึกษาความว่องไวของหมู่ไดเอมีนและไดออลบนสารประกอบเฮเทอโรไซคลิกที่มีต่อหมู่ไดไอโซไซยาเนตในการเกิดปฏิกิริยาพอลิเมอไรเซชันทำได้โดยใช้ปฏิกิริยาระหว่างไอโซฟอโรนไดไอโซไซยาเนต (IPI) และเฮเทอโรไซเคิลชนิดต่างๆ การติดตามความก้าวหน้าของปฏิกิริยาพอลิเมอไรเซชันทำได้โดยใช้เทคนิคอินฟราเรดสเปกโทรสโกปี โดยพีกของหมู่ไอโซไซยาเนตที่ 2270 ซม$^{-1}$ จะหายไปเมื่อปฏิกิริยาพอลิเมอไรเซชันเกิดขึ้นอย่างสมบูรณ์ ข้อมูลที่ได้ในขั้นนี้ใช้เป็นแนวทางสำหรับการสังเคราะห์เฮเทอโรไซคลิกพอลิยูเรีย พอลิยูรีเทน และ พอลิยูรีเทน-ยูเรียในขั้นถัดไป การพิสูจน์เอกลักษณ์พอลิเมอร์ทำได้โดยใช้เทคนิคอินฟราเรดสเปกโทรสโกปี เอ็นเอ็มอาร์สเปกโทรสโกปี การวิเคราะห์ธาตุองค์ประกอบ สมบัติการละลาย และความหนืด สมบัติการทนความร้อนตรวจสอบได้ด้วยเทอร์โมกราวิเมตริกอนาลิซิส (TGA) และวัดค่าลิมิตติงออกซิเจนอินเดกซ์ (LOI) จากผลการทดลองพบว่าพอลิยูเรียที่สังเคราะห์จากโพรฟลาวิน และ นิวฟุชซิน แสดงสมบัติการทนความร้อนได้ดี

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต.....นิภาภรณ์...ศุภะรัชฎเดช...............
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**# # 4672308923: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE**
**KEYWORD: HETEROCYCLIC POLYMERS**

**NIPAPORN SUPARATTADET: SYNTHESIS OF POLYUREAS AND POLYURETHANES CONTAINING HETEROCYCLES.**
**THESIS ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D. 77 pp. ISBN 974-53-2488-4.**

This research involved the synthesis of heterocyclic polyureas, polyurethanes and polyurethane-ureas, which was done by the polymerization reaction of heterocyclic compounds containing diamine and diol functional groups with diisocyanate compounds at the mole ratio 1:1. The heterocycles used were proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB). The diisocyanates employed were isophorone diisocyanate (IPI), 4,4′-methylenebis (phenyl isocyanate) (MDI), tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer (PB900) and tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer (PP1000). The reaction between isophorone diisocyanate (IPI) and different heterocycles were studied to obtain the information on the reactivity of diamine group or diol group in heterocyclic compounds towards diisocyanate group in the polymerization reaction. The progress of polymerization reaction was followed by using infrared spectroscopy. The disappearance of isocyanate peak at 2270 cm$^{-1}$ was observed when the polymerization was completed. The obtained information in this step was used in the synthesis of heterocyclic polyureas, polyurethanes and polyurethane-ureas in the next step. The polymers were characterized by FTIR spectroscopy, NMR spectroscopy, elemental analysis, solubility and viscometry. Heat resistance of polymers was investigated by thermogravimetric analysis (TGA) and measuring limiting oxygen index (LOI) values. It was found that the polyureas based on proflavine and new fuchsin showed good thermal stability.

Field of study Petrochemistry and polymer science Student's signature NIPAPORN SUPARATTADET
Academic year 2005.................. Advisor's signature N. Chantarasiri.......

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# LIST OF SYMBOLS AND ABBREVIATION

| | |
|---|---|
| BPB | Bromphenol blue |
| BPB-IPI | Polymer synthesized from bromphenol blue and isophorone diisocyanate |
| BPB-MDI | Polymer synthesized from bromphenol blue and 4,4′-methylenebis(phenyl isocyanate) |
| BPB-PB900 | Polymer synthesized from bromphenol blue and tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer |
| BPB-PP1000 | Polymer synthesized from bromphenol blue and tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer |
| DBTDL | Dibutyltin dilaurate |
| DMF | Dimethyl formamide |
| DMSO | Dimethyl sulfoxide |
| EA | Elemental analysis |
| IDT | Initial decomposition temperature |
| IPI | Isophorone diisocyanate |
| IR | Infrared spectroscopy |
| LOI | Limiting oxygen index |
| MDI | 4,4′-methylenebis(phenyl isocyanate) |
| NF | New fuchsin |
| NMR | Nuclear magnetic resonance |
| NF-IPI | Polymer synthesized from new fuchsin and isophorone diisocyanate |
| NF-MDI | Polymer synthesized from new fuchsin and 4,4′-methylenebis(phenyl isocyanate) |
| NF-PB900 | Polymer synthesized from new fuchsin and tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer |
| NF-PP1000 | Polymer synthesized from new fuchsin and tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer |

| | |
|---|---|
| PB900 | Tolylene 2,4-diisocynate terminated poly(1,4- butanediol) prepolymer, molecular weight 900 |
| PF | Proflavine |
| PP1000 | Tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer, molecular weight 1000 |
| PF-IPI | Polymer synthesized from proflavine and isophorone diisocyanate |
| PF-MDI | Polymer synthesized from proflavine and 4,4′-methylenebis(phenyl isocyanate) |
| PF-PB900 | Polymer synthesized from proflavine and tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer |
| PF-PP1000 | Polymer synthesized from proflavine and tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer |
| TGA | Thermogravimetric analysis |
| UV-visible | Ultraviolet-visible spectroscopy |

# CHAPTER I

# INTRODUCTION

## 1.1 Heterocyclic polyureas, polyurethanes and polyurethane-ureas

Heterocyclic polymers [1-11] are well known for high strength, heat resistance, solvent resistance, chemical resistance and stability to oxidation by heat because of their aromatic ring systems. From these properties, the polymer can be utilized at high temperature with a variety of applications, such as aerospace industry, automotive industry and electronic industry.

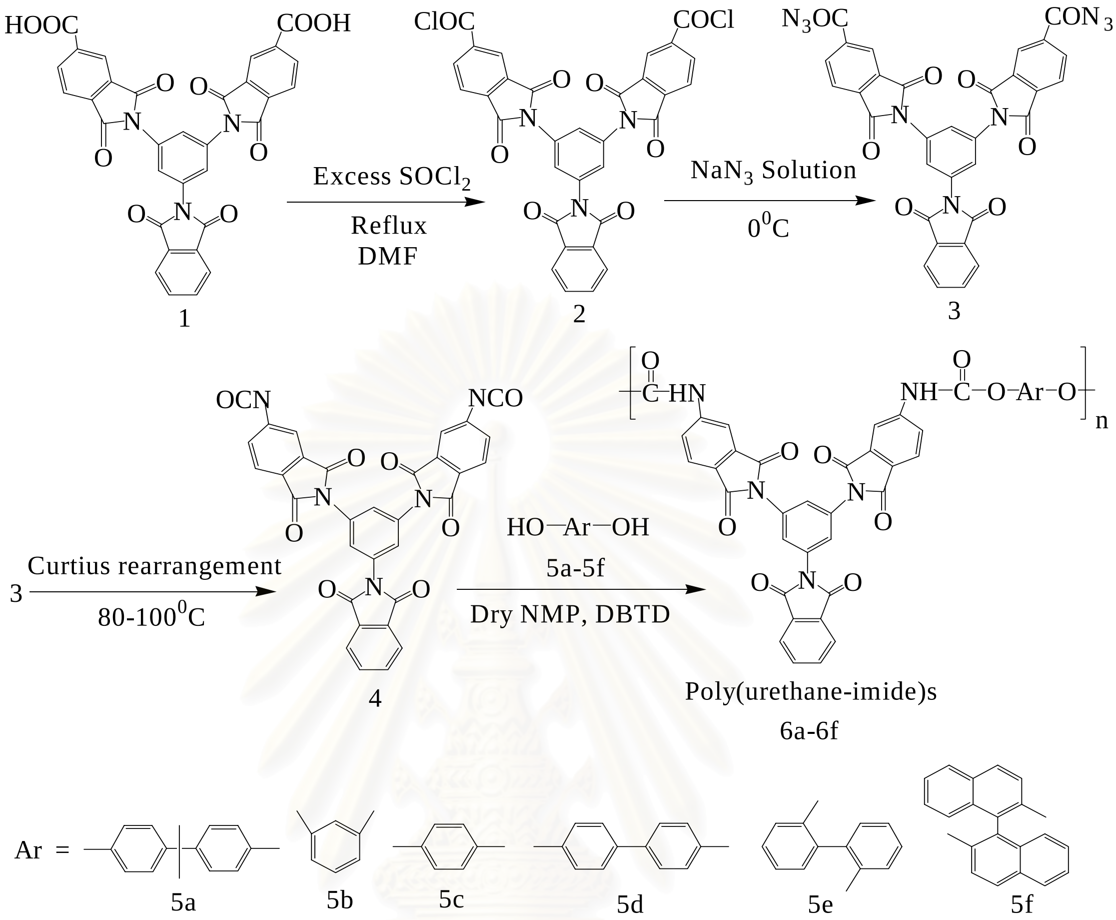
Heterocyclic polyureas, polyurethanes and polyurethane-ureas are considerable interesting due to their wide range of interesting properties and potential applications that can be obtained, such as foam, fiber, elastomer, coating and adhesive.

Heterocyclic polyureas, polyurethanes and polyurethane-ureas can be synthesized by using heterocyclic compound as a starting material. The functional groups of heterocyclic compound are diamine groups or diol groups. Heterocyclic polyureas are prepared by the reaction between isocyanates and amines. Heterocyclic polyurethanes or polyurethane-ureas are obtained by the reaction of isocyanates with diols and amines, respectively. Examples of common isocyanates used for preparing these polymers are isophorone diisocyanate (IPI), 4,4'-diphenylmethane diisocyanate (MDI), tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer (PB900) and tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer (PP1000).

## 1.2 Literature review

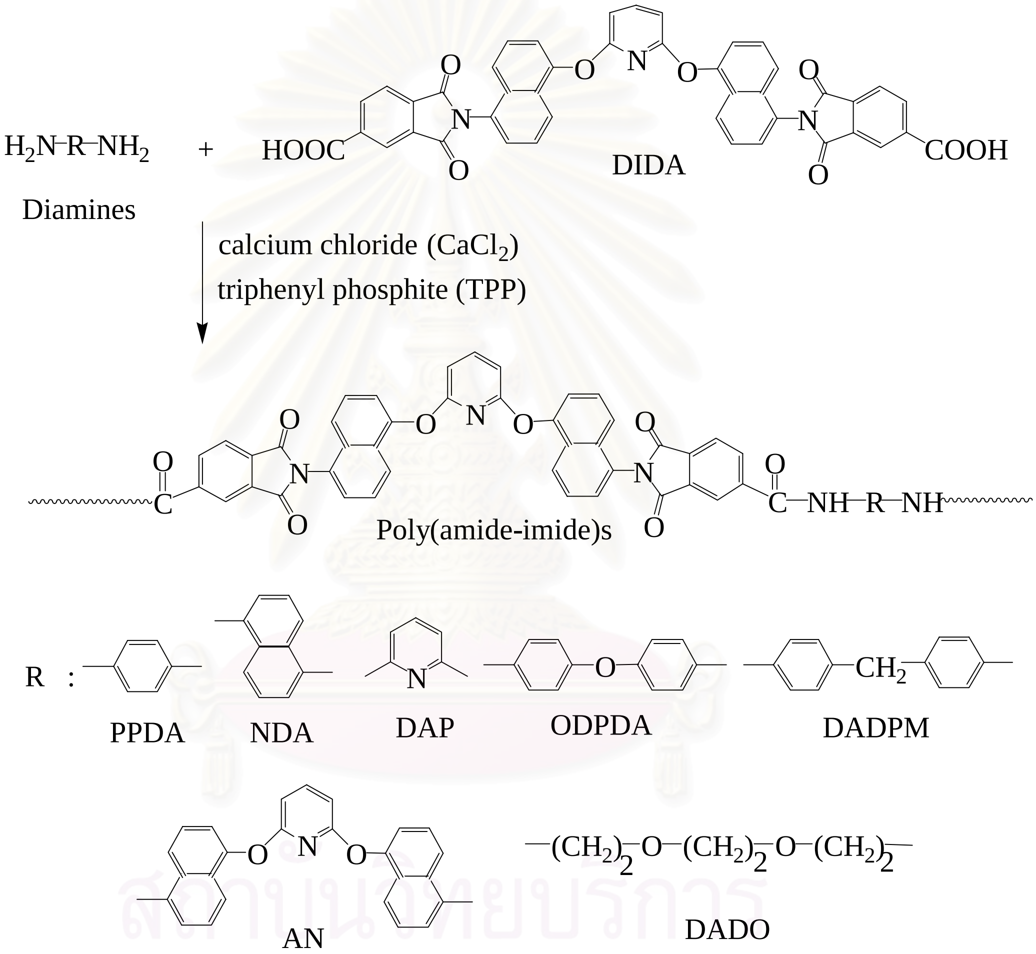
The preparation of heterocyclic polyureas, polyurethanes and polyurethane-ureas in the polymer backbone by using heterocyclic compounds as a starting materials have been studied. A number of papers concerning the synthesis and improvement of properties of heterocyclic polyureas, polyurethanes, polyurethane-ureas and their related polymers have been reported as follows:

Behniafar and coworkers [12] synthesized soluble and thermally stable poly(urethane-imide)s from a new triimide-dicarbonylazide (Scheme 1.1). The synthesis of poly (urethane-imide)s (6a-6f) from the polyaddition reactions of various aromatic dihydroxy compounds (5a-5f) with triimide-dicarbonylazide (3). Compounds (3) was prepared from triimide-dicarboxyl acid (1) and thionyl chloride to obtain triimide-dicarboxyl acid chloride (2) followed by nucleophilic reaction with sodium azide. The aromatic hydroxyl compounds used were bisphenol A (5a) *m*-phenylenedihydroxylic (5b), *p*-phenylenedihydroxylic (5c), 4,4′-dihydroxybiphenyl (5d), 2,2′-dihydroxybiphenyl (5e) and 2,2′-dihydroxy-1,1′-binaphthyl (5f). The prepared poly (urethane-imide)s had inherent viscosities of 0.19-0.24 dl g$^{-1}$ in *N*,*N*-dimethylacetamide (DMAc) at concentration of 0.5 g dl$^{-1}$ at 30°C, which GPC results showed that the resulting polymers had relatively low molecular weight. The poly(urethane-imide)s showed good solubility in variety of polar solvents. Differential scanning calorimetry (DSC) was determined the thermal behavior of the resulting poly(urethane-imide)s. The polymers exhibited hight glass transition temperature in the range between 197 and 219°C depending on the structure of aromatic dihydroxylic compounds. The thermal stability of poly(urethane-imide)s was evaluated by thermogravimetric analysis (TGA) in nitrogen. The TGA results showed that the heat resistance of polyurethane can be improved by chemical modification of their structure by incorporation of wholly aromatic imide group into polyurethane backbone. It was found that the poly(urethane-imide)s showed thermal stability up to 400°C and the 10% weight loss temperature of the these polymers was in the range 385-412°C, depending on aromatic structures.



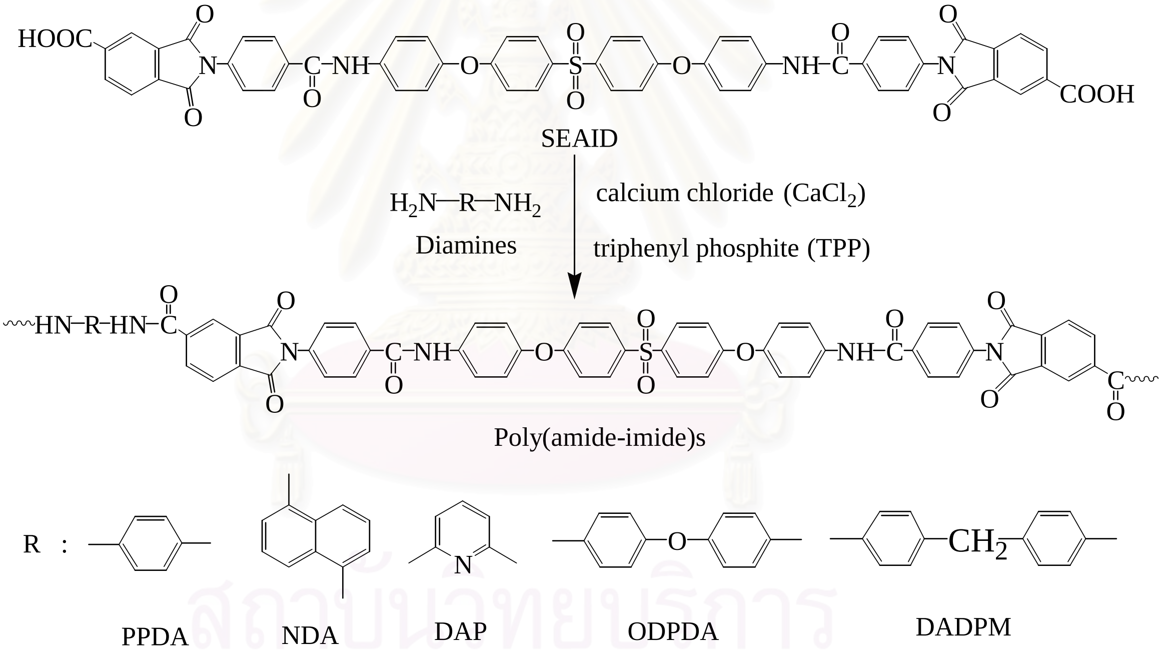
**Scheme 1.1** Synthesis of poly(urethane-imide)s from triimide-dicarbonylazide (3)

Mehdipour-Ataei and Amirshaghagi [13] synthesized novel poly(amide-imide)s by polycondensation reactions of diimide-diacid (DIDA) with various diamine, namely *p*-phenylenediamine (PPDA), 1,5-diaminonaphthalene (NDA), 2,6-diaminopyridine (DPA), 4,4′-diaminodiphenyl methane (DADPM), 4,4′-diamino diphenyl ether (ODPDA), 2,6-bis(5-amino-1-naphthoxy) pyridine (AN) and 2,2′-(ethylenedioxy) dietylamine (DADO) (Scheme 1.2). The inherent viscosity of the polymers was in the range 0.44-0.50 dl $g^{-1}$ in *N*-methyl-2-pyrrolidone (NMP) at concentration of 0.5 g $dl^{-1}$ at 30°C and from these results it can be concluded that the polymers showed reasonable molegular weights. $T_g$ of the polymers was about 138-225°C. The initial decomposition, 10% weight loss and char residue at 600°C of polymers were about 155-240°C, 326-432°C and 39-70%, respectively using TGA in air. TGA results also concluded that polymers based on fully aromatic diamines are more thermally stable than polymers based on aromatic diamines with flexible moieties and these polymers are more heat resistant than polymers based on aliphatic diamine with flexible units. All of polymers showed solubility in polar aprotic solvents. The incorporation flexible ether linkage, fully aromatic structure and pyridine heterocyclic ring into polymer backbone improve both solubility and thermal stability of polymers.



**Scheme 1.2** Synthesis of poly(amide-imide)s from diimide-diacids and diamines

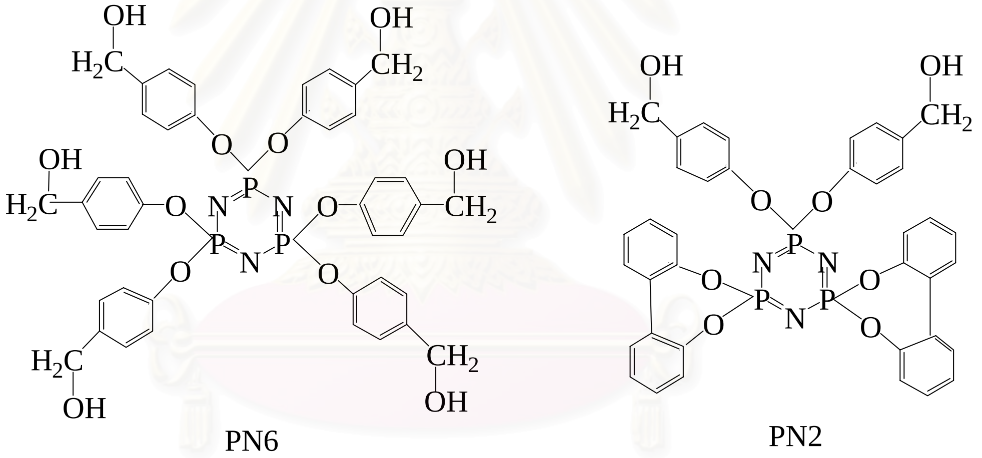
Mehdipour-Ataei and Hatami [14] synthesized novel heat resistant poly(amide-imide)s through the direct polycondensation reactions of a sulfone ether amide imide diacid (SEAID) with different aromatic diamines including *p*-phenylene diamine (PPDA), 1,5-diaminonaphthalene (NDA), 2,6-diaminopyridine (DAP), 4,4′-diamino diphenyl ether (ODPDA) and 4,4′-diamino diphenyl methane (DADPM) (Scheme 1.3). The inherent viscosity of all the polymers was in the range 0.43-0.51 g dl$^{-1}$ at a concentration of 0.5 g dl$^{-1}$ in *N*-methyl-2-pyrrolidone (NMP) at 30°C, and therefore the polymers had reasonable molecular weights. The prepared polymers exhibited improved solubility in polar aprotic solvents due to the presence of ether and sulfone groups. $T_g$ of the polymers was in the range 221-252°C. Thermal stability of the polymers was evaluated by using thermogravimetric analysis (TGA) in air. The initial decomposition temperature (IDT) and 10% weight loss of polymers were in the range of 255-295°C and 438-485°C, respectively. The char yield at 600°C of the polymers were about 64-78%. The polymers showed high thermal stability which could be attributed to the presence of imide and amide groups, phenylation of the backbone and symmetry of structures.



**Scheme 1.3** Synthesis of poly(amide-imide)s from sulfone ether amide imide diacid and diamines

Modesti and coworkers [15] studied thermally stable hybrid foams based on cyclophosphazines and polyurethanes. The foams were prepared by mixing of the components (polyols, cyclotriphosphazine, catalysts, blowing agents, and surfactants) with 4,4′-diphenylmethane diisocyanate (MDI). The two cyclotriphosphazines used were hexakis[*p*-(hydroxymethyl)phenoxy]cyclotriphosphazene (PN6) and

2,2-di-[*p*-(hydroxymethyl)phenoxy]-4,4,6,6-bis[spiro(2′,2′′-dioxy-1′,1′′-biphenyl) cyclotriphosphazene (PN2) (Figure 1.1). The content of PN2 and PN6 in the hybrid foams were varied. The TGA results showed that 10% weight loss of hybrid foams were 300-323°C and 295-328°C in $N_2$ and air, respectively. The char yield at 600°C of hybrid foams were about 34-59% and 16-53% in $N_2$ and air atmosphere, respectively. The LOI of hybrid foams was 21.8-30.7. TGA and LOI results concluded that the incorporation of phosphazene lead to improvement of both thermal stability and flame retardant, increasing the phosphazene content  increases char yield and LOI values of foams. Moreover, it was found that the foams containing PN2 showed better behavior than the foams containing PN6 because the higher content of phosphazine.

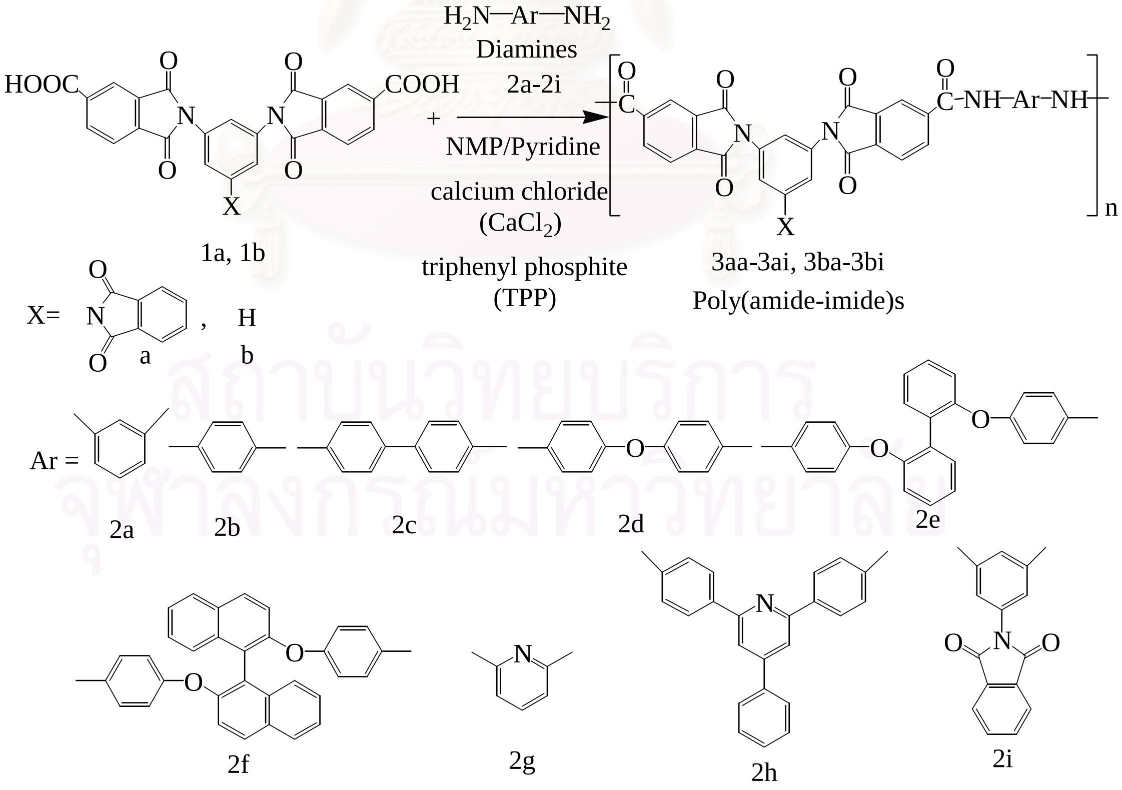


PN6 PN2

**Figure 1.1** Cyclophosphazines (PN6 and PN2)

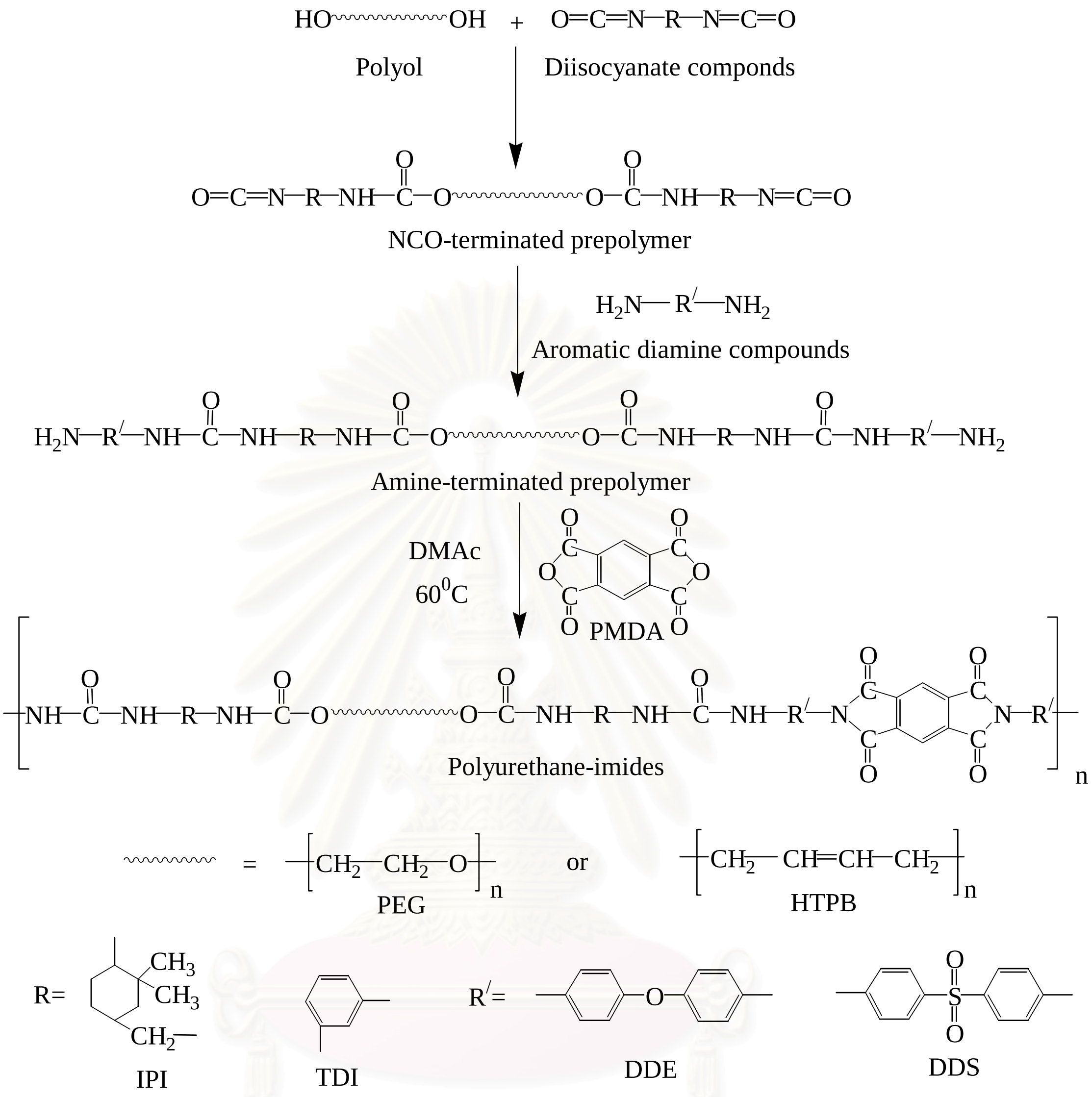
Behniafar and Banihashemi [16] synthesized new soluble and thermally stable aromatic poly(amide-imide)s based on *N*-[3,5-bis(*N*-trimellitoyl)phenyl]phthalimide. The preparation of wholly aromatic poly(amide-imide)s were obtained by polycondensation from *N*-[3,5-bis(*N*-trimellitoyl)phenyl]phthalimide (1a) and 1,3-bis(*N*-trimellitoly)benzene (1b) with various aromatic diamines, including *m*-phenylenediamine (2a), *p*-phenylenediamine (2b), 4,4′-diaminobiphenyl (2c), 4,4′-diaminodiphenylether (2d), 2,2′-bis(*p*-aminophenoxy)biphenyl (2e), 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl (2f), 2,6-diaminopyridine (2g), 4-phenyl-2,6-bis(4-trimellitimidophenyl)pyridine (2h) and

*N*-3,5-diaminophenylphthalimide (2i) (Scheme 1.4). The inherent vicosities of 3aa-3ai and 3ba-3bi were around 0.68-1.01 and 0.63-1.09 dl $g^{-1}$, respectively at a concentration of 0.5 g $dl^{-1}$ in *N,N*-dimethylacetamide (DMAc) at 30°C. The results exhibited high molecular weight. The polymers containing phthalimide pendent group showed better solubility in various polar solvents than the polymers missing phthalimide pendent group because the chain is interrupted by phthalimide bulky pendent group. The thermal transition showed that the $T_g$ of 3aa-3ai was found in the range 334-403°C, which are more than that of 3ba-3bi, which was found in the range 309-361°C. The high $T_g$ may be due to the effect of polar and rigid structure containing of the polymers chains. The 10% weight loss of 3aa-3ai and 3ba-3bi obtained from TGA in nitrogen atmosphere were found in the range 541-568°C and 528-547°C, respectively. The TGA results obviously showed that 3aa-3ai had more thermal stability than 3ba-3bi because of the presence phthalimide pendant group which effectively enhanced heat resistance of polymers.



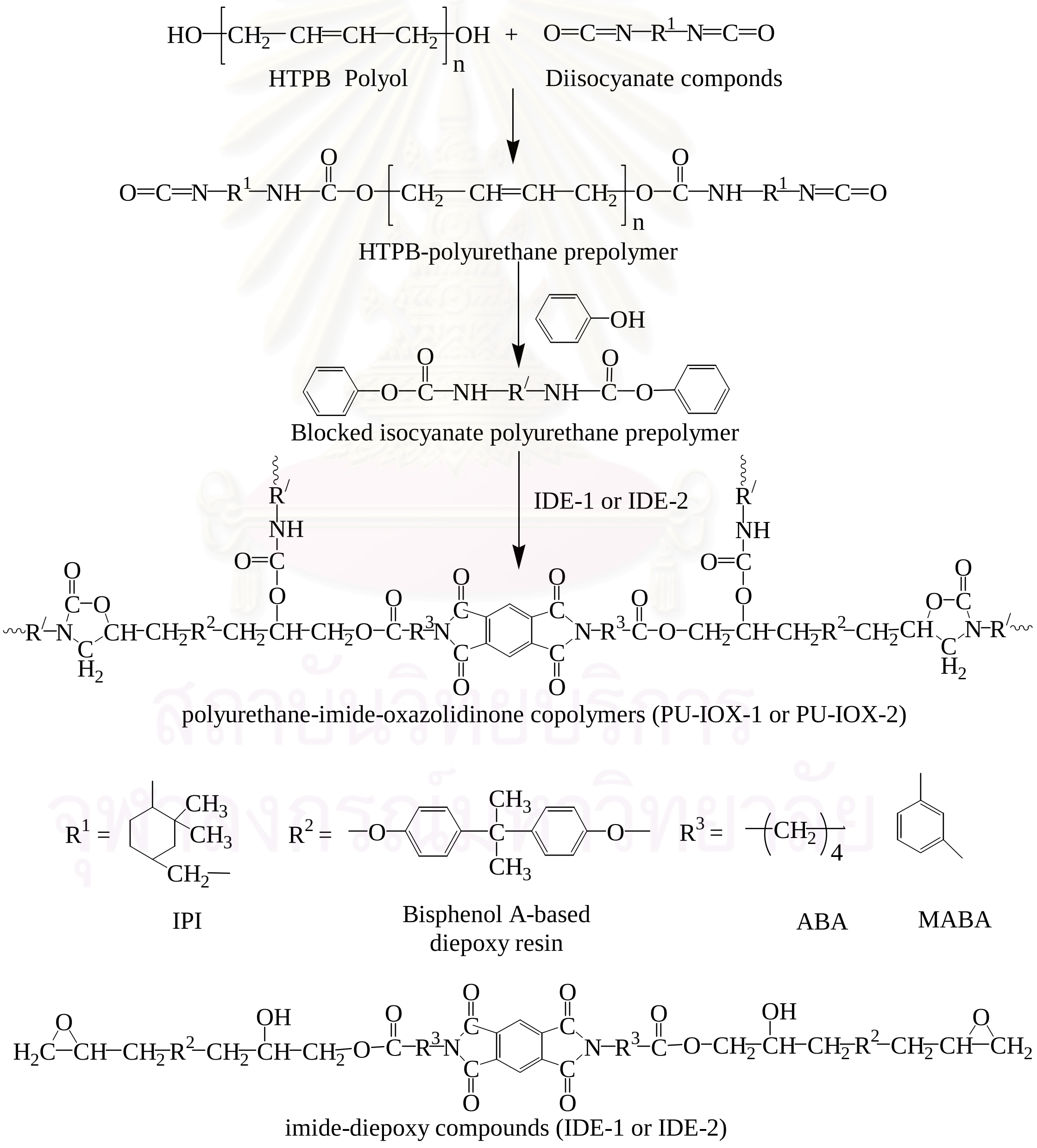
**Scheme 1.4** Synthesis aromatic poly(amide-imide)s based on *N*-[3,5-bis(*N*-trimellitoyl) phenyl]phthalimide

Nair and coworkers [17] concerned syntheses, thermal and mechanical characteristics of imide-modified polyurethanes. Polyurethane-imides were synthesized by the reaction of pyromellitic dianhydride (PMDA) with amine-terminated prepolymer prepared from transformation the polyol to the isocyanate terminated prepolymers and supsequent and capping with a diamine (Scheme 1.5). The polyol used were hydroxyl-terminated polybutadiene (HTPB) and polyethylene glycol (PEG, of molecular weights 600 and 100). The isocyanate used were isophorone diisocyanate (IPI) and tolylene diisocyanate (TDI). The aromatic diamine used were diamino diphenyl sulfone (DDS) and diamino diphenyl ether (DDE). From the experimental, aromatic diisocyanate (TDI) was found more reactive than aliphatic diisocyanate (IPI) and IPI has obvious better than other aliphatic diisocyanate because its reaction with the polyol produce to the secondary isocyanate terminals. These secondary isocyanate groups, because of their still reduced reactivity, dose not cause crosslinking in chain extending or capping with the aromatic diamine. The inherent viscosity of the PEG-based polyurethane-imides was in the range 0.81-0.91 dl $g^{-1}$ and the PUI derived from higher molecular weight polyols were soluble in *N,N*-dimethylacetamide (DMAc). The enhancement of the inherent viscosity of the polymers caused by the rigidity and enhanced intermolecular dipolar interaction by aromatic imide groups. The heat resistance of polyurethane-imides was determined by thermogravimetric analysis (TGA). The initial decomposition and residue weight (%) at 600°C of polymers were 275-300°C and 22-35%, respectively. From the results, it was found that thermal and mechanicanical properties of polyurethanes were improved by introducing of urea and imide groups in the backbone. In addition DDS-modifies PUIs has higher than DDE-modified PUIs due to higher polality sulfone group, which imparts higher cohesive strength.



**Scheme 1.5** Synthesis of imide-modified polyurethanes

Nair and coworkers [18] studied the effect of imide-oxazolidinone modification on thermal and mechanical properties of HTPB-polyurethanes. The blocked isocyanate polyurethane prepolymer was reacted imide-diepoxy compounds (IDE-1 and IDE-2) to produce the polyurethane-imide-oxazolidinone copolymers (PU–IOX-1 and PU–IOX-2, repectively) as shown in Scheme 1.6. The blocked isocyanated polyurethane prepolymer was prepared by reacting hydroxyl terminated polybutadiene (HTPB) with isophorone diisocyanate (IPI) and then encapping through phenol. The *m*-aminobenzoic acid (MADA) or 4-aminobutyric acid (ABA) was reacted with pyromellitic dianhydride (PMDA) to generate imide-diepoxy compounds (IDAs) and followed by reacting IDAs with the bisphenol A-based diepoxy resin to give imide-diepoxy compounds (IDEs). The mechanical and thermal properties of polyurethane were improved by combination of imide and oxazolidinone into polyurethane backbone. The improvement in properties is caused by the rigidity and enhanced cohesive interactions of the aromatic rings and polar heterocyclic groups in proportionation to the hard-segment content. It was found that initial decomposition temperature (IDT) of PU-IOXs appeared at around 315°C and residue at 600°C was around 38-40% by thermogravimetric analysis (TGA) under nitrogen atmosphere.



**Scheme 1.6** Synthesis of polyurethane-imide-oxazolidinone copolymers

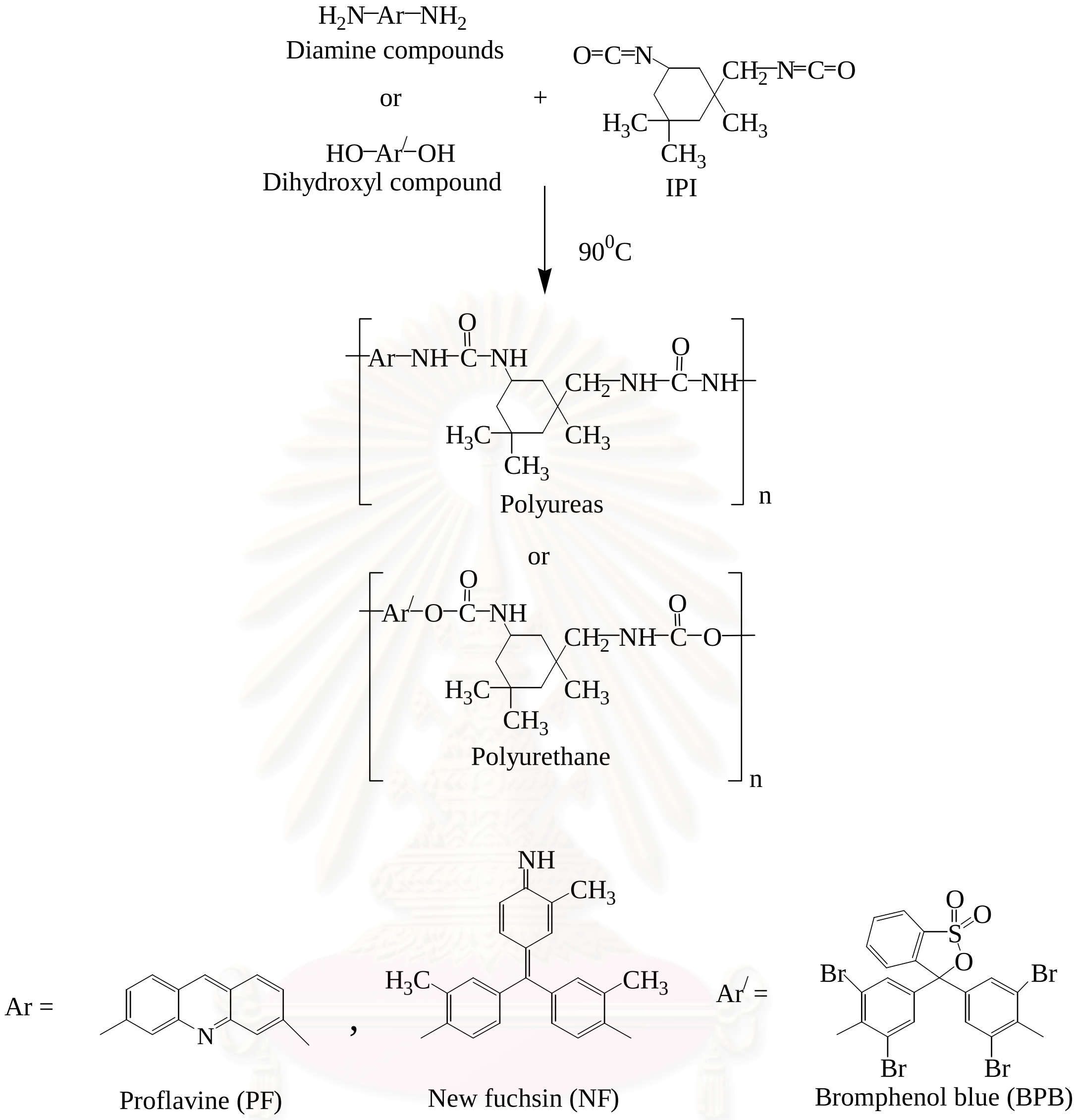
## 1.3 Objective and Scope of the Research

From the research work described above, heterocyclic polymers are well known for their high strength, solvent and chemical resistance, heat resistance and stability to oxidation by heat because of the aromatic ring systems. The target of this research was to use heterocyclic compounds as starting materials in the synthesis of heterocyclic polyureas, polyurethanes and polyurethane-ureas. Three commercially available heterocyclic compounds, namely proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB) were employed in this study.

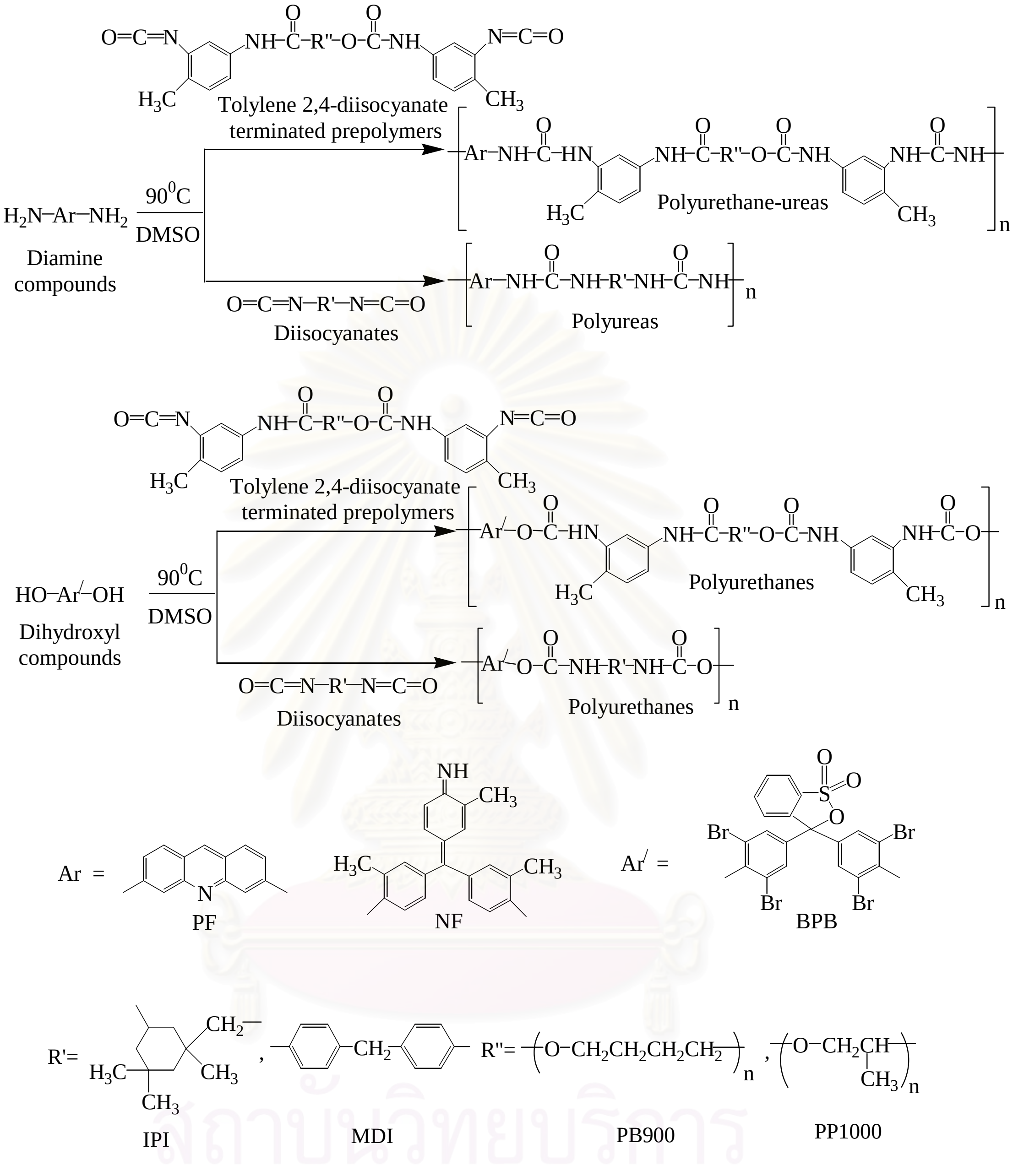
In the first step, investigation the reactivity between isophorone diisocyanate and heterocycles, namely proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB) to give heterocyclic polyureas and polyurethane was done as shown in Scheme 1.7. The progress of polymerization reaction was followed by IR spectroscopy. The obtained polymers were characterized by IR spectroscopy. This would give an information on the reactivity of the heterocycles towards diisocyanate which could be applied in the synthesis of heterocyclic polyureas polyurethanes and polyurethane-ureas in the next step.

In the next step, polymerization was performed to obtain heterocyclic polyureas, polyurethanes and polyurethane-ureas as shown in Scheme 1.8. Polymerization was done by reacting of heterocycles, namely proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB) with diisocyanates, namely isophorone diisocyanate (IPI), 4,4'-diphenylmethane diisocyanate (MDI), tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer (PB900) and tolylene 2,4-diisocynate terminated poly(propylene glycol) prepolymer (PP1000).

Finally, the polymer structures were characterized by IR, NMR and elemental analysis. Physical properties of polymers investigated were inherent viscosity and solubility. Thermal stability of the polymers was investigated by thermogravimetric analysis (TGA). Flammability of the polymers was studied by measuring limiting oxygen index (LOI).



**Scheme 1.7** Reaction between isophorone diisocyanate and heterocycles to give heterocyclic polyureas and polyurethane



**Scheme 1.8** Synthesis of polyureas, polyurethanes and polyurethane-ureas containing heterocycles

# CHAPTER II

# EXPERIMENTAL

## 2.1 Materials

All reagents and solvents were analytical grade quality. The solvents were obtained from Lab-Scan. Dimethyl sulfoxide (DMSO) was dried over calcium hydride ($CaH_2$) and distilled under reduced pressure before use. Proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB) were obtained from Fluka. PF and NF were purified before use. Purification [19-20] was done by dissolving of PF or NF in boiling distilled water and then the solution was allowed to cool to room temperature, followed by adding dropwise of 1 M sodium hydroxide until the precipitation of neutralized PF or NF were complete and the precipitate was washed with 100 ml of distilled mixture of water and methanol. Isophorone diisocyanate (IPI), 4,4′-methylene-bis(phenyl isocyanate) (MDI), tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer (PB900), tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer (PP1000) and dibutyltin dilaurate (DBTDL) were obtained from Aldrich.

## 2.2 Analytical Procedures

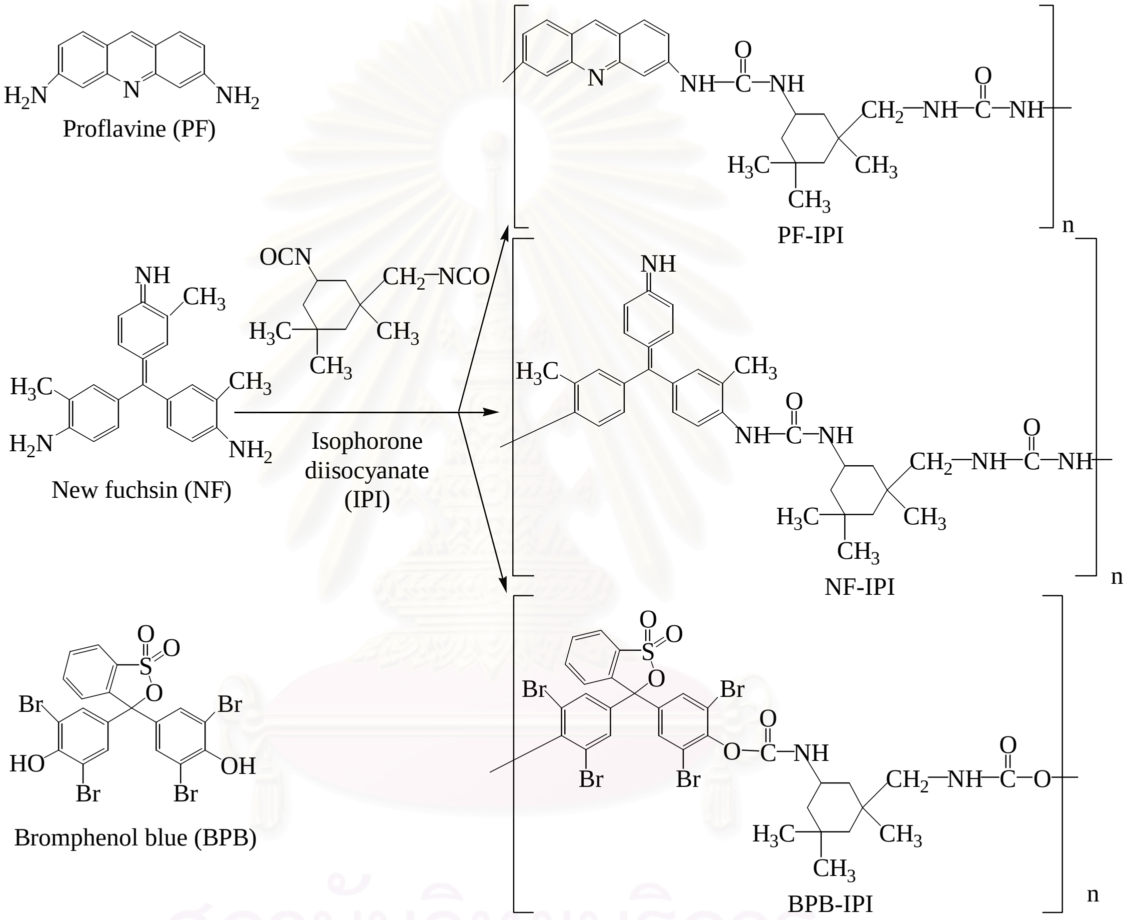
IR spectra were recorded on a Nicolet Impact 410 using KBr pellet method. NMR spectra were recorded in $CDCl_3$ and DMSO-$d_6$ solution on a Varian Mercury-400 BB instrument. Chemical shifts are given in parts per million (ppm) using the proton residual as internal reference. Elemental analyses were carried out on a Perkin Elmer 2400 CHN Elemental Analyzer. Thermogravimetric measurements were performed on a Netzsch thermogravimetric analyzer (STA 409C) at the heating rate $20^{o}$C/min under air/nitrogen (50/50) atmosphere. Initial decomposition temperature (IDT) was reported at the temperature where weight loss of the samples were observed. Inherent viscosities of the polymers were determined at a concentration of 0.5g/100ml in DMSO at 40°C using Cannon-Fenske viscometer. Limiting oxygen index (LOI) data were obtained on an apparatus produced in. accordance with ASTM-D2863-70 standard. The solubility of the polymers was tested in various polar and nonpolar solvents by addition of 10 mg samples to 2 ml of a solvent. All UV-Vis absorption spectra have been recorded in a 1 cm path length SuperQuartz spectrophotometric cell (STE) by a Varian Cary 50 Probe UV-Vis spectrometer at 25°C using a Julabo F 33 refrigerated circulator as temperature controller.

### 2.3 Nomenclature of polymers

In the polymer codes, the synthesized polymers are called PF-IPI, PF-MDI, PF-PB900, PF-PP1000, NF-IPI, NF-MDI, NF-PB900, NF-PP1000, BPB-IPI, BPB-MDI, BPB-PB900 and BPB-PP1000. PF, NF and BPB represent the heterocyclic compounds, namely proflavine, new fuchsin and bromphenol blue, respectively. IPI, MDI, PB900 and PP1000 indicate the type of diisocyanate compounds, namely isophorone diisocyanate, 4,4′-methylene-bis(phenyl isocyanate), tolylene 2,4-diisocynate terminated poly(1,4-butanediol) prepolymer and tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer, respectively. For example, PF-IPI is the polymer synthesized from proflavine and isophorone diisocyanate.

## 2.4 Synthetic Procedures

### 2.4.1 Investigation the reactivity between heterocycles and isophorone diisocyanate to give heterocyclic polyureas and polyurethane



The heterocycles used were proflavine (PF), new fuchsin (NF), and bromphenol blue (BPB). The diisocyanate used was isophorone diisocyanate (IPI). The synthetic method was as follows: heterocycles and isophorone diisocyanate were mixed at the mole ratio of heterocycle:IPI = 1:1 and was then heated in a hot air oven at 90$^{o}$C to give polyureas and polyurethane containing heterocycles. IR spectroscopy was used to follow the progress of the reaction. The completeness of reaction was confirmed by the disappearance of the characteristic band of the isocyanate group at 2270 cm$^{-1}$ and the appearance of absorption band of the carbonyl group between 1680-1725 cm$^{-1}$. The isolation of polymers containing heterocycles was done by dissolving the product mixture in DMSO and the resulting solution was then added to water or methanol to precipitate the polymer. The polymer was washed with water or methanol and dried under vacuo to remove traces of the solvent.

**Table 2.1** Composition of starting materials in the investigation of the polymerization reactivity between heterocycles and isophorone diisocyanate

| **Polymers** | **Starting materials** | | | | **Reaction time (hr)** | **Yield (%)** |
|---|---|---|---|---|---|---|
| | **Heterocycles** | | | **Isocyanate** | | |
| | **PF** | **NF** | **BPB** | **IPI** | | |
| PF-IPI | 0.145 g, 0.694 mmol | - | - | 0.145 mL, 0.693 mmol | 48 | 32 |
| NF-IPI | - | 0.178 g, 0.541 mmol | - | 0.113 mL, 0.540 mmol | 72 | 33 |
| BPB-IPI | - | - | 0.226 g, 0.337 mmol | 0.071 mL, 0.337 mmol | 48 | 37 |

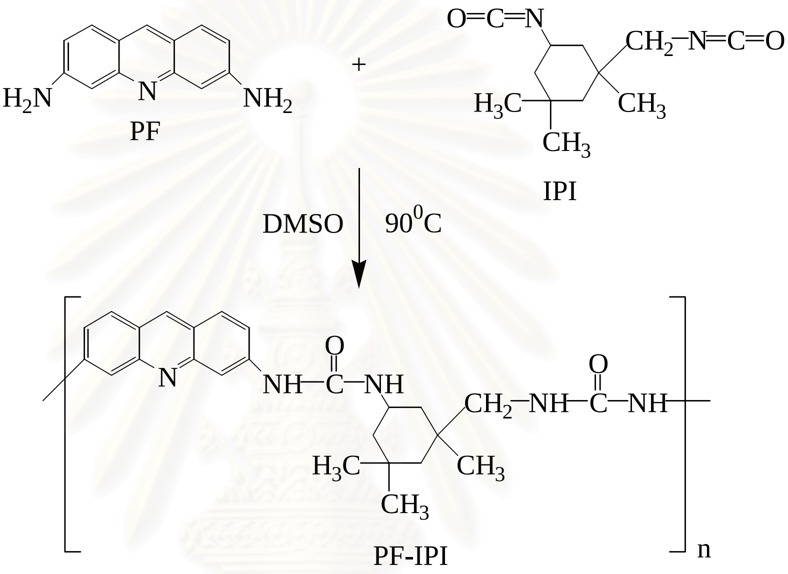
**PF-IPI:** IR (KBr, cm$^{-1}$); 3362 (NH), 3218, 2953, 2922, 2844, 1706 (C=O), 1642 (C=N), 1618 (C=C), 1552, 1466 (C=C), 1385, 1307, 1233, 1159, 1066, 914, 867, 805, 777, 649.

**NF-IPI:** IR (KBr, cm$^{-1}$); 3354 (NH), 3222, 2945, 2926, 2852, 1704 (C=O), 1638 (C=N), 1591 (C=C), 1552, 1513 (C=C), 1466, 1365, 1307, 1233, 1147, 1066, 890, 824, 762, 626.

**BPB-IPI:** IR (KBr, cm$^{-1}$); 3393 (NH), 3070, 2953, 2922, 2856, 1708 (C=O), 1630, 1572 (C=C), 1466 (C=C), 1396, 1311, 1225, 1190, 1136, 1085, 1023, 945, 887, 766, 711, 618.

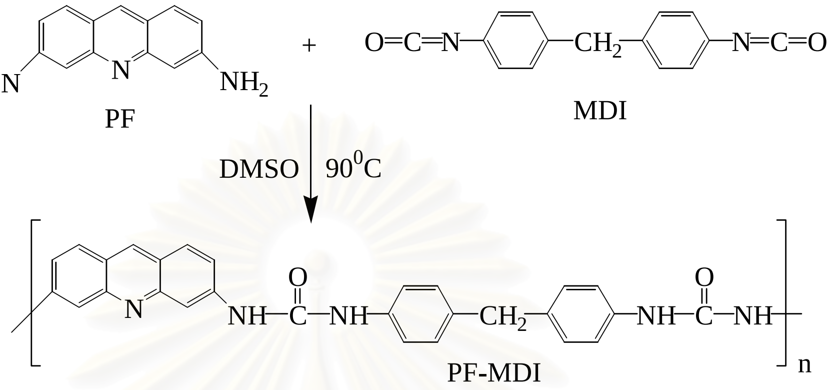
## 2.4.2 Synthesis of polyureas and polyurethane-ureas containing proflavine units

### 2.4.2.1 Synthesis of PF-IPI from the reaction between proflavine and IPI



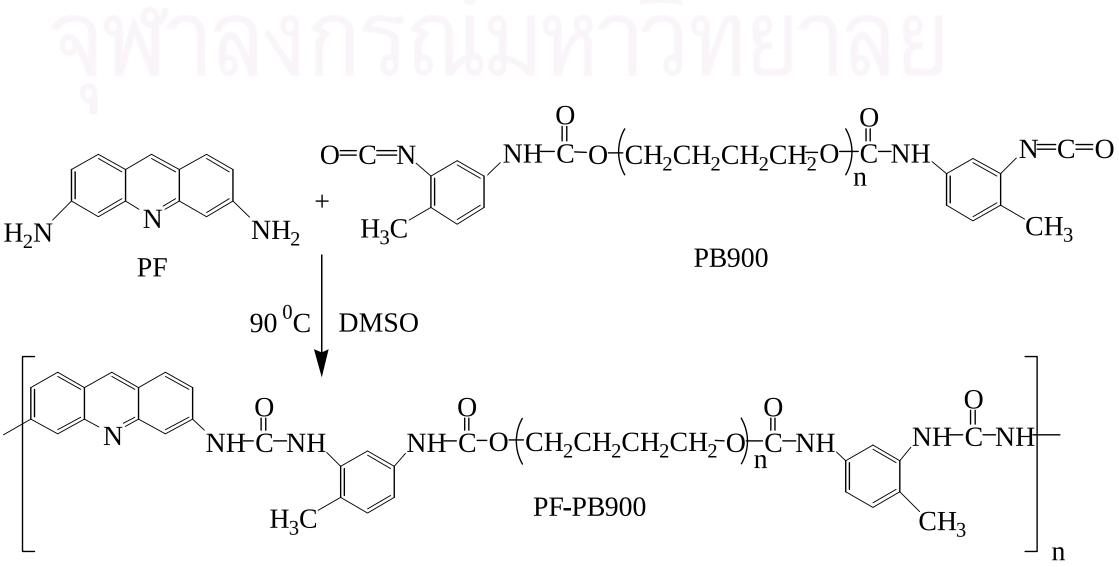
A solution of proflavine (0.146 g, 0.70 mmol) in dimethyl sulfoxide (1 mL) was added to the solution of IPI (0.146 mL, 0.70 mmol) in dimethyl sulfoxide (2 mL) with stirring under nitrogen atmosphere. Then, dibutyltin dilaurate (0.421 mL, 0.70 mmol) was added to the mixture as a catalyst. After heating under nitrogen atmosphere for 5 days at 90°C, the polymer was precipitated by pouring the reaction mixture into a mixture of water and methanol (1:1). The precipitated polymer was filtered off and dried under vacuum to remove traces of solvent. The polymer was obtained as yellow-brown powder (0.217 g, 72%): IR (KBr, $cm^{-1}$); 3346 (NH), 3218, 2945, 2914, 2840, 1704 (C=O), 1642 (C=N), 1618 (C=C), 1552, 1466 (C=C), 1389, 1307, 1229, 1159, 1066, 914, 867, 805, 774, 645. $^1H$ NMR (400 MHz, $CDCl_3$:DMSO-$d_6$, ppm); δ 8.25 (1H, *s*, Ar-H), 7.57 (2H, *d*, Ar-H, $J$ = 9.2 Hz), 6.87 (2H, *d*, Ar-H, $J$ = 9.2 Hz), 6.84 (2H, *s*, Ar-H), 5.57 (4H, *s*, NHCO), 3.63-3.84 (1H, *m*, NCH), 2.63-2.92 (2H, *m*, $NCH_2$), 0.78-1.70 (15H, *m*, $CH_2$ and $CH_3$ of isophorone unit). UV-visible; $\lambda_{max}$ 411, 464.

#### 2.4.2.2 Synthesis of PF-MDI from the reaction between proflavine and MDI



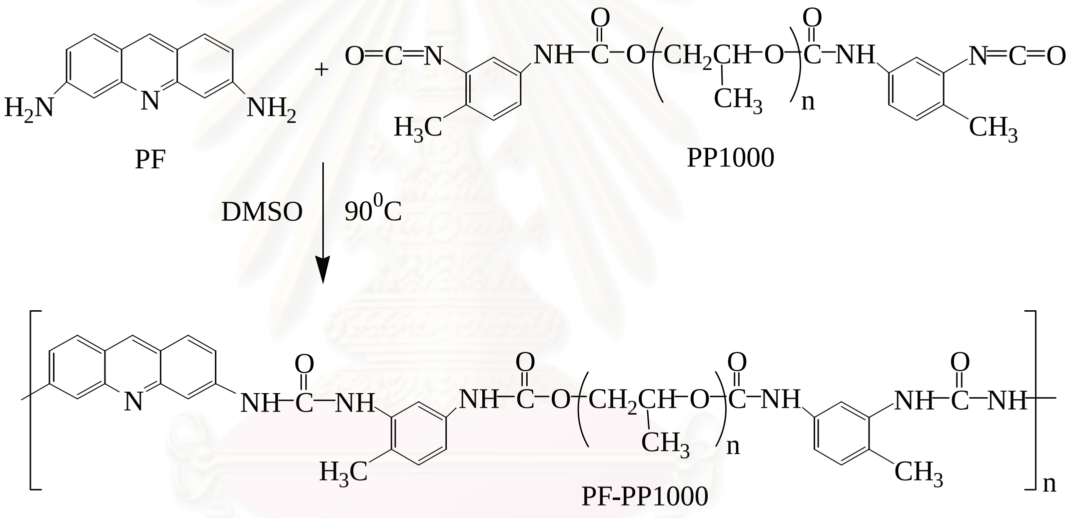
The experiment was performed according to the procedure described in experiment 2.4.2.1 employing proflavine (0.137 g, 0.66 mmol) and MDI (0.164 g, 0.66 mmol). The reaction mixture was stirred at 90°C for 5 days. The polymer was obtained as yellow-brown powder (0.169 g, 56%): IR (KBr, cm$^{-1}$); 3303 (NH), 3031, 2903, 1700 (C=O), 1642 (C=N), 1599 (C=C), 1544, 1513, 1466 (C=C), 1408, 1311, 1229, 1019, 914, 855, 809, 778, 645. $^1$H NMR (400 MHz, DMSO-$d_6$, ppm); δ 7.64-8.83 (3H, *m*, Ar-H), 7.32-7.44 (4H, *m*, Ar-H), 7.00-7.18 (4H, *m*, Ar-H ), 6.03-6.86 (4H, *m*, Ar-H), 3.69-3.84 (2H, *m*, CH$_2$). UV-visible; $\lambda_{max}$ 393.

#### 2.4.2.3 Synthesis of PF-PB900 from the reaction between proflavine and PB900



The experiment was performed according to the procedure described in experiment 2.4.2.1 employing proflavine (0.057 g, 0.27 mmol) and PB900 (0.244 g, 0.27 mmol). The reaction mixture was stirred at 90°C for 7 days. The polymer was obtained as yellow-brown elastomer (0.139 g, 46%): IR (KBr, $cm^{-1}$); 3342 (NH), 3222, 2930, 2860, 1716 (C=O), 1638 (C=N), 1607 (C=C), 1544, 1466 (C=C), 1381, 1229, 1112, 875, 848, 803, 774. UV-visible; $\lambda_{max}$ 394.

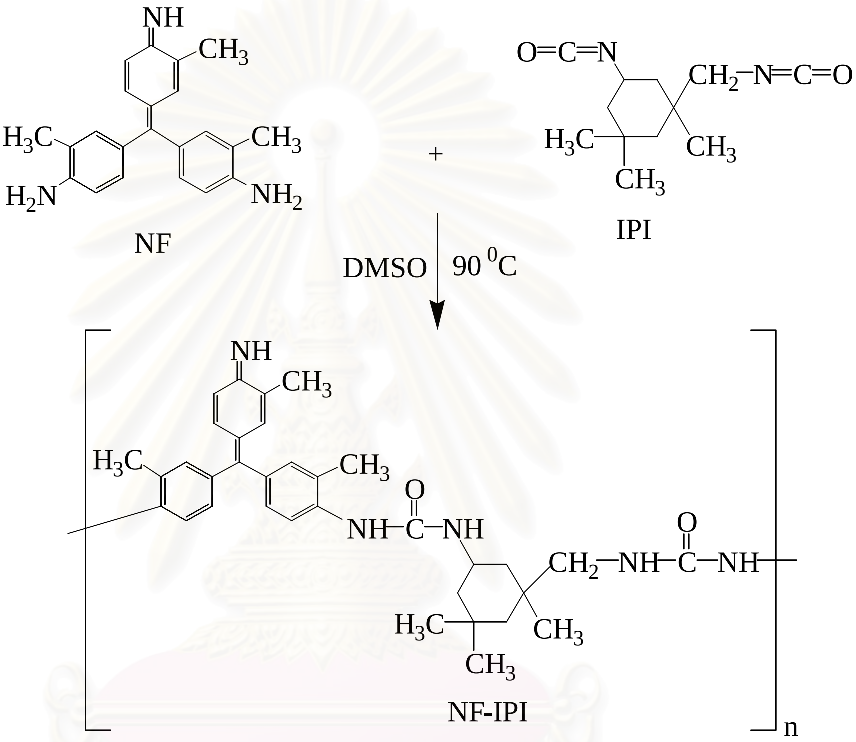
#### 2.4.2.4 Synthesis of PF-PP1000 from the reaction between proflavine and PP1000



The experiment was performed according to the procedure described in experiment 2.4.2.1 employing proflavine (0.052 g, 0.25 mmol) and PP1000 (0.248 g, 0.25 mmol). The reaction mixture was stirred at 90°C for 7 days. The polymer was obtained as yellow-brown elastomer (0.159 g, 53%): IR (KBr, $cm^{-1}$); 3358 (NH), 3222, 2969, 2922, 2860, 1708 (C=O), 1642 (C=N), 1599 (C=C), 1540, 1466 (C=C), 1380, 1229, 1108, 1019, 923, 867, 809, 770, 645. UV-visible; $\lambda_{max}$ 394.

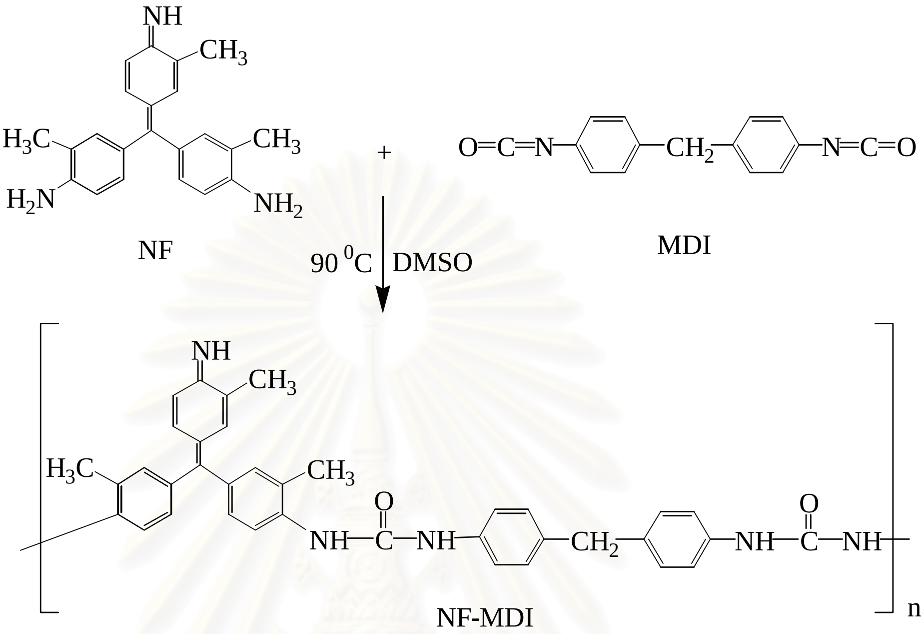
## 2.4.3 Synthesis of polyureas and polyurethane-ureas containing new fuchsin units

### 2.4.3.1 Synthesis of NF-IPI from the reaction between new fuchsin and IPI



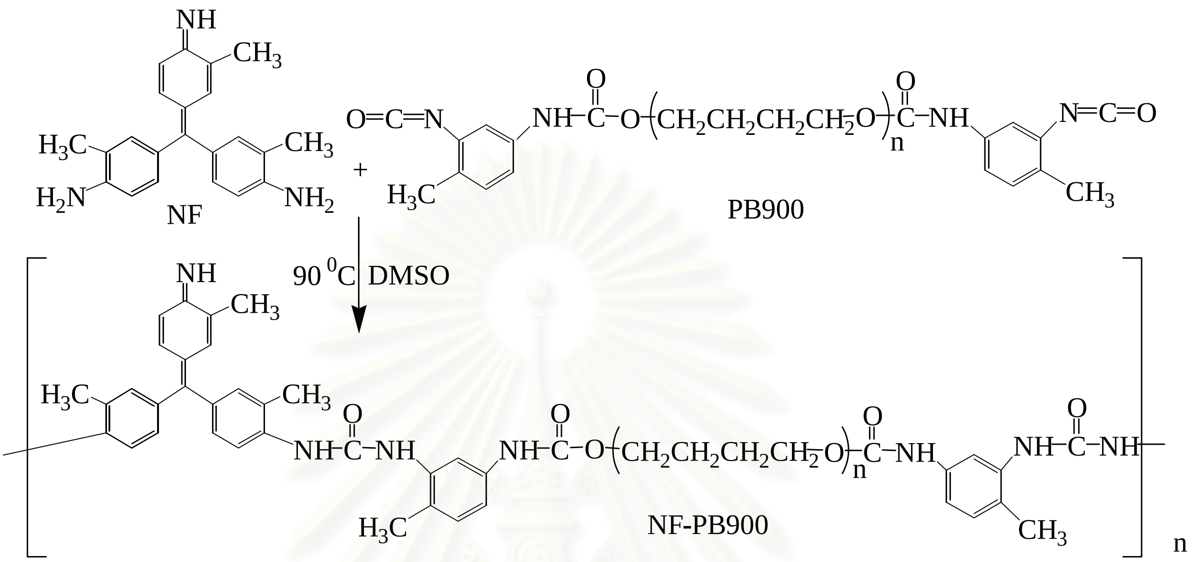
A solution of new fuchsin (0.179 g, 0.54 mmol) in dimethyl sulfoxide (1 mL) was added to the solution of IPI (0.114 mL, 0.54 mmol) in dimethyl sulfoxide (2 mL) with stirring under nitrogen atmosphere. Then, dibutyltin dilaurate (0.325 mL, 0.54 mmol) were added to the mixture as a catalyst. After heating under nitrogen atmosphere for 5 days at 90°C, the polymer was precipitated by pouring the reaction mixture into a mixture of water and methanol (1:1). The precipitated polymer was filtered off and dried under vacuum to remove traces of solvent. The polymer was obtained as violet-brown powder (0.234 g, 78%): IR (KBr, $cm^{-1}$); 3366 (NH), 3218, 2945, 2922, 2860, 1708 (C=O), 1634 (C=N), 1552, 1513 (C=C), 1466, 1365, 1311, 1241, 1147, 1066, 890, 828, 758, 618. $^1H$ NMR (400 MHz, DMSO-$d_6$, ppm); $\delta$ 5.60-7.74 (9H, *m*, Ar-$\underline{H}$), 3.61-3.80 (1H, *m*, NC$\underline{H}$), 2.61-2.93 (2H, *m*, NC$\underline{H}_2$), 0.77-2.27 (24H, *m*, C$\underline{H}_2$ and C$\underline{H}_3$ of isophorone and NF units). UV-visible; $\lambda_{max}$ 555.

### 2.4.3.2 Synthesis of NF-MDI from the reaction between new fuchsin and MDI



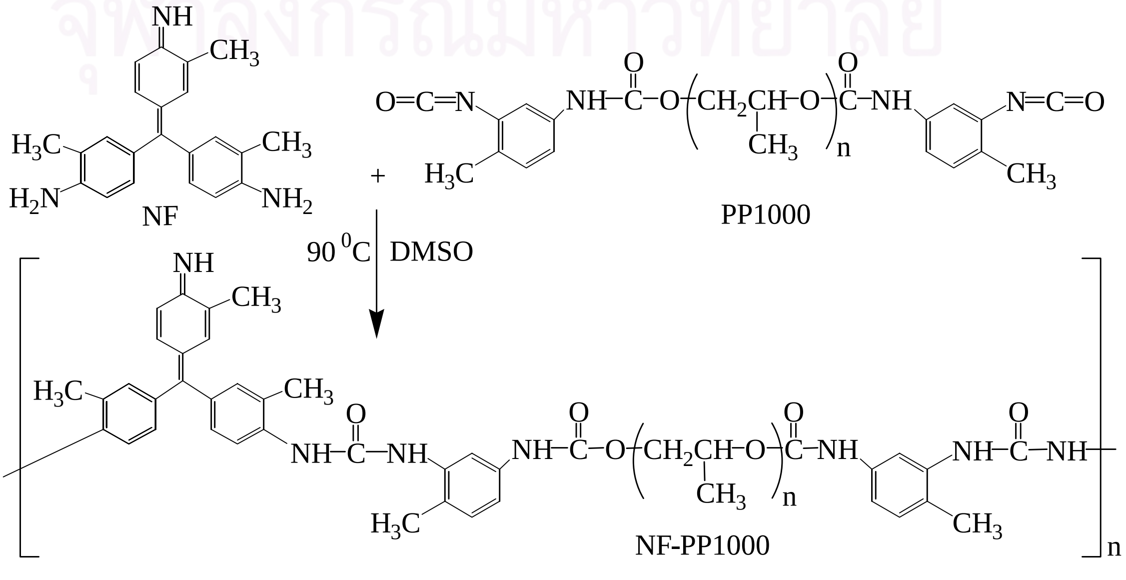
The experiment was performed according to the procedure described in experiment 2.4.3.1 employing new fuchsin (0.171 g, 0.52 mmol) and MDI (0.130 g, 0.52 mmol). The reaction mixture was stirred at 90°C for 5 days. The polymer was obtained as violet-brown powder (0.235 g, 78%): IR (KBr, $cm^{-1}$); 3354 (NH), 3023, 2914, 1680 (C=O), 1591 (C=C), 1513 (C=C), 1447, 1408, 1311, 1229, 1120, 1015, 898, 816, 758, 618. $^1$H NMR (400 MHz, DMSO-$d_6$, ppm); δ 6.48-7.85 (9H, *m*, Ar-H), 7.34-7.36 (4H, *m*, Ar-H), 7.10-7.12 (4H, *m*, Ar-H), 3.68-3.81 (2H, *m*, $CH_2$), 1.92-2.39 (9H, *m*, $CH_3$). UV-visible; $\lambda_{max}$ 557.

### 2.4.3.3 Synthesis of NF-PB900 from the reaction between new fuchsin and PB900



The experiment was performed according to the procedure described in experiment 2.4.3.1 employing new fuchsin (0.080 g, 0.24 mmol) and PB900 (0.220 g, 0.24 mmol). The reaction mixture was stirred at 90°C for 7 days. The polymer was obtained as violet-black elastomer (0.201 g, 67%): IR (KBr, $cm^{-1}$); 3362 (NH), 2922, 2852, 1712 (C=O), 1591 (C=C), 1536, 1459, 1373, 1229, 1108, 871, 824, 762, 618. UV-visible; $\lambda_{max}$ 565.

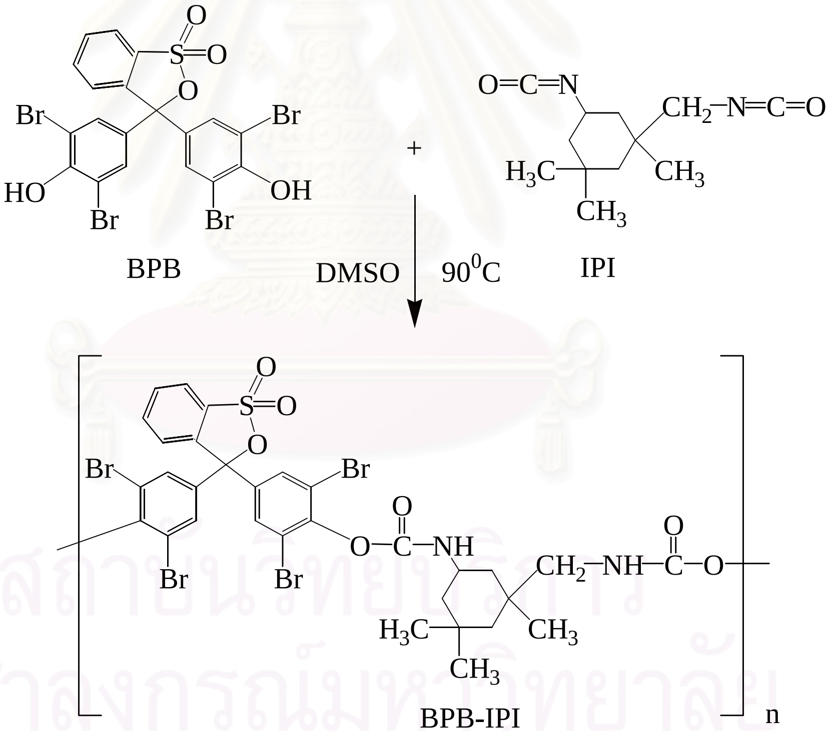
### 2.4.3.4 Synthesis of NF-PP1000 from the reaction between new fuchsin and PP1000



The experiment was performed according to the procedure described in experiment 2.4.3.1 employing new fuchsin (0.074 g, 0.23 mmol) and PP1000 (0.226 g, 0.23 mmol). The reaction mixture was stirred at 90°C for 7 days. The polymer was obtained as violet-black elastomer (0.213 g, 71%): IR (KBr, cm$^{-1}$); 3366 (NH), 2969, 2926, 2860, 1712 (C=O), 1591 (C=C), 1540, 1455, 1373, 1229, 1104, 875, 824, 766, 622. UV-visible; $\lambda_{max}$ 565.

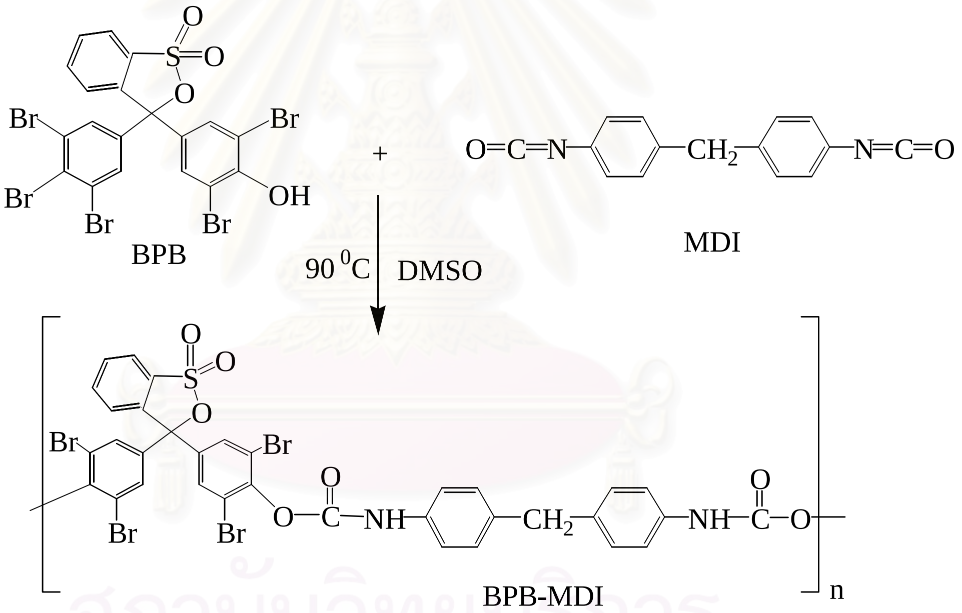
### 2.4.4 Synthesis of polyurethane containing bromphenol blue units

#### 2.4.4.1 Synthesis of BPB-IPI from the reaction between bromphenol blue and IPI



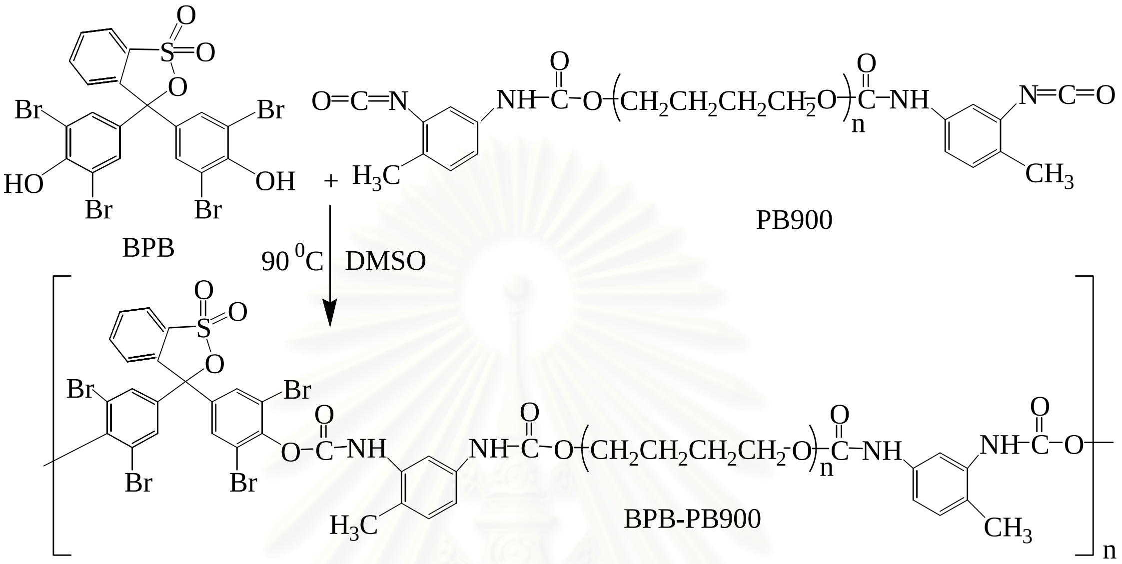
A solution of bromphenol blue (0.225 g, 0.34 mmol) in dimethyl sulfoxide (1 mL) was added to the solution of IPI (0.071 mL, 0.34 mmol) in dimethyl sulfoxide (2 mL) with stirring under nitrogen atmosphere. Then, dibutyltin dilaurate (0.205 mL, 0.34 mmol) were added to the mixture as a catalyst. After heating under nitrogen atmosphere for 5 days at 90°C, the polymer was precipitated by pouring the reaction mixture into water (10 mL). The precipitated polymer was filtered off and dried under vacuum to remove traces of solvent. The polymer was obtained as green-brown powder (0.252 g, 84%): IR (KBr, cm$^{-1}$); 3381 (NH), 3058, 2953, 2922, 2852, 1708 (C=O), 1630, 1575 (C=C), 1466 (C=C), 1396, 1303, 1221, 1194, 1136, 1089, 1019, 945, 887, 762, 711, 622. $^1$H NMR (400 MHz, $CDCl_3$:DMSO-$d_6$, ppm); δ 8.03 (1H, *d*, Ar-H, $J$ = 7.6 Hz), 7.52 (4H, *s*, Ar-H), 7.49 (1H, *t*, Ar-H, $J$ = 6.8 Hz), 7.43 (1H, *t*, Ar-H, $J$ = 7.4 Hz), 7.03 (1H, *d*, Ar-H, $J$ = 8.0 Hz), 1.49-1.66 (3H, *m*, $CH_2$), 0.81-1.11 (17H, *m*, $CH_2$ and $CH_3$ of isophorone unit). UV-visible; $\lambda_{max}$ 605.

### 2.4.4.2 Synthesis of BPB-MDI from the reaction between bromphenol blue and MDI



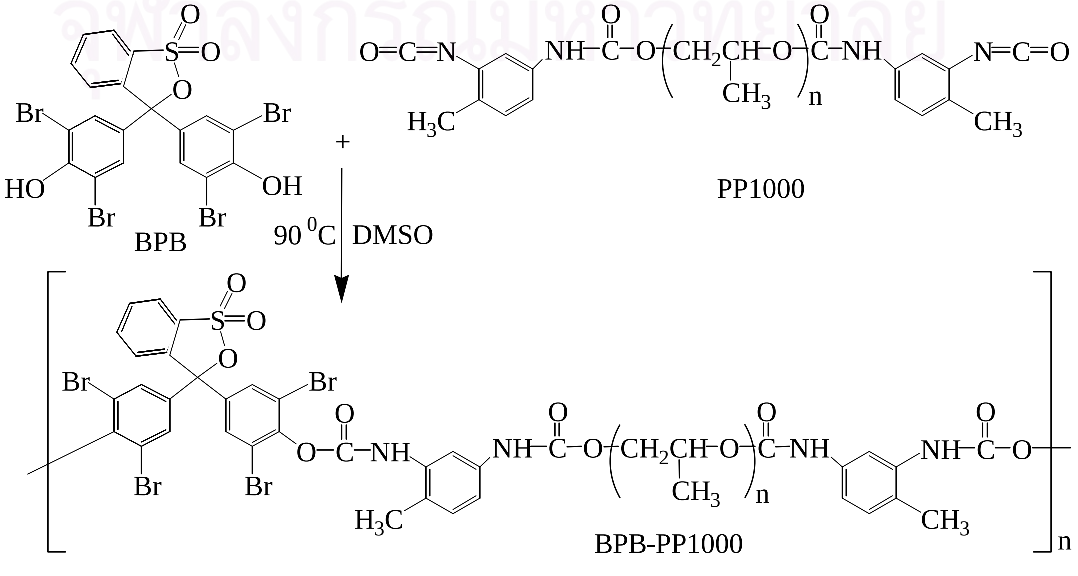
The experiment was performed according to the procedure described in experiment 2.4.4.1 employing bromphenol blue (0.219 g, 0.33 mmol) and MDI (0.082 g, 0.33 mmol). The reaction mixture was stirred at 90°C for 5 days. The polymer was obtained as green-brown powder (0.238 g, 79%): IR (KBr, cm$^{-1}$); 3389 (NH), 3054, 2922, 2852, 1704 (C=O), 1630, 1599 (C=C), 1544, 1513, 1474 (C=C), 1408, 1311, 1233, 1178, 1085, 1015, 937, 820, 766, 711, 618. $^1$H NMR (400 MHz, $CDCl_3$:DMSO-$d_6$, ppm); δ 8.00 (1H, *d*, Ar-H, $J$ = 7.6 Hz), 7.53 (4H, *s*, Ar-H), 7.49 (1H, *t*, Ar-H, $J$ = 8.2 Hz), 7.43 (1H, *t*, Ar-H, $J$ = 7.4 Hz), 7.18-7.30 (4H, *m*, Ar-H), 7.01-7.14 (5H, *m*, Ar-H of BPB and MDI units), 3.79-3.98 (2H, *m*, $CH_2$). UV-visible; $\lambda_{max}$ 603.

### 2.4.4.3 Synthesis of BPB-PB900 from the reaction between bromphenol blue and PB900



The experiment was performed according to the procedure described in experiment 2.4.4.1 employing bromphenol blue (0.128 g, 0.19 mmol) and PB900 (0.172 g, 0.19 mmol). The reaction mixture was stirred at 90°C for 7 days. The polymer was obtained as black elastomer (0.204 g, 68%): IR (KBr, $cm^{-1}$); 3377 (NH), 2926, 2856, 1723 (C=O), 1638, 1599 (C=C), 1533, 1470 (C=C), 1412, 1369, 1307, 1233, 1112, 1027, 933, 887, 766, 711, 618. UV-visible; $\lambda_{max}$ 604.

### 2.4.4.4 Synthesis of BPB-PP1000 from the reaction between bromphenol blue and PP1000



The experiment was performed according to the procedure described in experiment 2.4.4.1 employing bromphenol blue (0.120 g, 0.18 mmol) and PP1000 (0.180 g, 0.18 mmol). The reaction mixture was stirred at 90°C for 7 days. The polymer was obtained as black elastomer (0.219 g, 73%): IR (KBr, cm$^{-1}$); 3397 (NH), 2957, 2922, 2860, 1723 (C=O), 1634, 1603 (C=C), 1536, 1466 (C=C), 1373, 1303, 1229, 1112, 1019, 937, 875, 774, 708, 618. UV-visible; $\lambda_{max}$ 603.

**Table 2.2** Composition of starting materials in the synthesis heterocyclic polymers

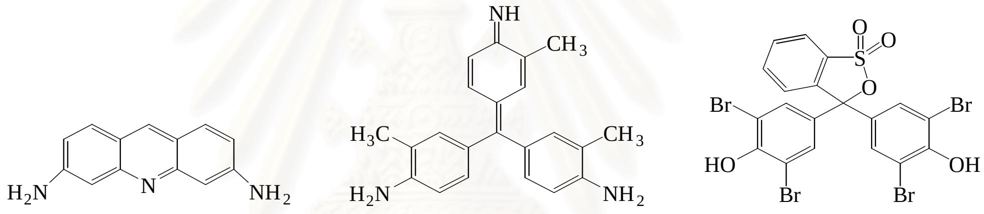
| **Polymers** | **Starting materials** | | | | | | | **Yield (%)** |
|---|---|---|---|---|---|---|---|---|
| | **Heterocycles** | | | **Isocyanates** | | | | |
| | **PF** | **NF** | **BPB** | **IPI** | **MDI** | **PB900** | **PP1000** | |
| PF-IPI | 0.146 g,<br>0.70 mmol | - | - | 0.146 mL,<br>0.70 mmol | - | - | - | 72 |
| PF-MDI | 0.137 g,<br>0.66 mmol | - | - | - | 0.164 g,<br>0.66 mmol | - | - | 56 |
| PF-PB900 | 0.057 g,<br>0.27 mmol | - | - | - | - | 0.244 g,<br>0.27 mmol | - | 46 |
| PF-PP1000 | 0.052g,<br>0.25 mmol | - | - | - | - | - | 0.248 g,<br>0.25 mmol | 53 |
| NF-IPI | - | 0.179 g,<br>0.54 mmol | - | 0.114 mL,<br>0.54 mmol | - | | - | 78 |
| NF-MDI | - | 0.171 g,<br>0.52 mmol | - | - | 0.130 g,<br>0.52 mmol | - | - | 78 |
| NF-PB900 | - | 0.080 g,<br>0.24 mmol | - | - | - | 0.220 g,<br>0.24 mmol | - | 67 |
| NF-PP1000 | - | 0.074 g,<br>0.23 mmol | - | - | - | - | 0.226 g,<br>0.23 mmol | 71 |
| BPB-IPI | - | - | 0.225 g,<br>0.34 mmol | 0.071 mL,<br>0.34 mmol | - | - | - | 84 |
| BPB-MDI | - | - | 0.219 g,<br>0.33mmol | - | 0.082 g,<br>0.33 mmol | - | - | 79 |
| BPB-PB900 | - | - | 0.128 g,<br>0.19 mmol | - | - | 0.172 g,<br>0.19 mmol | - | 68 |
| BPB-PP1000 | - | - | 0.120 g,<br>0.18 mmol | - | - | - | 0.180 g,<br>0.18 mmol | 73 |

# CHAPTER III

# RESULTS AND DISCUSSION

Heterocycles have good thermal stability because they contain aromatic systems. Therefore, they were used as monomers in the synthesis of polyurethanes and polyureas. It was expected that the obtained polymers would show good thermal stability.

The heterocycles used were proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB). Their structures are shown in Figure 3.1.



Proflavine (PF) New fuchsin (NF) Bromphenol blue (BPB)

**Figure 3.1** Structure of heterocycles used in this study

## 3.1 Investigation of the reactivity between heterocycles and isophorone diisocyanate to give heterocyclic polyureas and polyurethane

The reactivity of the amine group and alcohol group in heterocycles with isocyanate group in isophorone diisocyanate (IPI) to give urea and urethane group, respectively, was followed in this step. The heterocycles used were proflavine, new fuchsin and bromphenol blue. Proflavine and new fuchsin contain $NH_2$ groups and the polymers obtained from their reactions with isophorone diisocyanate are polyureas (PF-IPI and NF-IPI, respectively). Bromphenol blue contains OH groups and its reaction with isophorone diisocyanate gives polyurethane (BPB-IPI). IR spectroscopy was used to follow the progress of the reaction. The completeness of reaction could be observed by the disappearance of the strong -NCO- absorption in IPI at 2270 $cm^{-1}$ and the appearance of new -NCON- or -NCOO- absorption band at 1680-1720 cm$^{-1}$.

Figures 3.2, 3.3 and 3.4 show the IR spectra of the reaction mixture of PF:IPI, NF:IPI and BPB:IPI, respectively, at different reaction times. The polymerization was done at 90°C. After heating the reaction mixture of PF:IPI and NF:IPI, the new -NCON- peak could not be clearly observed since it overlaps with the C=N band which results in a broad absorption band. In the case of BPB:IPI reaction, a new -NCOO- peak was observed at 1708 cm$^{-1}$. The completeness of the reactions between PF:IPI, NF:IPI and BPB:IPI was supported by the absence of the NCO peak at 2270 cm$^{-1}$ after heating for 48, 72 and 48 hours, respectively.

IR data of PF-IPI, NF-IPI and BPB-IPI are presented in Table 3.1. The N-H stretching signals of urea and urethane groups appeared between 3300-3400 cm$^{-1}$. The urea carbonyl peak of PF-IPI and NF-IPI, which should be observed at 1704-1706 cm$^{-1}$, overlapped with the C=N bands of the heterocycles and broad peaks were observed. The urethane carbonyl peak of BPB-IPI was observed as a sholder at 1708 cm$^{-1}$. The C=C absorption band was observed around 1466-1630 cm$^{-1}$.

**Table 3.1** IR data of PF-IPI, NF-IPI and BPB-IPI

| Polymers | Wavenumber (cm$^{-1}$) | | |
|---|---|---|---|
| | $\nu_{N-H}$ | $\nu_{C=O}$ | $\nu_{C=C}$ |
| PF-IPI | 3362 | 1706 | 1618, 1466 |
| NF-IPI | 3354 | 1704 | 1591, 1513 |
| BPB-IPI | 3393 | 1708 | 1572, 1466 |

It was found that order of reactivity of heterocycle towards the polymerization with IPI was proflavine > bromphenol blue > new fuchsin. It has been known that the reactivity data of diisocyanate that the order of reactivity is aromatic > aliphatic. This would give the information in the synthesis of polyureas and polyurethanes containing heterocycles in the next step.

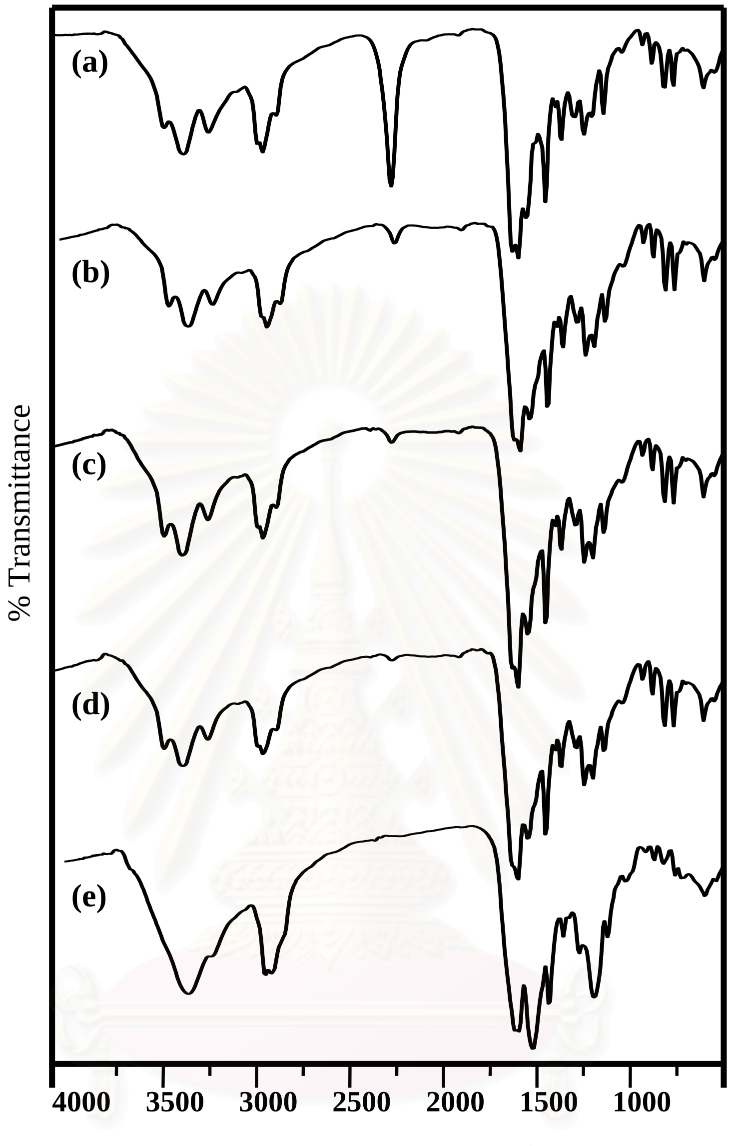


**Figure 3.2** IR spectra of the reaction mixture of PF-IPI at different times (a) 0 h; (b) 4 h; (c) 6 h; (d) 24 h; (e) 30 h

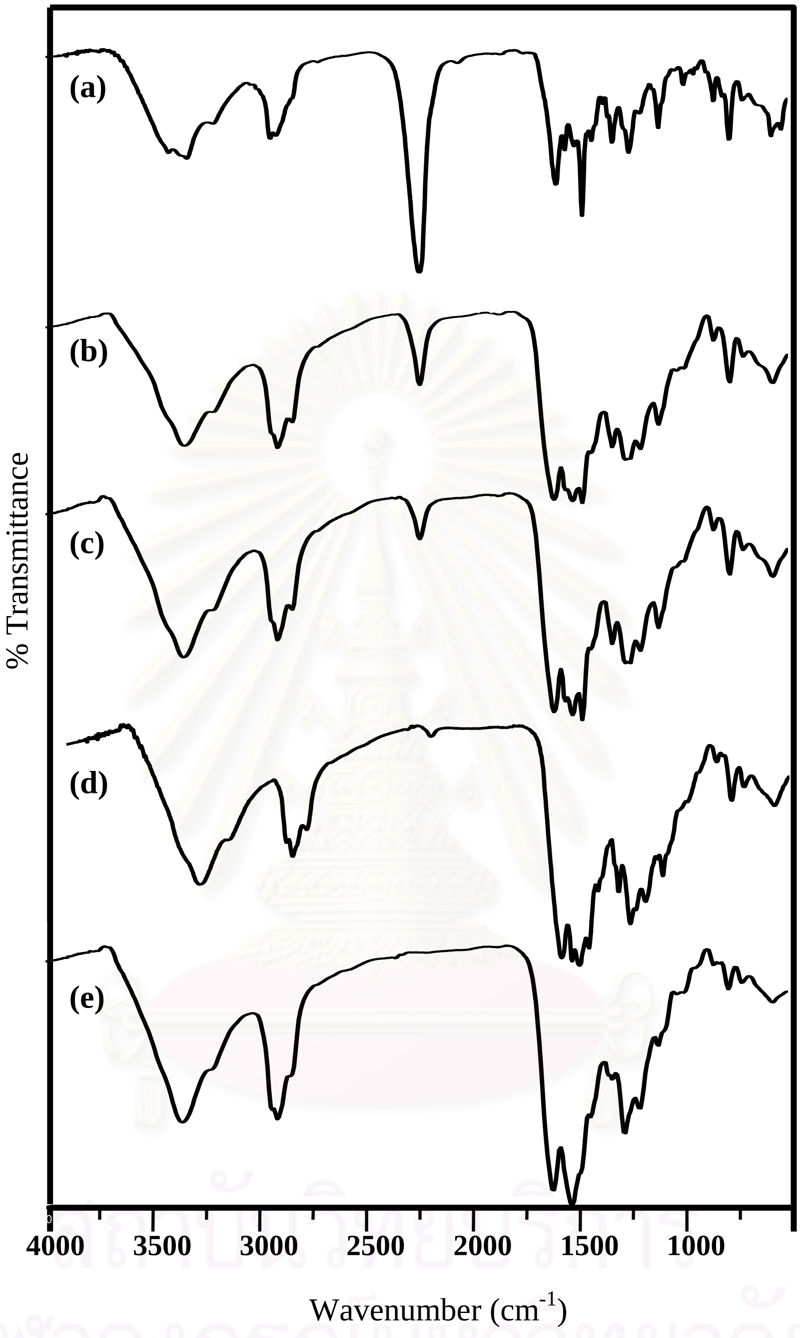


**Figure 3.3** IR spectra of the reaction mixture of NF-IPI at different times (a) 0 h; (b) 6 h; (c) 24 h; (d) 48 h; (e) 72 h

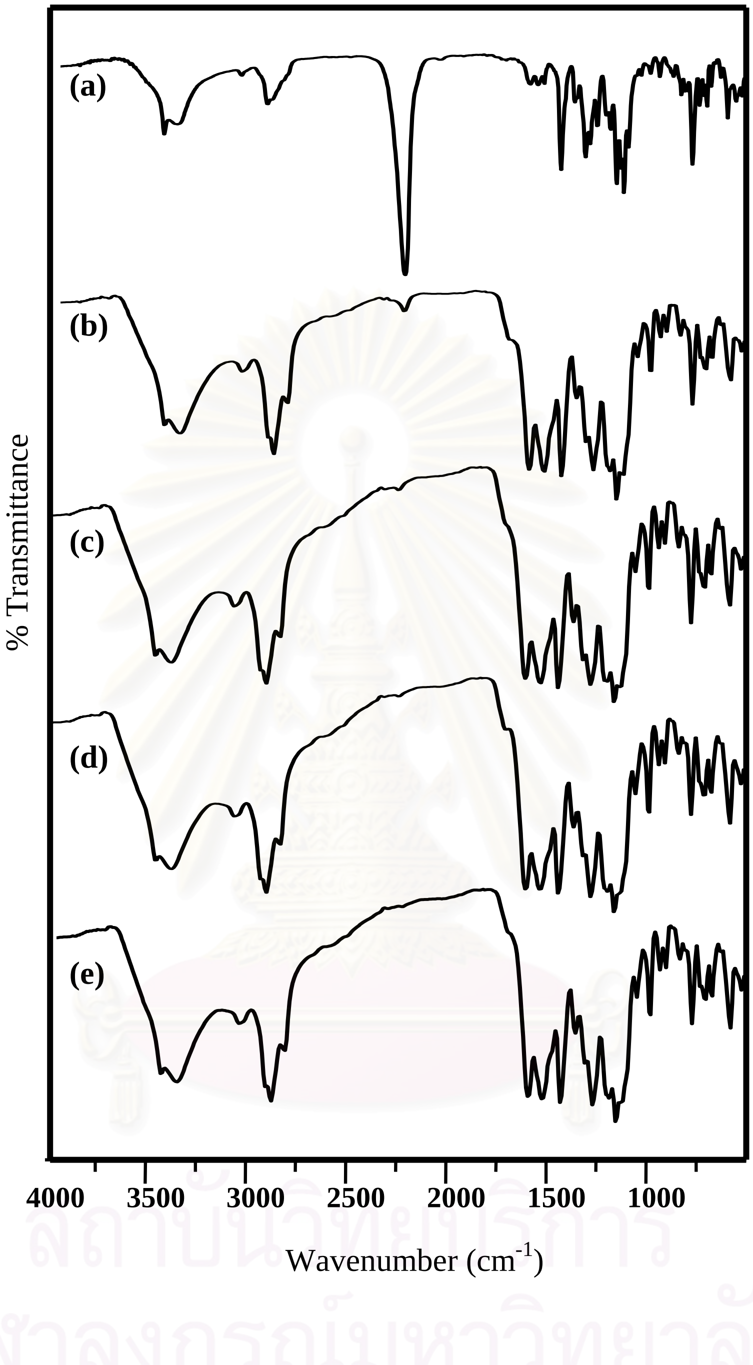
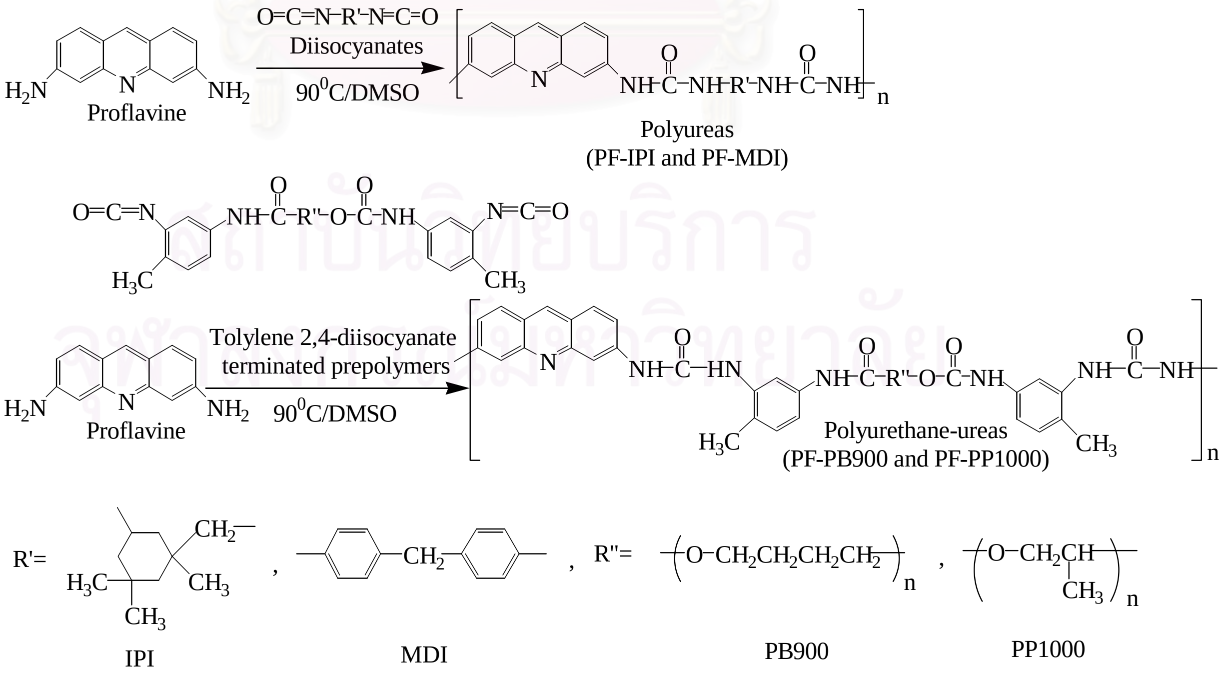


**Figure 3.4** IR spectra of the reaction mixture of BPB-IPI at different times (a) 0 h; (b) 6 h; (c) 24 h; (d) 30 h; (e) 48 h

## 3.2 Synthesis of heterocyclic polyureas, polyurethanes and polyurethane-ureas

### 3.2.1 Synthesis of polyureas and polyurethane-ureas containing proflavine units

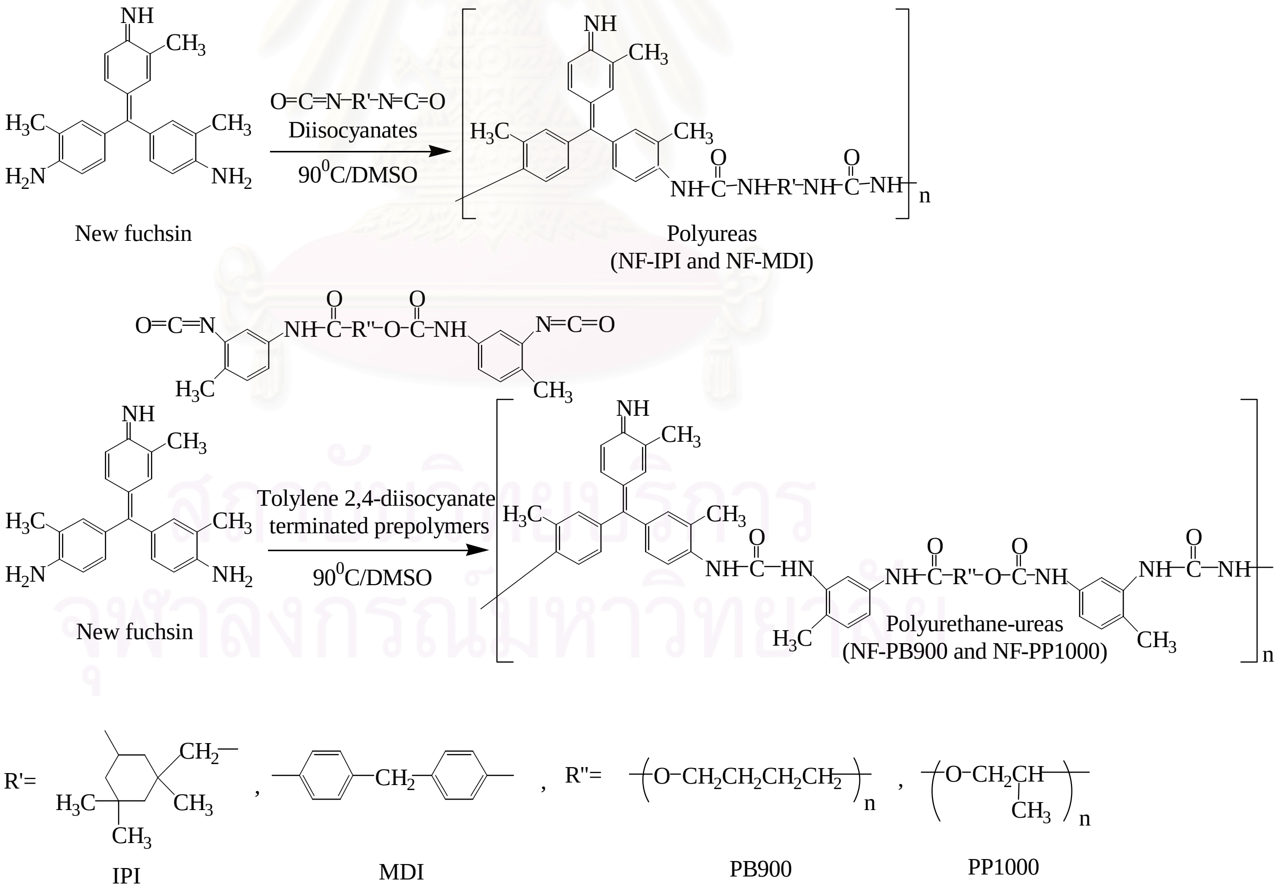
Polyureas and polyurethane-ureas containing proflavine units in the main chain were synthesized from the reaction between proflavine and diisocyanates. The diisocyanates used were IPI, MDI, PB900 and PP1000. The reaction of proflavine with diisocyanates for polyureas and polyurethanes synthesis was done at the mole ratio of diisocyanate:proflavine = 1:1 to avoid crosslinking of the polymers. The reaction mixture was heated until the polymer could be precipitated by addition of reaction mixture into water and methanol. The reaction of proflavine with different diisocyanates is shown in Scheme 3.1. The obtained polymers from proflavine (PF) with IPI, MDI, PB900 and PP1000 are called PF-IPI, PF-MDI, PF-PB900 and PF-PP1000, respectively. PF-IPI and PF-MDI are polyureas which are yellow brown powder. PF-PB900 and PF-PP1000 are polyurethane-ureas and they were obtained as yellow brown elastomers. The yield of these polymers were 46-72 %.



**Scheme 3.1** Synthesis of polyureas and polyurethane-ureas containing proflavine units from proflavine and diisocyanates

### 3.2.2 Synthesis of polyureas and polyurethane-ureas containing new fuchsin units

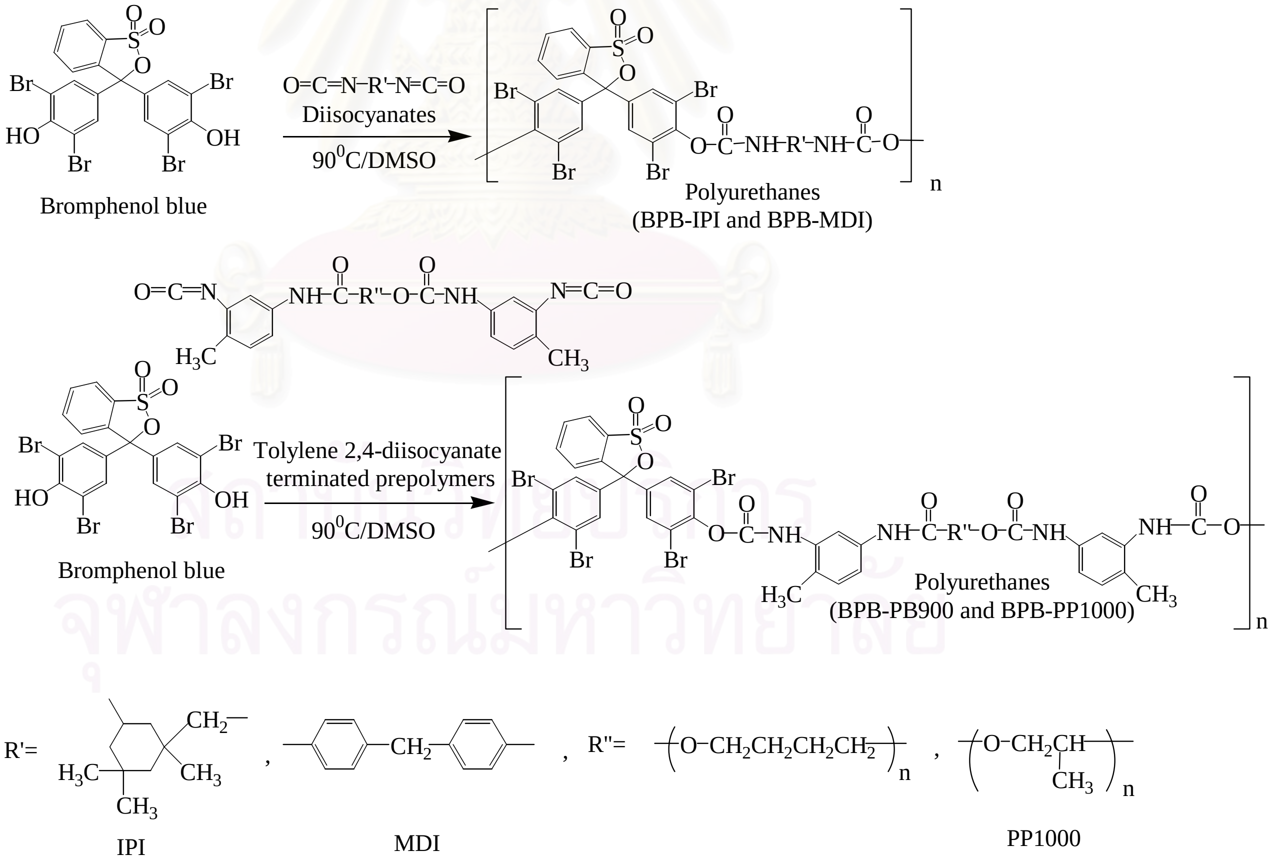
Polyureas and polyurethane-ureas containing new fuchsin units in the main chain were synthesized from the reaction between new fuchsin and diisocyanates. The diisocyanates used were IPI, MDI, PB900 and PP1000. The reaction between new fuchsin and diisocyanates was done by the same method and condition as described in section 3.2.1. The outline for this reaction is shown in Scheme 3.2. The obtained polymers were called NF-IPI, NF-MDI, NF-PB900 and NF-PP1000. The obtained polyureas, namely NF-IPI and NF-MDI, are violet-brown powder. The obtained polyurethanes, namely NF-PB900 and NF-PP1000, are violet-black elastomers. Yield of the polymers based on new fuchsin were 67-78 %.



**Scheme 3.2** Synthesis of polyureas and polyurethane-ureas containing new fuchsin units from new fuchsin and diisocyanates

### 3.2.3 Synthesis of polyurethanes containing bromphenol blue units

Polyurethanes containing bromphenol blue units in the main chain were synthesized from the reaction between bromphenol blue and diisocyanates. The diisocyanates used were IPI, MDI, PB900 and PP1000. The reaction between bromphenol blue and diisocyanates was doned by the same method and condition as described in section 3.2.1. The outline for this reaction is shown in Scheme 3.3. The obtained polyurethanes were called BPB-IPI, BPB-MDI, BPB-PB900 and BPB-PP1000. BPB-IPI and BPB-MDI are green-brown powder. BPB-PB900 and BPB-PP1000 are black elastomers since BPB-PB900 and BPB-PP100 were synthesized from high molecular weight prepolymer. Yield of the polymers based on bromphenol blue were 68-84 %.



**Scheme 3.3** Synthesis of polyurethanes containing bromphenol blue units from bromphenol blue and diisocyanates

## 3.3 Characterization of polymers

### 3.3.1 Infrared spectroscopy

#### 3.3.1.1 Infrared spectra of polyureas and polyurethane-ureas containing proflavine units

IR spectra and absorption data of proflavine and the polymers based on proflavine are shown in Figure 3.5 and Table 3.2, respectively. All polyureas and polyurethane-ureas showed N-H band of the urea group and urethane group between 3300-3400 cm$^{-1}$. For PF-IPI, PF-PB900 and PF-PP1000, the C-H stretching signals appeared between 2980-2840 cm$^{-1}$. The urea carbonyl absorption of PF-MDI appeared as a shoulder at 1700 cm$^{-1}$. The urea carbonyl absorption of PF-IPI appeared as a broad peak due to the overlapping with -C=N- absorption. The urea carbonyl absorption of PF-PB900 and PF-PP1000 at 1708-1716 cm$^{-1}$ was not clearly observed because this peak overlapped with the urethane carbonyl peak at 1725 cm$^{-1}$. The C=C absorption band was observed around 1466-1618 cm$^{-1}$.

#### 3.3.1.2 Infrared spectra of polyureas and polyurethane-ureas containing new fuchsin units

IR spectra and absorption data of new fuchsin and the polymers based on new fuchsin are shown in Figure 3.6 and Table 3.2, respectively. All polyureas and polyurethane-ureas showed N-H band of the urea group and urethane group between 3300-3400 cm$^{-1}$. The C-H stretching signals appeared between 2980-2840 cm$^{-1}$. The urea carbonyl absorption of NF-MDI appeared as a shoulder at 1680 cm$^{-1}$. The urea carbonyl absorption of NF-IPI appeared as a broad peak due to the overlapping with -C=N- absorption. The urea carbonyl absorption of NF-PB900 and NF-PP1000 at 1712 cm$^{-1}$ was not clearly observed because this peak overlapped with the urethane carbonyl peak at 1725 cm$^{-1}$. The C=C absorption band was observed around 1513-1591 cm$^{-1}$.

### 3.3.1.3 Infrared spectra of polyurethanes containing bromphenol blue units

IR spectra and absorption data of bromphenol blue and the polymers based on bromphenol blue are shown in Figure 3.7 and Table 3.2, respectively. All polyurethanes showed N-H band of the urethane group between 3300-3400 cm$^{-1}$. For BPB-IPI, BPB-PB900 and BPB-PP1000, the C-H stretching signals appeared between 2980-2840 cm$^{-1}$. The urethane carbonyl absorption appeared as a shoulder around 1704-1723 cm$^{-1}$. The C=C absorption band was observed around 1466-1638 cm$^{-1}$.

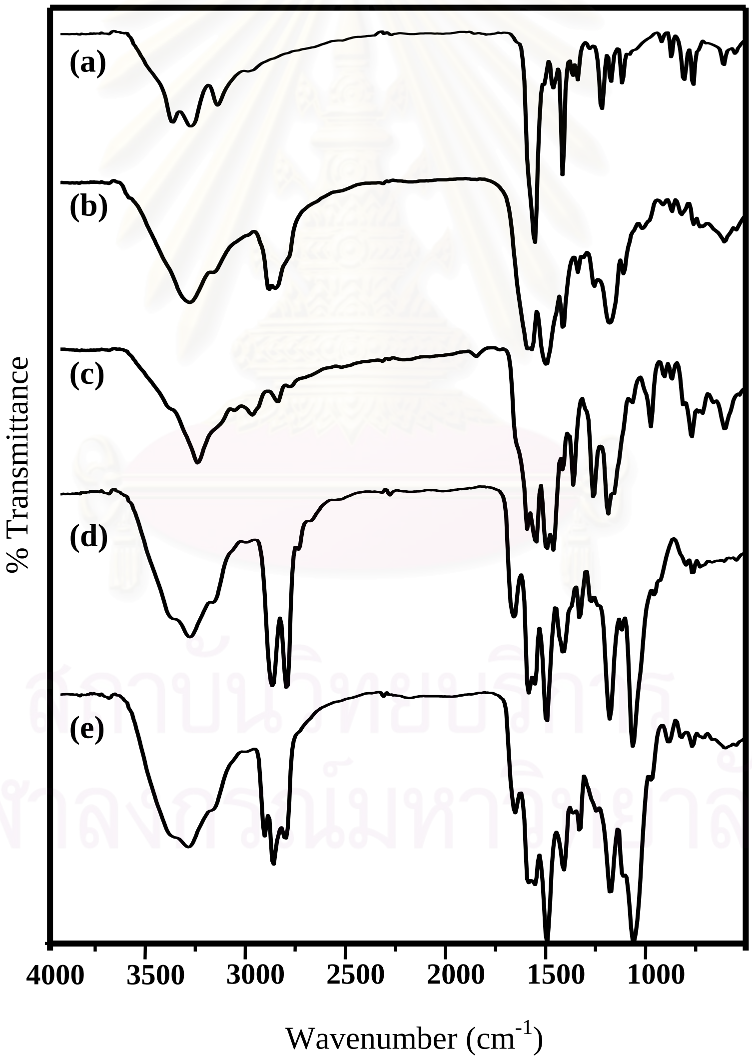


**Figure 3.5** IR spectra of polyureas and polyurethane-ureas containing proflavine units: (a) proflavine; (b) PF-IPI; (c) PF-MDI; (d) PF-PB900; (e) PF-PP1000

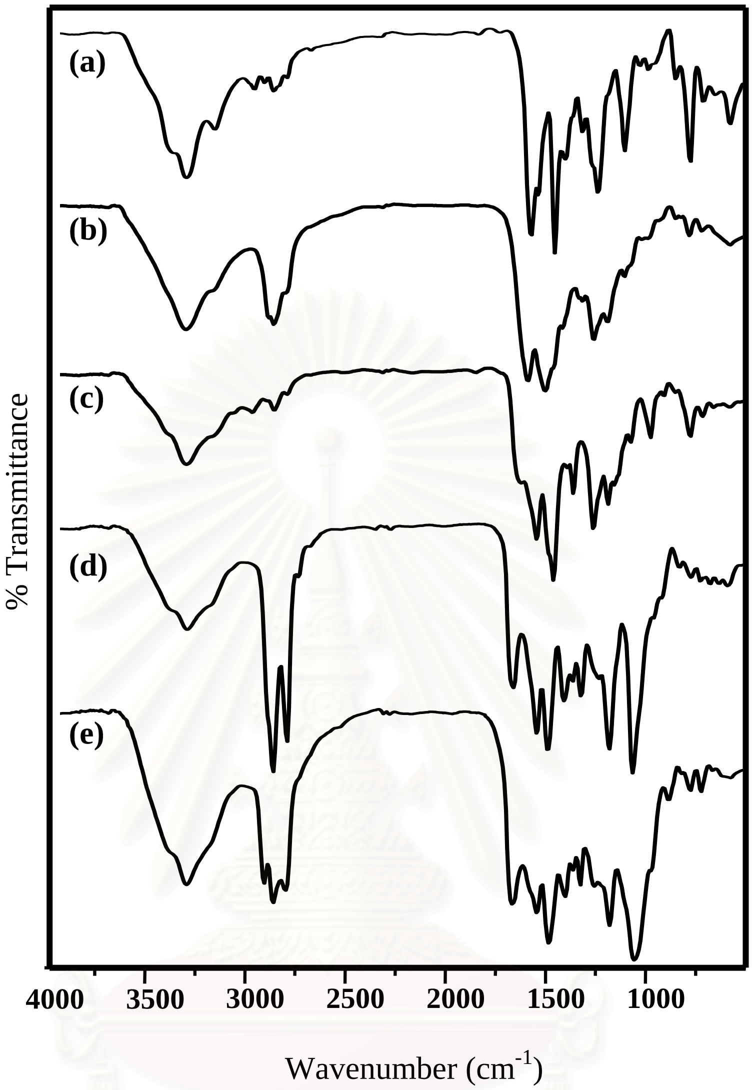


**Figure 3.6** IR spectra of polyureas and polyurethane-ureas containing new fuchsin units: (a) new fuchsin; (b) NF-IPI; (c) NF-MDI; (d) NF-PB900; (e) NF-PP1000

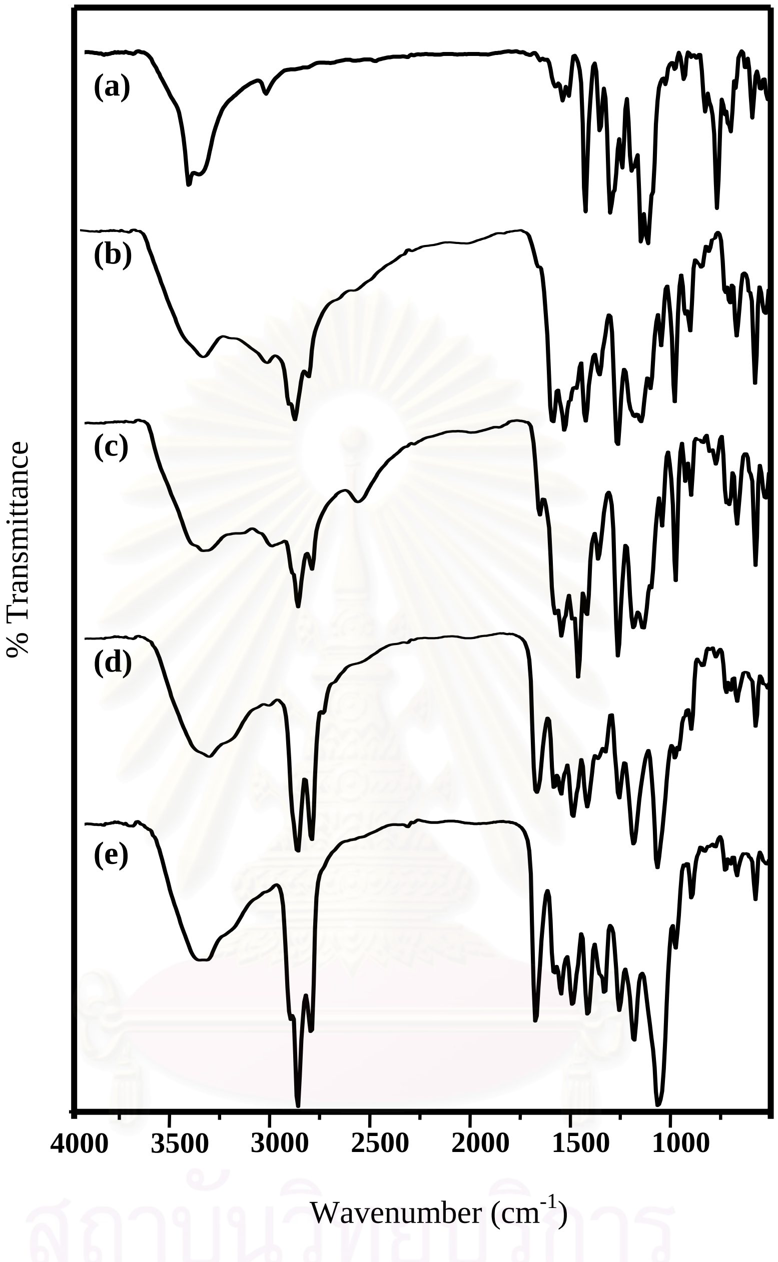


**Figure 3.7** IR spectra of polyurethanes containing bromphenol blue units: (a) bromphenol blue; (b) BPB-IPI; (c) BPB-MDI; (d) BPB-PB900; (e) BPB-PP1000

**Table 3.2** IR data of polyureas, polyurethanes and polyurethane-ureas containing heterocycles

| Polymers | Characteristic signals ($\text{cm}^{-1}$) |
|---|---|
| PF-IPI[a] | 3346 (NH), 3218, 2945, 2914, 2840, 1704 (C=O), 1642 (C=N), 1618 (C=C), 1552, 1466 (C=C), 1389, 1307, 1229, 1159, 1066, 914, 867, 805, 774, 645 |
| PF-MDI[b] | 3303 (NH), 3031, 2903, 1700 (C=O), 1642 (C=N), 1599 (C=C), 1544, 1513, 1466 (C=C), 1408, 1311, 1229, 1019, 914, 855, 809, 778, 645 |
| PF-PB900[b] | 3342 (NH), 3222, 2930, 2860, 1716 (C=O), 1638 (C=N), 1607 (C=C), 1544, 1466 (C=C), 1381, 1229, 1112, 875, 848, 803, 774 |
| PF-PP1000[b] | 3358 (NH), 3222, 2969, 2922, 2860, 1708 (C=O), 1642 (C=N), 1599 (C=C), 1540, 1466 (C=C), 1380, 1229, 1108, 1019, 923, 867, 809, 770, 645 |
| NF-IPI[a] | 3366 (NH), 3218, 2945, 2922, 2860, 1708 (C=O), 1634 (C=N), 1552, 1513 (C=C), 1466, 1365, 1311, 1241, 1147, 1066, 890, 828, 758, 618 |
| NF-MDI[b] | 3354 (NH), 3023, 2914, 1680 (C=O), 1591 (C=C), 1513 (C=C), 1447, 1408, 1311, 1229, 1120, 1015, 898, 816, 758, 618 |
| NF-PB900[b] | 3362 (NH), 2922, 2852, 1712 (C=O), 1591 (C=C), 1536, 1459, 1373, 1229, 1108, 871, 824, 762, 618 |
| NF-PP1000[b] | 3366 (NH), 2969, 2926, 2860, 1712 (C=O), 1591 (C=C), 1540, 1455, 1373, 1229, 1104, 875, 824, 766, 622 |
| BPB-IPI[c] | 3381 (NH), 3058, 2953, 2922, 2852, 1708 (C=O), 1630, 1575 (C=C), 1466 (C=C), 1396, 1303, 1221, 1194, 1136, 1089, 1019, 945, 887, 762, 711, 622 |
| BPB-MDI[c] | 3389 (NH), 3054, 2922, 2852, 1704 (C=O), 1630, 1599 (C=C), 1544, 1513, 1474 (C=C), 1408, 1311, 1233, 1178, 1085, 1015, 937, 820, 766, 711, 618 |
| BPB-PB900[c] | 3377 (NH), 2926, 2856, 1723 (C=O), 1638, 1599 (C=C), 1533, 1470 (C=C), 1412, 1369, 1307, 1233, 1112, 1027, 933, 887, 766, 711, 618 |
| BPB-PP1000[c] | 3397 (NH), 2957, 2922, 2860, 1723 (C=O), 1634, 1603 (C=C), 1536, 1466 (C=C), 1373, 1303, 1229, 1112, 1019, 937, 875, 774, 708, 618 |

[a] Urea carbonyl peak was not observed since it overlaps with C=N absorption which results in a broad peak

[b] Urea carbonyl peak was observed as shoulder or peak

[c] Urethane carbonyl peak was observed as a shoulder or peak

### 3.3.2 $^1$H NMR spectroscopy

#### 3.3.2.1 $^1$H NMR spectra of polyureas containing proflavine units

$^1$H NMR spectra of PF, PF-IPI and PF-MDI were recorded in a mixture of DMSO-$d_6$ and $CDCl_3$. Their spectra and data are presented in Figures 3.8-3.11 and Table 3.3, respectively.

$^1$H NMR spectrum of PF showed the characteristic $-NH_2$ protons at $\delta$ 5.83. The aromatic protons of PF showed signals at $\delta$ 8.30 (1H, *s*, Ar-H), 7.59 (2H, *d*, Ar-H, *J* = 9.4 Hz), 6.87 (2H, *d*, Ar-H, *J* = 9.4 Hz), 6.81 (2H, *s*, Ar-H). For PF-IPI, the aromatic protons showed peaks due to the proflavine unit in the same chemical shift range observed in proflavine at $\delta$ 8.25 (1H, *s*, Ar-H), 7.57 (2H, *d*, Ar-H, *J* = 9.2 Hz), 6.87 (2H, *d*, Ar-H, *J* = 9.2 Hz), 6.84 (2H, *s*, Ar-H) and the aliphatic protons of IPI showed signals at $\delta$ 3.63-3.84 (1H, *m*, NCH), 2.63-2.92 (2H, *m*, $NC\underline{H}_2$), 0.78-1.70 (15H, *m*, $C\underline{H}_2$ and $C\underline{H}_3$ of isophorone unit). In PF-MDI sprectrum, the aromatic protons showed peaks due to the proflavine unit in different pattern to those observed in proflavine at $\delta$ 7.64-8.83 (3H, *m*, Ar-H) and 6.03-6.86 (4H, *m*, Ar-H) because the product contained the mixture of starting material, oligomer and polymer. The aromatic and aliphatic peaks due to MDI were observed at 7.32-7.44 (4H, *m*, Ar-H), 7.00-7.18 (4H, *m*, Ar-H) and 3.69-3.84 (2H, *m*, $C\underline{H}_2$), respectively.

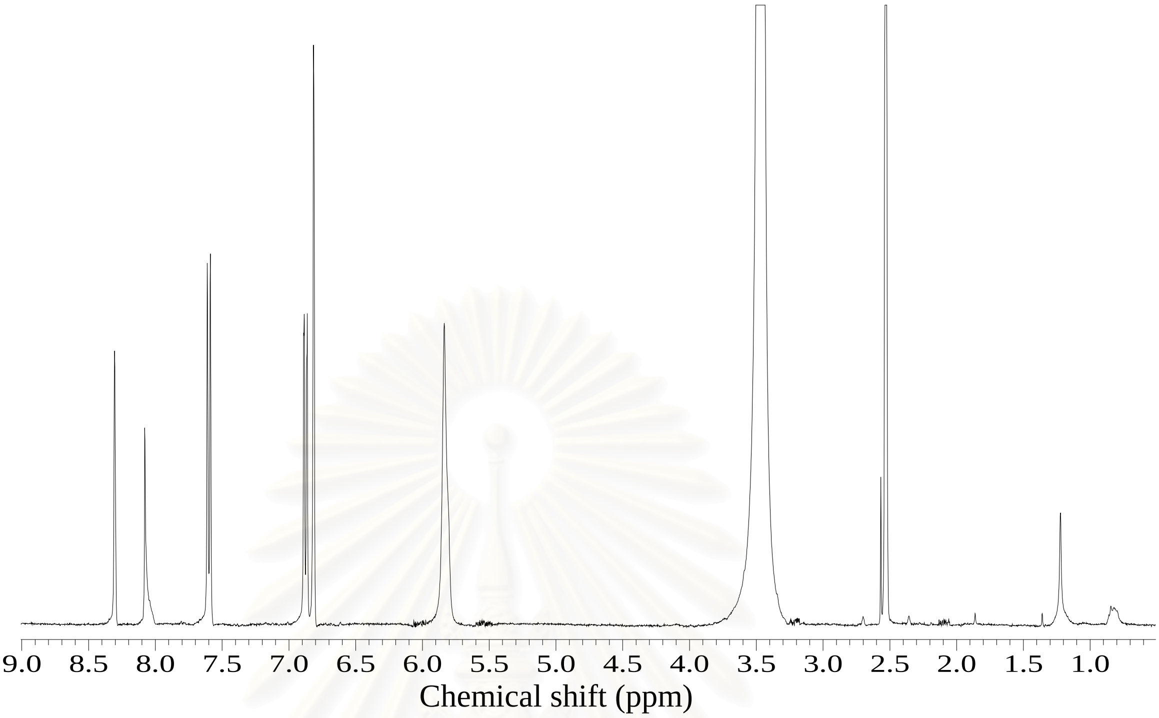


**Figure 3.8** $^1$H-NMR spectrum of PF in $CDCl_3$: DMSO-$d_6$

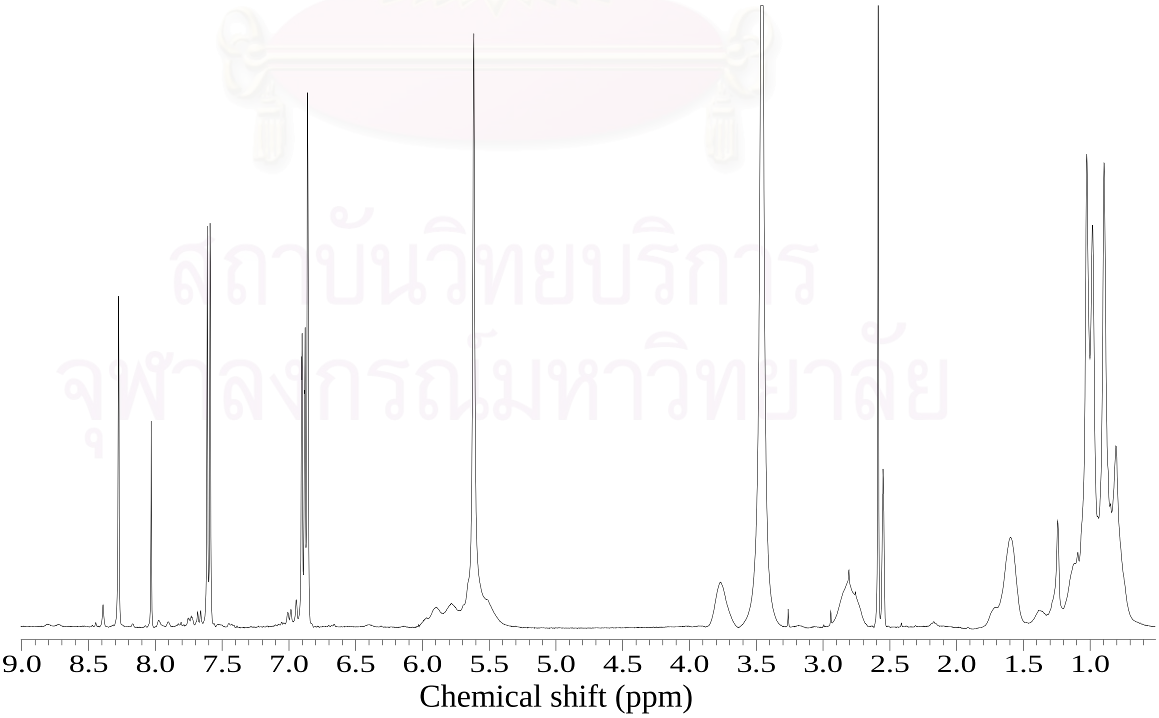


**Figure 3.9** $^1$H-NMR spectrum of PF-IPI in $CDCl_3$: DMSO-$d_6$

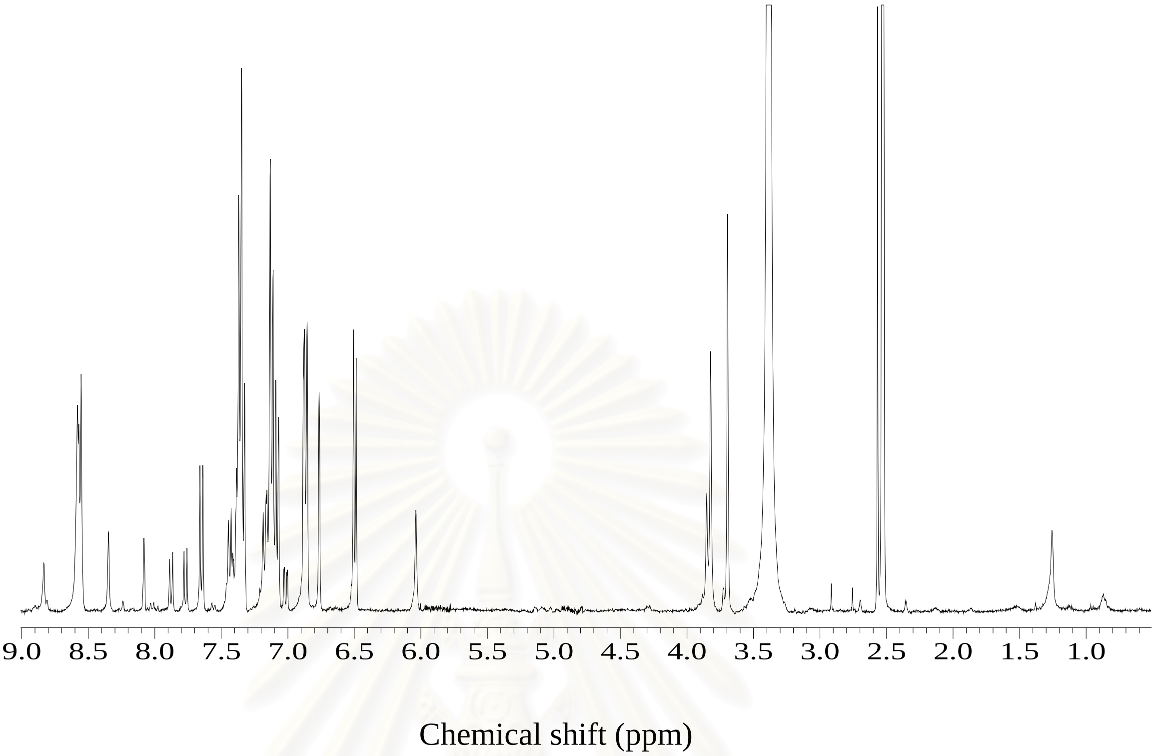


**Figure 3.10** $^1$H-NMR spectrum of PF-MDI in DMSO-$d_6$

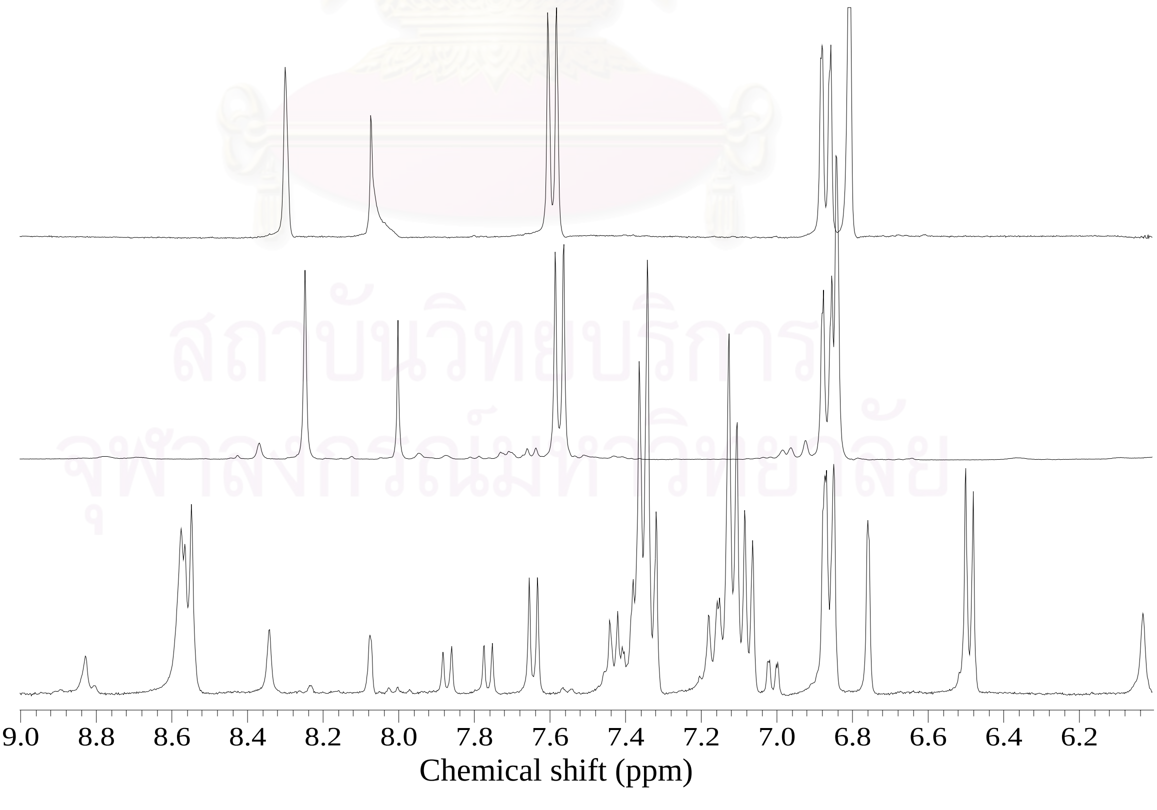


**Figure 3.11** $^1$H-NMR spectra of PF, PF-IPI and PF-MDI in aromatic region

### 3.3.2.2 $^1$H NMR spectra of polyureas containing new fuchsin units

$^1$H NMR spectra of NF, NF-IPI and NF-MDI were recorded in a mixture of DMSO-$d_6$ and $CDCl_3$. Their spectra and data are presented in Figures 3.12-3.15 and Table 3.3, respectively.

$^1$H NMR spectrum of NF showed the characteristic $-NH_2$ protons at δ 3.82. The aliphatic protons of NF showed signals at δ 2.01-2.20 (9H, *m*, $C\underline{H}_3$). The aromatic protons of NF showed signals at δ 6.48-7.02 (9H, *m*, Ar-$\underline{H}$). For NF-IPI, the aromatic protons showed broad peaks due to the new fuchsin unit in the same chemical shift range observed in new fuchsin at δ 5.60-7.74 (9H, *m*, Ar-$\underline{H}$). The aliphatic protons of IPI and NF showed signals at δ 3.61-3.80 (1H, *m*, $NC\underline{H}$), 2.61-2.93 (2H, *m*, $NC\underline{H}_2$), 0.77-2.27 (24H, *m*, $C\underline{H}_2$ and $C\underline{H}_3$ of isophorone and NF units). In NF-MDI sprectrum, the aromatic protons showed peaks due to the new fuchsin unit in the same chemical shift range observed in new fuchsin at δ 6.48-7.85 (9H, *m*, Ar-$\underline{H}$) and aromatic peaks due to MDI were observed at δ 7.34-7.36 (4H, *m*, Ar-$\underline{H}$) and 7.10-7.12 (4H, *m*, Ar-$\underline{H}$), which the aromatic peaks of NF overlapped with those of MDI. The aliphatic protons showed peaks due to NF at δ 1.92-2.39 (9H, *m*, $C\underline{H}_3$) and aliphatic peaks due to MDI were observed at δ 3.68-3.81 (2H, *m*, $C\underline{H}_2$), respectively.

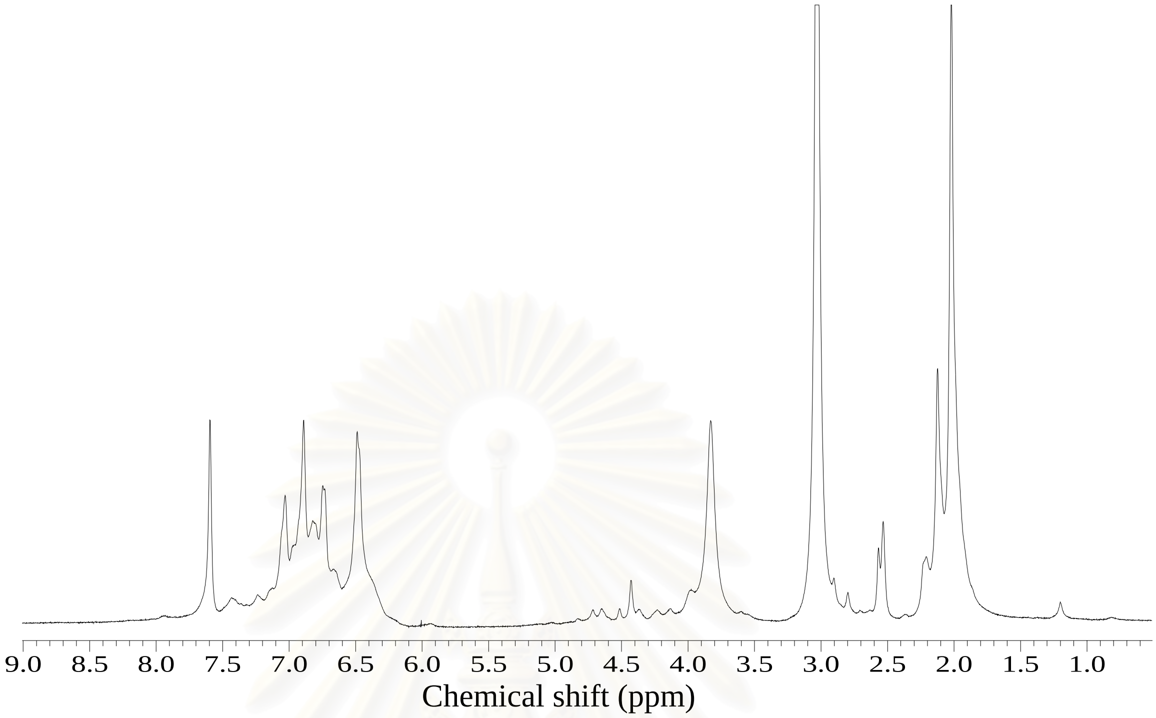


**Figure 3.12** $^{1}$H-NMR spectrum of NF in $CDCl_3$: DMSO-$d_6$

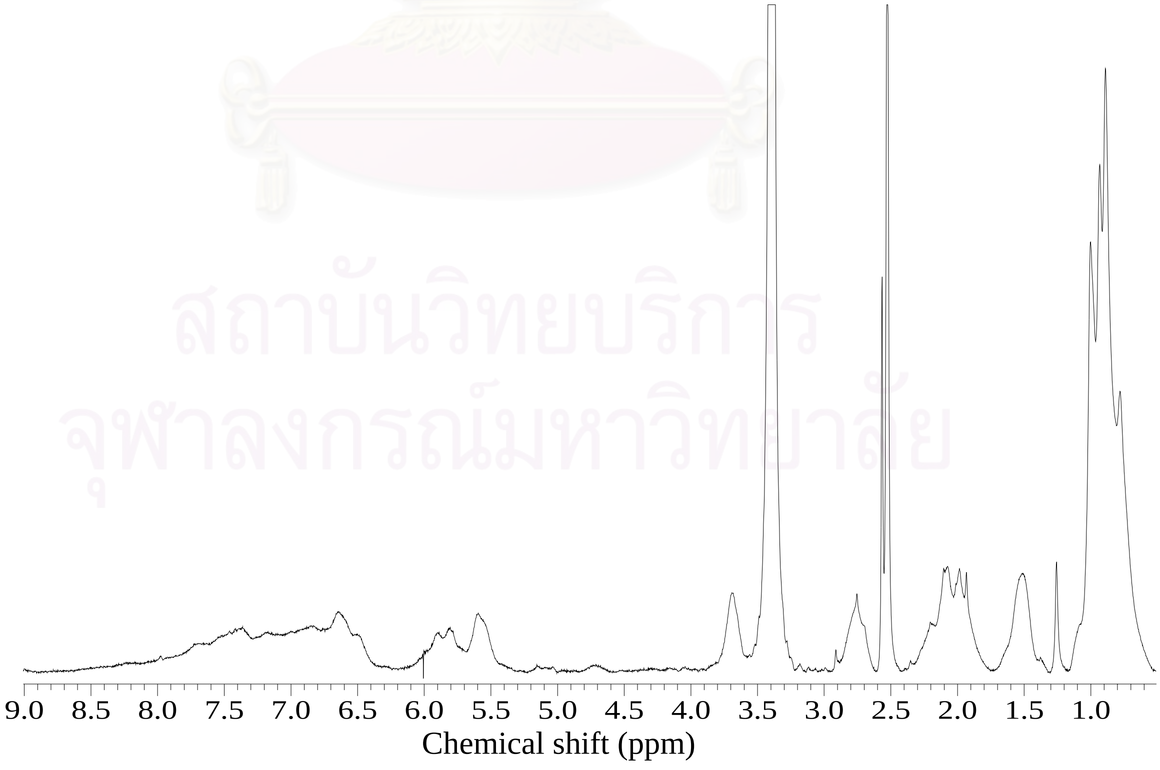


**Figure 3.13** $^{1}$H-NMR spectrum of NF-IPI in DMSO

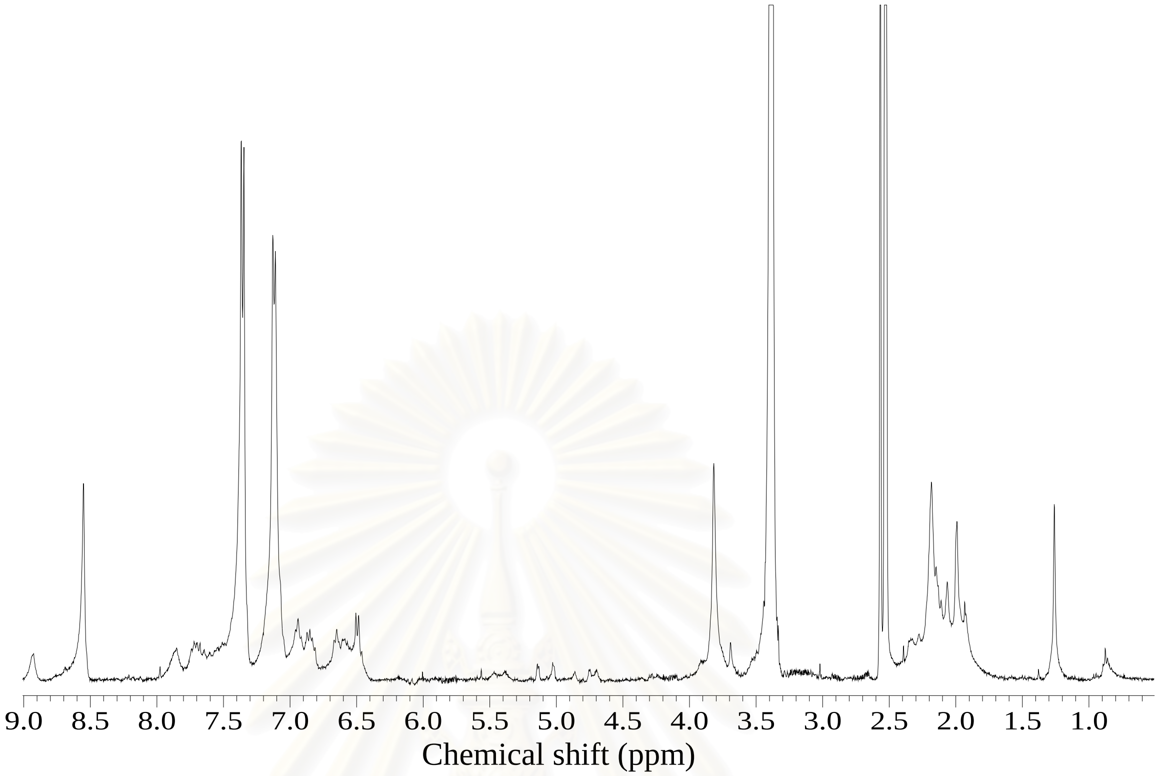


**Figure 3.14** $^{1}$H-NMR spectrum of NF-MDI in DMSO- $d_6$

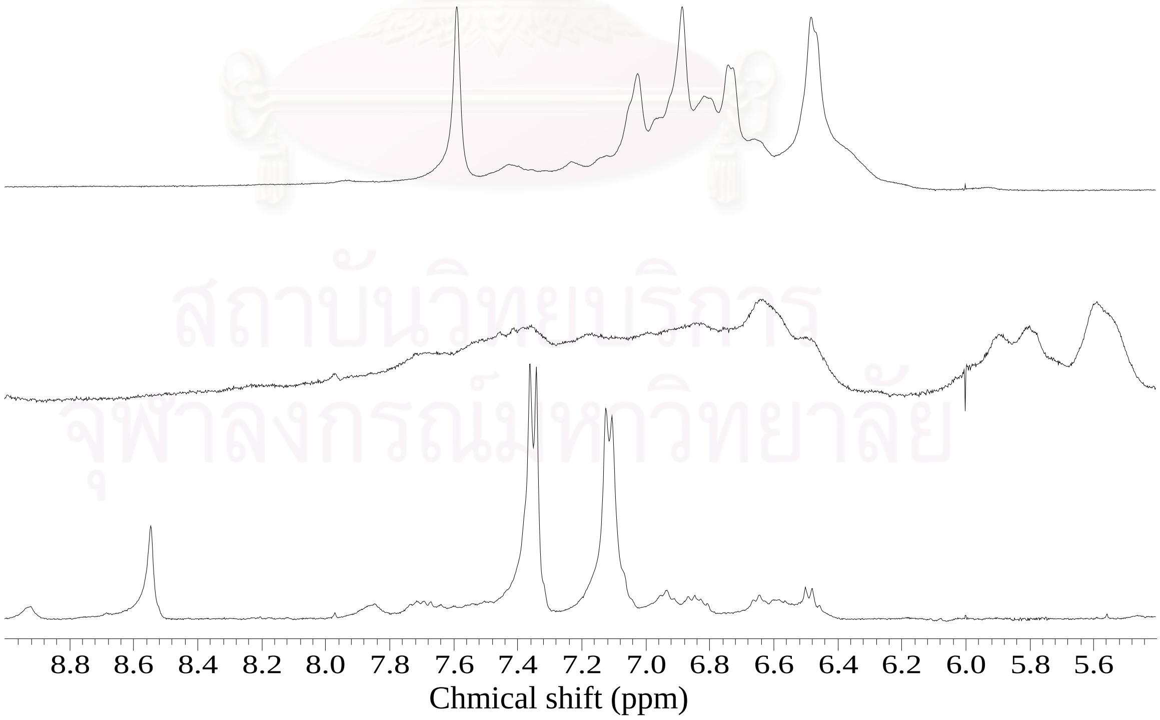


**Figure 3.15** $^{1}$H-NMR spectra of NF, NF-IPI and NF-MDI in aromatic region

### 3.3.2.3 $^1$H NMR spectrum of polyurethanes containing bromphenol blue units

$^1$H NMR spectra of BPB, BPB-IPI and BPB-MDI were recorded in a mixture of DMSO-$d_6$ and $CDCl_3$. Their spectra and data are presented in Figures 3.16-3.19 and Table 3.3, respectively.

$^1$H NMR spectrum of BPB showed the characteristic -OH protons at δ 6.02. The aromatic protons of BPB showed signals at δ 7.84 (1H, *d*, Ar-H, *J* = 8.0 Hz), 7.71 (1H, *t*, Ar-H, *J* = 7.0 Hz), 7.64 (1H, *t*, Ar-H, *J* = 7.6 Hz), 7.26-7.31 (1H, *m*, Ar-H), 7.29 (4H, *s*, Ar-H). For BPB-IPI, the aromatic protons showed peaks due to the bromphenol blue in the same chemical shift range observed in bromphenol blue at δ 8.03 (1H, *d*, Ar-H, *J* = 7.6 Hz), 7.52 (4H, *s*, Ar-H), 7.49 (1H, *t*, Ar-H, *J* = 6.8 Hz), 7.43 (1H, *t*, Ar-H, *J* = 7.4 Hz), 7.03 (1H, *d*, Ar-H, *J* = 8.0 Hz), and the aliphatic protons of IPI showed signals at δ 1.49-1.66 (3H, *m*, $CH_2$), 0.81-1.11 (17H, *m*, $CH_2$ and $CH_3$ of isophorone unit). The aliphatic region of IPI in the region δ 3.68-3.89 (1H, *m*, NCH) and 2.69-2.99 (2H, *m*, $NCH_2$) could not be clearly observed due to large peaks of $H_2O$ in DMSO. In BPB-MDI sprectrum, the aromatic protons showed peaks due to the bromphenol blue unit in the same chemical shift range observed in bromphenol blue at δ 8.00 (1H, *d*, Ar-H, *J* = 7.6 Hz), 7.53 (4H, *s*, Ar-H), 7.49 (1H, *t*, Ar-H, *J* = 8.2 Hz), 7.43 (1H, *t*, Ar-H, *J* = 7.4 Hz), 7.01-7.14 (4H, *m*, Ar-H), which overlapped with the peaks from MDI protons. The aromatic and aliphatic peaks due to MDI were observed at 7.18-7.30 (4H, *m*, Ar-H), 7.01-7.14 (4H, *m*, Ar-H, which this chemical shift range overlapping with proton of BPB) and 3.79-3.98 (2H, *m*, $CH_2$), respectively.

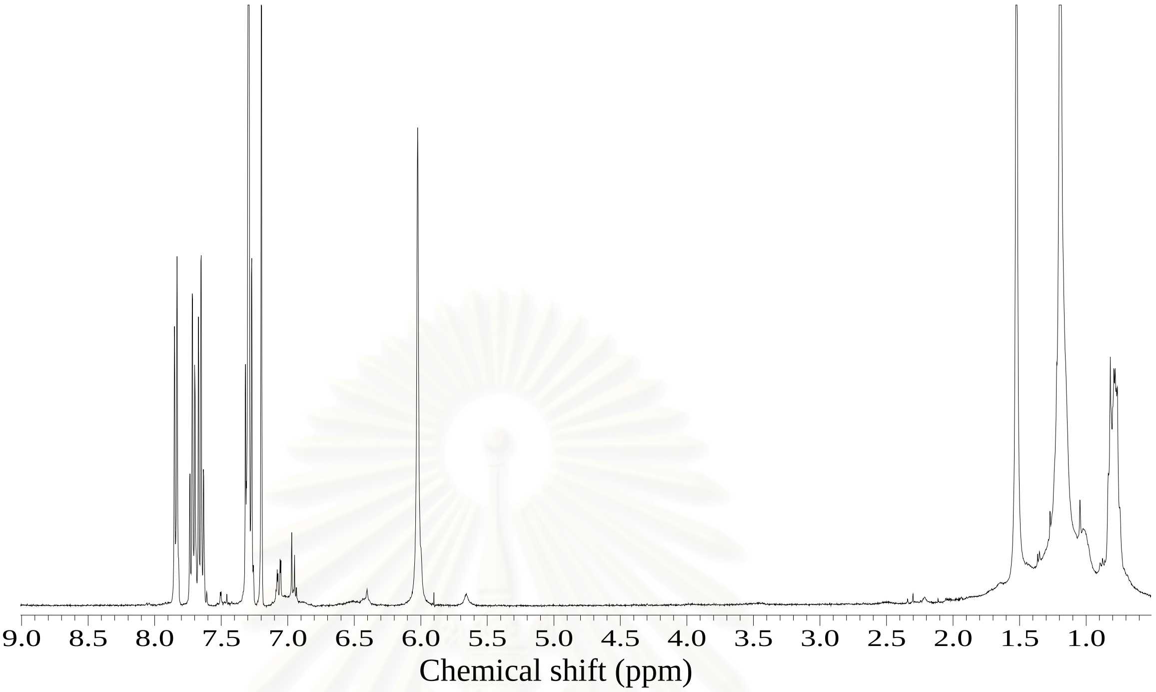


**Figure 3.16** $^1$H-NMR spectrum of BPB in $CDCl_3$

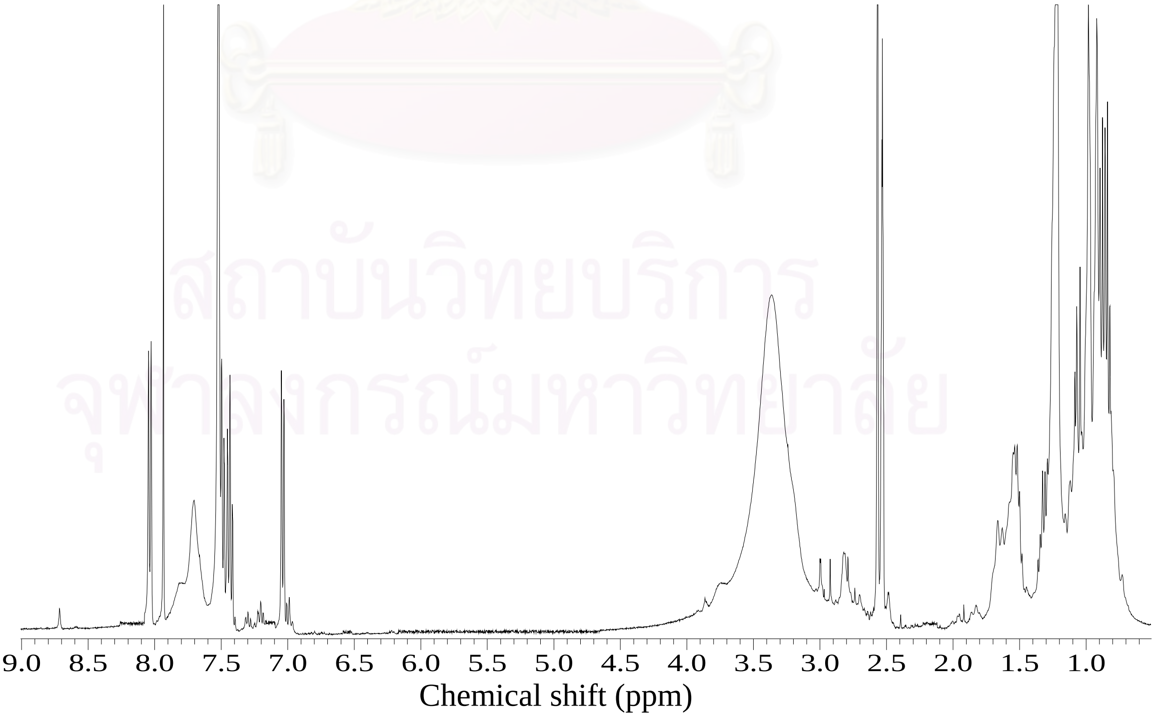


**Figure 3.17** $^1$H-NMR spectrum of BPB-IPI in $CDCl_3$: DMSO-$d_6$

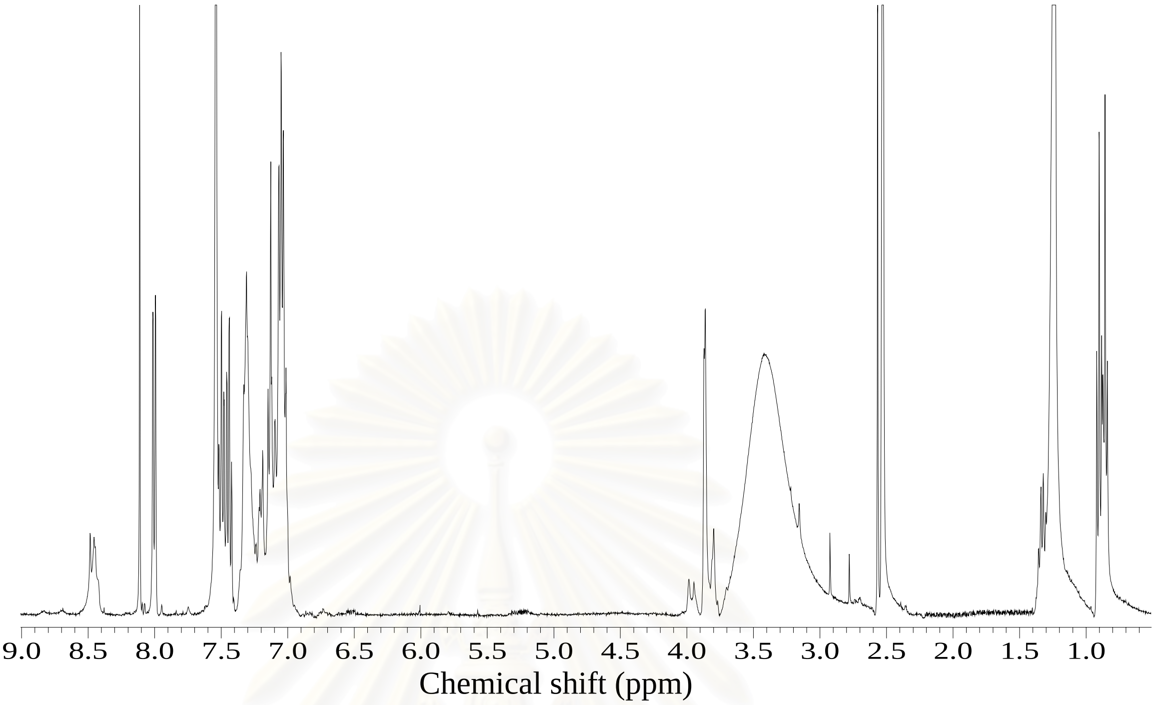


**Figure 3.18** $^{1}$H-NMR spectrum of BPB-MDI in $CDCl_3$: DMSO-$d_6$

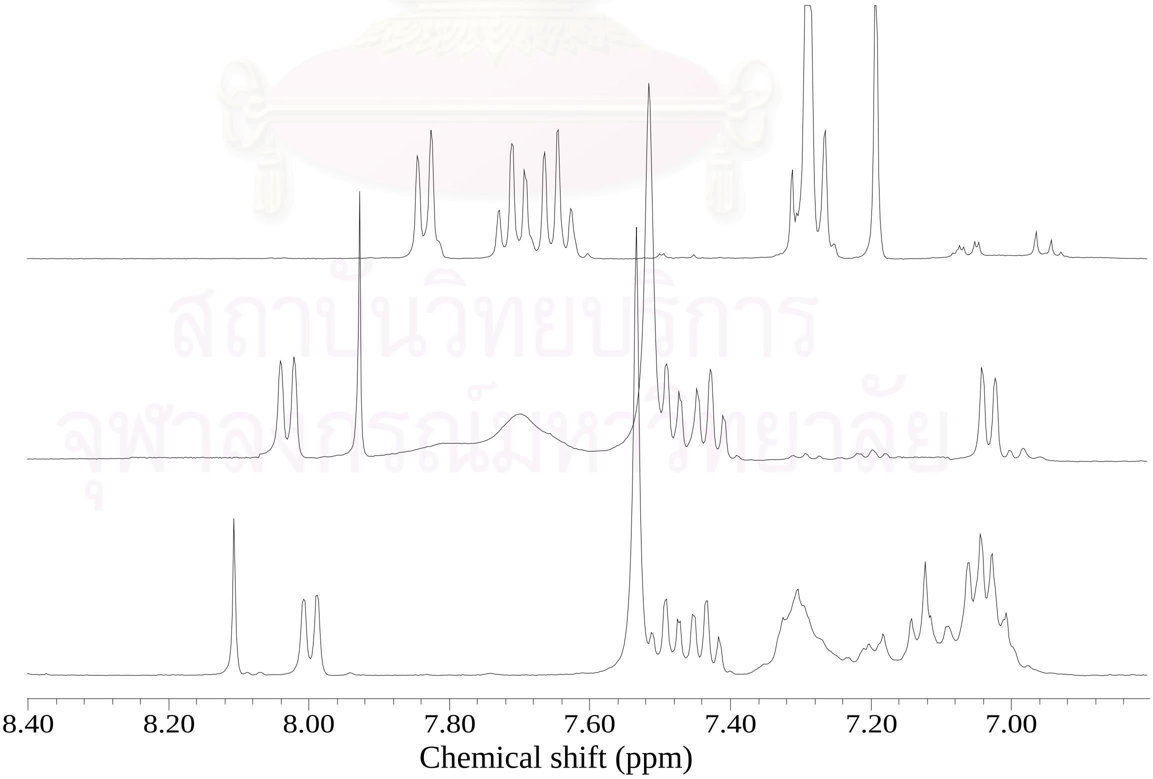


**Figure 3.19** $^{1}$H-NMR spectra of BPB, BPB-IPI and BPB-MDI in aromatic region

**Table 3.3** $^1$H NMR data of heterocycles, polyureas and polyurethanes containing heterocycles

| heterocycles and Polyureas | Characteristic signals |
|---|---|
| PF | 8.30 (1H, *s*, Ar-H), 7.59 (2H, *d*, Ar-H, *J* = 9.4 Hz), 6.87 (2H, *d*, Ar-H, *J* = 9.4 Hz), 6.81 (2H, *s*, Ar-H), 5.83 (4H, *br*, NH$_2$) |
| PF-IPI | 8.25 (1H, *s*, Ar-H), 7.57 (2H, *d*, Ar-H, *J* = 9.2 Hz), 6.87 (2H, *d*, Ar-H, *J* = 9.2 Hz), 6.84 (2H, *s*, Ar-H), 5.57 (4H, *s*, NHCO), 3.63-3.84 (1H, *m*, NCH), 2.63-2.92 (2H, *m*, NCH$_2$), 0.78-1.70 (15H, *m*, CH$_2$ and CH$_3$ of isophorone unit) |
| PF-MDI | 7.64-8.83 (3H, *m*, Ar-H), 7.32-7.44 (4H, *m*, Ar-H), 7.00-7.18 (4H, *m*, Ar-H ), 6.03-6.86 (4H, *m*, Ar-H), 3.69-3.84 (2H, *m*, CH$_2$) |
| NF | 6.48-7.02 (9H, *m*, Ar-H), 4.15-4.70 (1H, *m*, NH), 3.82 (4H, *br*, NH$_2$), 2.01-2.20 (9H, *m*, CH$_3$) |
| NF-IPI | 5.60-7.74 (9H, *m*, Ar-H), 3.61-3.80 (1H, *m*, NCH), 2.61-2.93 (2H, *m*, NCH$_2$), 0.77-2.27 (24H, *m*, CH$_2$ and CH$_3$ of isophorone and NF units) |
| NF-MDI | 6.48-7.85 (9H, *m*, Ar-H), 7.34-7.36 (4H, *m*, Ar-H), 7.10-7.12 (4H, *m*, Ar-H), 3.68-3.81 (2H, *m*, CH$_2$), 1.92-2.39 (9H, *m*, CH$_3$) |
| BPB | 7.84 (1H, *d*, Ar-H, *J* = 8.0 Hz), 7.71 (1H, *t*, Ar-H, *J* = 7.0 Hz), 7.64 (1H, *t*, Ar-H, *J* = 7.6 Hz), 7.26-7.31 (1H, *m*, Ar-H), 7.29 (4H, *s*, Ar-H), 6.02 (2H, *br*, OH) |
| BPB-IPI | 8.03 (1H, *d*, Ar-H, *J* = 7.6 Hz), 7.52 (4H, *s*, Ar-H), 7.49 (1H, *t*, Ar-H, *J* = 6.8 Hz), 7.43 (1H, *t*, Ar-H, *J* = 7.4 Hz), 7.03 (1H, *d*, Ar-H, *J* = 8.0 Hz), 1.49-1.66 (3H, *m*, CH$_2$), 0.81-1.11 (17H, *m*, CH$_2$ and CH$_3$ of isophorone unit) |
| BPB-MDI | 8.00 (1H, *d*, Ar-H, *J* = 7.6 Hz), 7.53 (4H, *s*, Ar-H), 7.49 (1H, *t*, Ar-H, *J* = 8.2 Hz), 7.43 (1H, *t*, Ar-H, *J* = 7.4 Hz), 7.18-7.33 (4H, *m*, Ar-H), 7.01-7.14 (5H, *m*, Ar-H of BPB and MDI units), 3.79-3.98 (2H, *m*, CH$_2$) |

### 3.3.3 UV-visible analysis

#### 3.3.3.1 UV-visible spectra of polyureas and polyurethane-ureas containing proflavine units

UV-visible spectra and absorption data of proflavine and the polymers based on proflavine are shown in Figure 3.20 and Table 3.4, respectively. The absorption maxima of PF was 411 nm. For PF-IPI, there was two absorption maxima at 411 and 464 nm. The absorption maxima of PF-MDI, PF-PB900 and PF-PP1000 were 393, 394 and 394 nm, respectively. Compared with their dye monomer (PF) and the polymers based on PF, PF-MDI, PF-PB900 and PF-PP1000 showed a slight hypsochromic shift, except PF-IPI that showed bathochromic shift.

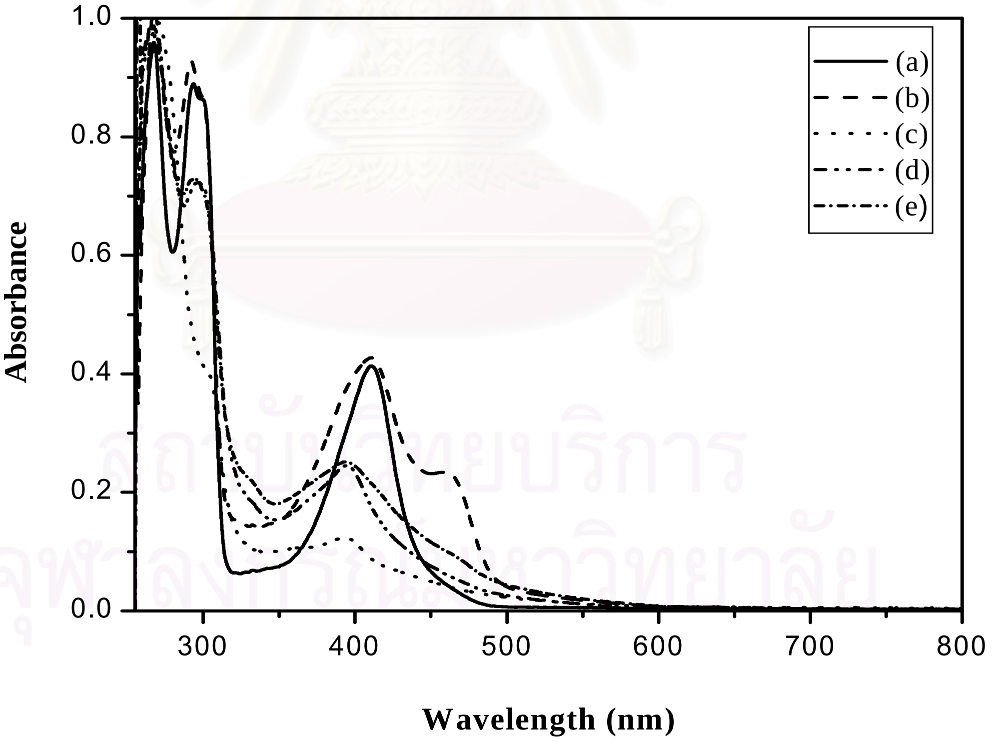


**Figure 3.20** UV-visible spectra of polyureas and polyurethane-ureas containing proflavine units: (a) proflavine; (b) PF-IPI; (c) PF-MDI; (d) PF-PB900; (e) PF-PP1000

### 3.3.3.2 UV-visible spectra of polyureas and polyurethane-ureas containing new fuchsin units

UV-visible spectra and absorption data of new fuchsin and the polymers based on new fuchsin are shown in Figure 3.21 and Table 3.4, respectively. The absorption maxima of NF was 565 nm. Compared with their dye monomer (NF) and the polymers based on NF, NF-IPI and NF-MDI showed a slight hypsochromic shift, that is, the absorption maxima of NF-IPI and NF-MDI were 555 and 557 nm. For NF-PB900 and NF-PP1000, the absorption maxima were 565 and 565 nm, respectively, which was the same as that of NF.

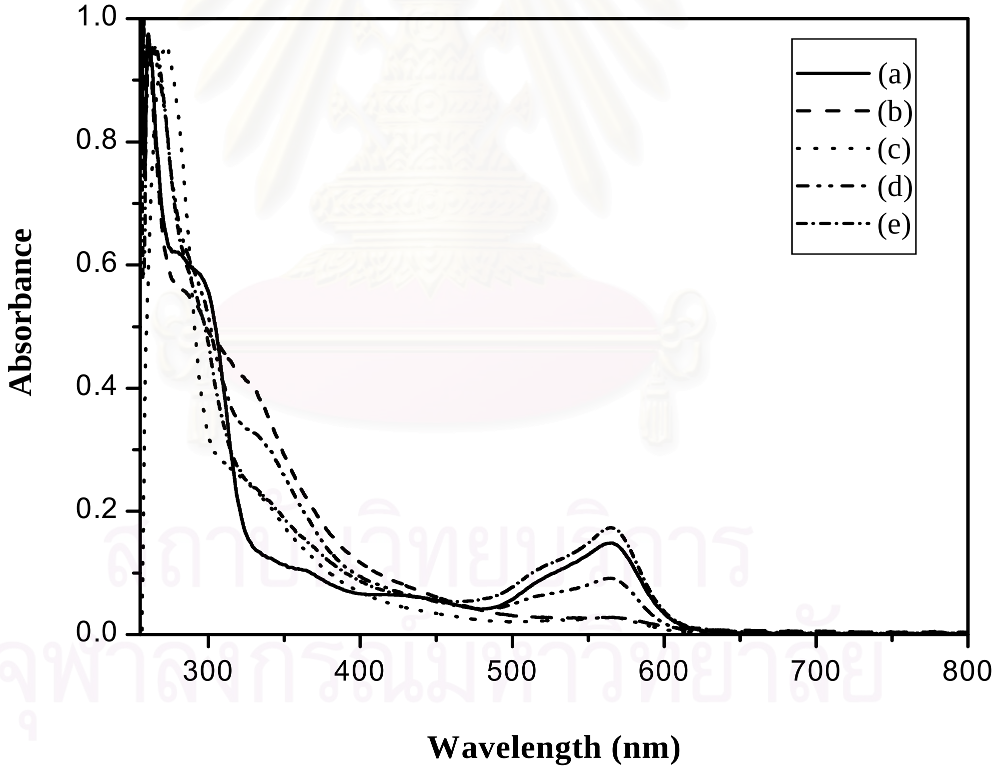


**Figure 3.21** UV-visible spectra of polyureas and polyurethane-ureas containing new fuchsin units: (a) new fuchsin; (b) NF-IPI; (c) NF-MDI; (d) NF-PB900; (e) NF-PP1000

### 3.3.3.3 UV-visible spectra of polyurethanes containing bromphenol blue units

UV-visible spectra and absorption data of bromphenol blue and the polymers based on bromphenol blue are shown in Figure 3.22 and Table 3.4, respectively. The absorption maxima of BPB was 424 and 605 nm. Compared with their dye monomer (BPB) and the polymers based on BPB, all polymers showed bathochromic shift, that is, the absorption maxima of BPB-IPI, BPB-MDI, BPB-PB900 and BPB-PP1000 were 605, 603, 604 and 603 nm, respectively.

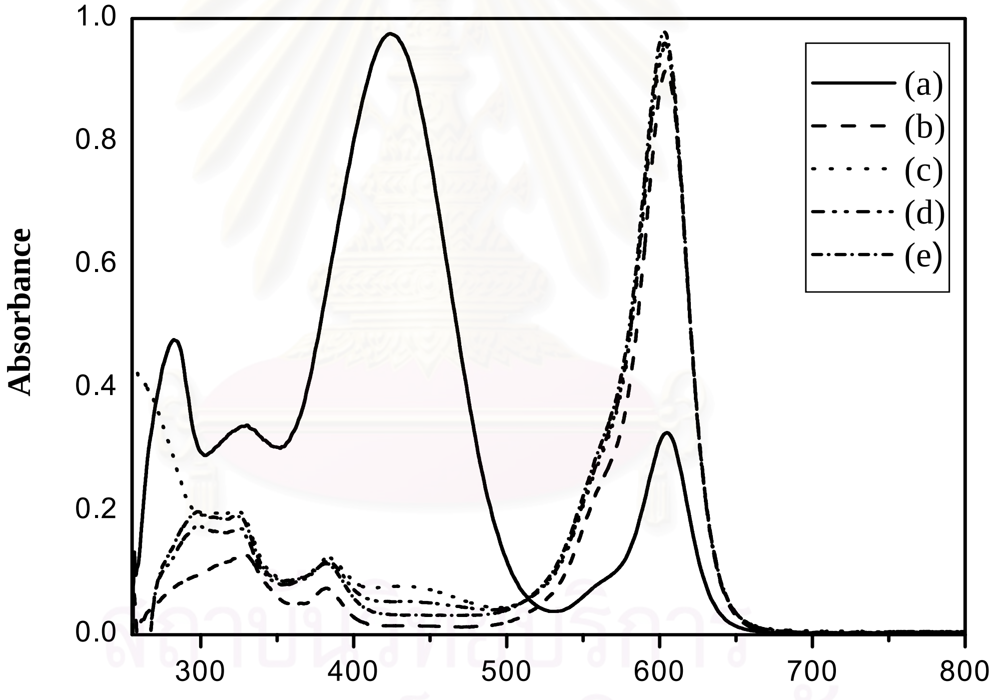


**Figure 3.22** UV-visible spectra of polyurethanes containing bromphenol blue units: (a) bromphenol blue; (b) BPB-IPI; (c) BPB-MDI; (d) BPB-PB900; (e) BPB-PP1000

**Table 3.4** UV-visible maximum absorption data of polyureas, polyurethanes, polyurethane-ureas containing heterocycles and heterocycles

| **Codes** | **Wavelength (nm)** |
|---|---|
| PF | 411 |
| PF-IPI | 411, 464 |
| PF-MDI | 393 |
| PF-PB900 | 394 |
| PF-PP1000 | 394 |
| NF | 565 |
| NF-IPI | 555 |
| NF-MDI | 557 |
| NF-PB900 | 565 |
| NF-PP1000 | 565 |
| BPB | 424, 605 |
| BPB-IPI | 605 |
| BPB-MDI | 603 |
| BPB-PB900 | 604 |
| BPB-PP1000 | 603 |

### 3.3.4 Thermal analysis

#### 3.3.4.1 Polyureas and polyurethane-ureas containing proflavine units

TGA curves and weight loss data of proflavine, polyureas and polyurethane-ureas containing proflavine units are presented in Figure 3.23 and Table 3.5, respectively. Initial decomposition temperature (IDT) of the polyureas and polyurethane was found to be in the range 277-327°C. Initial decomposition temperature (IDT) of proflavine was found to be at 354°C. The 10% weight loss of PF and polymers based on PF was found in the range 390°C and 302-336°C, respectively. The residual weight percentages at 600°C of PF, PF-IPI, PF-MDI and PF-PB900 were 71%, 45%, 59% and 27%, respectively.

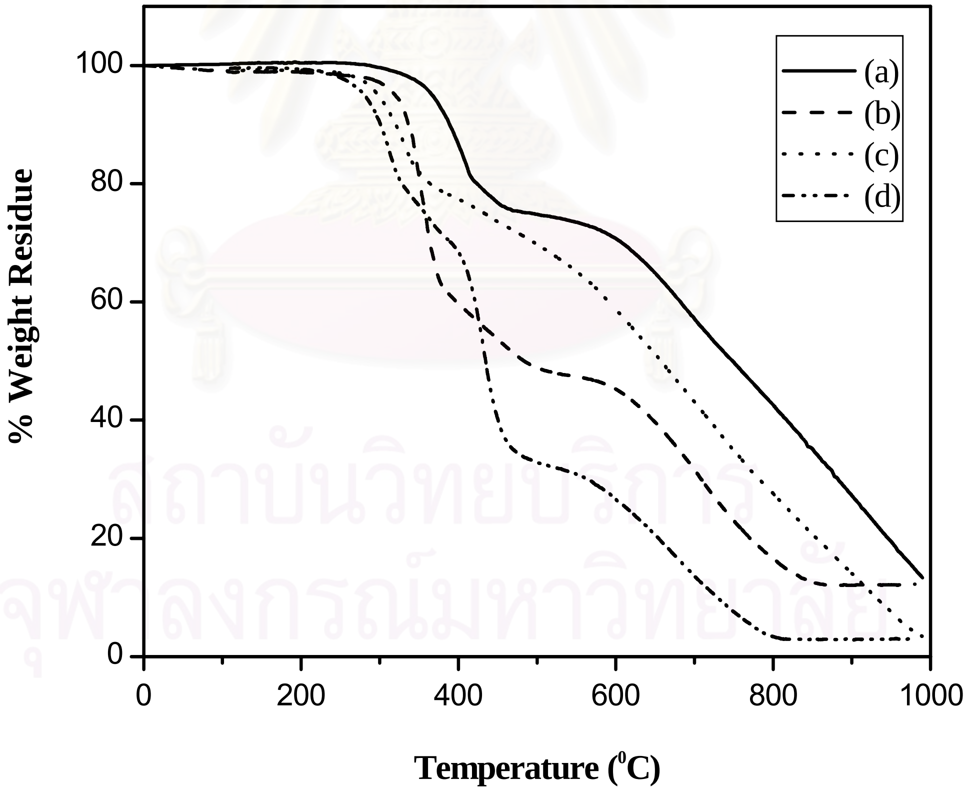


**Figure 3.23** TGA thermograms of (a) PF; (b) PF-IPI; (c) PF-MDI; (d) PF-PB900

**Table 3.5** TGA data of proflavine, polyureas and polyurethane-ureas containing proflavine units

| **Codes** | **IDTs** | **Weight loss (%) at various temperature ($^{o}$C)** | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **(°C)** | **300** | **400** | **500** | **600** | **700** | **800** | **900** |
| PF | 354 | 0 | 13 | 25 | 29 | 43 | 57 | 73 |
| PF-IPI | 327 | 3 | 40 | 51 | 55 | 69 | 84 | 88 |
| PF-MDI | 286 | 5 | 23 | 30 | 41 | 57 | 72 | 86 |
| PF-PB900 | 277 | 10 | 32 | 67 | 73 | 86 | 97 | 97 |

TGA thermograms showed that proflavine showed higher thermal stability than the polymers containing proflavine units. Among all proflavine-based polymers, PF-MDI was the most stable at high temperature because of the presence of aromatic rings in the main chain of the polymer. PF-IPI was slightly more stable than PF-PB900. PF-PB900 showed the lowest stable at high temperature because of the presence of aliphatic part in the main chain of the polymer.

#### 3.3.4.2 Polyureas and polyurethane-ureas containing new fuchsin units

TGA curves and weight loss data of new fuchsin, polyureas and polyurethane-ureas containing new fuchsin units are presented in Figure 3.24 and Table 3.6, respectively. Initial decomposition temperature (IDT) of the polyureas and polyurethane was found to be in the range 240-257°C. Initial decomposition temperature (IDT) of new fuchsin was found to be at 158°C. The 10% weight loss of NF and polymers based on NF was found in the range 432°C and 284-296°C, respectively. The residual weight percentages at 600°C of NF, NF-IPI, NF-MDI, NF-PB900 were 46%, 29%, 62% and 27%, respectively.

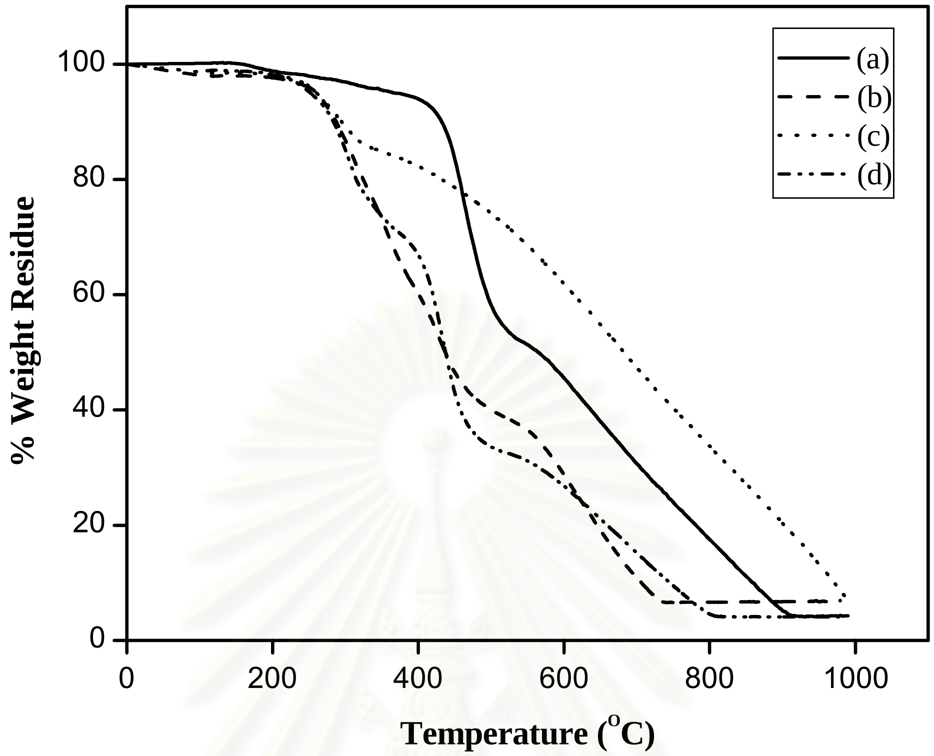


**Figure 3.24** TGA thermograms of (a) NF; (b) NF-IPI; (c) NF-MDI; (d) NF-PB900

**Table 3.6** TGA data of new fuchsin, polyureas and polyurethane-ureas containing new fuchsin units

| Codes | IDTs | Weight loss (%) at various temperature ($^oC$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | (°C) | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
| NF | 158 | 3 | 6 | 42 | 54 | 69 | 82 | 95 |
| NF-IPI | 257 | 13 | 40 | 60 | 71 | 89 | 93 | 93 |
| NF-MDI | 240 | 11 | 18 | 26 | 38 | 53 | 66 | 80 |
| NF-PB900 | 255 | 15 | 33 | 66 | 73 | 85 | 95 | 96 |

TGA thermograms showed that new fuchsin showed higher thermal stability than the polymers containing new fuchsin units except NF-MDI. Among all new fuchsin-based polymers, NF-MDI was the most stable at high temperature because of the presence of aromatic rings in the main chain of the polymer. NF-IPI showed the same thermal stability as NF-PB900.

### 3.3.4.3 Polyurethanes containing bromphenol blue units

TGA curves and weight loss data of bromphenol blue and polyurethanes containing bromphenol blue units are presented in Figure 3.25 and Table 3.7, respectively. Initial decomposition temperature (IDT) of the polyurethanes was found to be in the range 230-273°C. Initial decomposition temperature (IDT) of bromphenol blue was found to be at 258°C. The 10% weight loss of BPB and polymers based on BPB was found in the range 288°C and 246-286°C, respectively. The residual weight percentages at 600°C of BPB, BPB-IPI, BPB-MDI, BPB-PB900 were 29%, 24%, 37% and 25%, respectively.

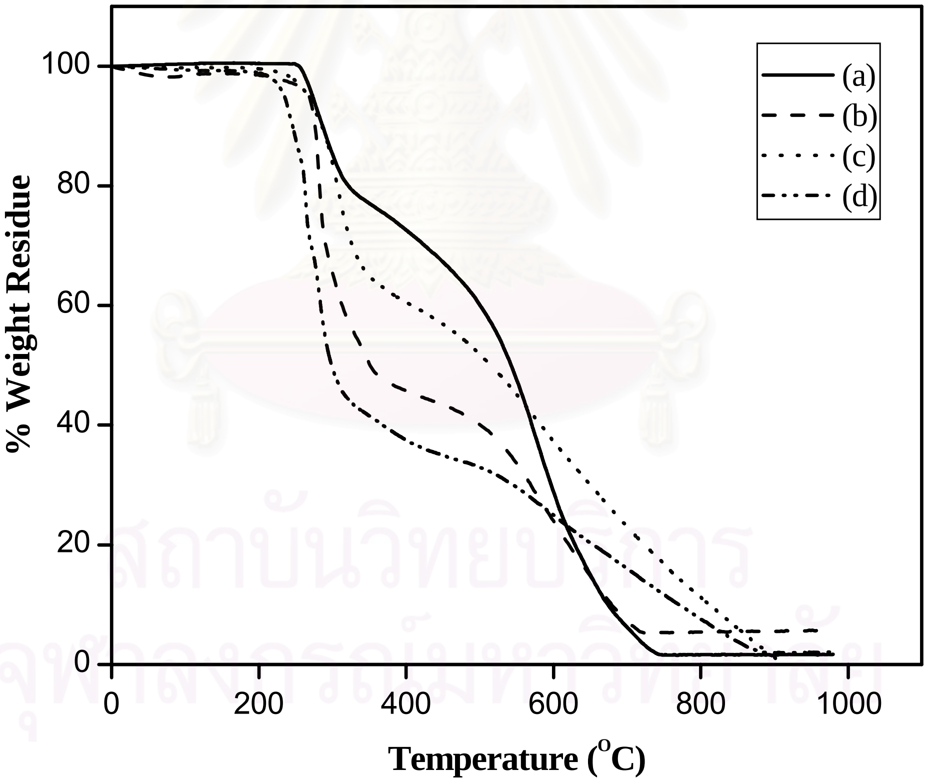


**Figure 3.25** TGA thermograms of (a) BPB; (b) BPB-IPI; (c) BPB-MDI; (d) BPB-PB900

**Table 3.7** TGA data of bromphenol blue and polyurethanes containing bromphenol blue units

| Codes | IDTs (°C) | Weight loss (%) at various temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
| BPB | 258 | 15 | 27 | 40 | 71 | 94 | 98 | 98 |
| BPB-IPI | 273 | 35 | 54 | 60 | 76 | 93 | 95 | 95 |
| BPB-MDI | 273 | 16 | 39 | 48 | 63 | 77 | 89 | 99 |
| BPB-PB900 | 230 | 51 | 63 | 67 | 75 | 84 | 92 | 98 |

TGA thermograms showed that bromphenol blue showed higher thermal stability than the polymers containing bromphenol blue units at low temperature, however, bromphenol blue less thermal stability than polyurethanes at high temperature. Among all bromphenol blue-based polymers, BPB-MDI was the most stable at high temperature because of the presence of aromatic rings in the main chain of the polymer. BPB-IPI showed the same thermal stability as BPB-PB900.

Among all of polymers, the polymers obtained from PF and NF are more thermally stable than the polymers obtained from BPB. This was because polyureas are more stability than polyurethanes. At the same polyurethanes, the polymers obtained from series-BPB are less thermal stability than the polymers obtained from series-PF and series-NF. This was because chemical structure of PF and NF are more stability than BPB. The thermal stability of the polymers obtained from series-PF was similar to the polymers obtained from series-NF.

Comparing with the hybrid foams based on cyclophosphazines and polyurethanes synthesis from polyols, cyclotriphosphazine and 4,4'-diphenylmethane diisocyanate [15], 10% weight loss of hybrid foams are about 300-323°C in $N_2$, and the char yield at 600°C are about 34-59%.

### 3.3.5 Solubility

Solubility of heterocyclic polyureas, polyurethanes, polyurethane-ureas and heterocycles was tested in various polar and non-polar solvents (Table 3.8).

**Table 3.8** Solubility of heterocyclic polyureas, polyurethanes, polyurethane-ureas and heterocycles [a]

| **Polymers** | **Hexane** | **Toluene** | **Diethyl ether** | **THF** | **$CH_2Cl_2$** | **$CHCl_3$** | **DMF** | **DMSO** | **MeOH** | **$H_2O$** |
|---|---|---|---|---|---|---|---|---|---|---|
| **PF** | -+ | -+ | -+ | ++ | -+ | -+ | ++ | ++ | + | -+ |
| **PF-IPI** | - | -+ | -+ | -+ | -+ | -+ | ++ | ++ | -+ | - |
| **PF-MDI** | - | -+ | -+ | -+ | -+ | -+ | -+ | + | -+ | - |
| **PF-PB900** | - | -+ | ++ | ++ | ++ | ++ | ++ | ++ | -+ | - |
| **PF-PP1000** | - | -+ | -+ | -+ | -+ | -+ | ++ | ++ | -+ | - |
| **NF** | -+ | -+ | -+ | ++ | -+ | -+ | ++ | ++ | ++ | -+ |
| **NF-IPI** | - | -+ | -+ | -+ | -+ | -+ | ++ | ++ | -+ | - |
| **NF-MDI** | - | -+ | -+ | -+ | -+ | -+ | -+ | + | -+ | - |
| **NF-PB900** | - | -+ | ++ | ++ | ++ | ++ | ++ | ++ | ++ | - |
| **NF-PP1000** | - | -+ | ++ | ++ | ++ | ++ | ++ | ++ | ++ | - |
| **BPB** | -+ | -+ | ++ | ++ | ++ | -+ | ++ | ++ | ++ | ++ |
| **BPB-IPI** | - | -+ | -+ | -+ | -+ | -+ | ++ | ++ | ++ | - |
| **BPB-MDI** | - | -+ | -+ | -+ | -+ | -+ | ++ | ++ | -+ | - |
| **BPB-PB900** | - | -+ | ++ | ++ | ++ | ++ | ++ | ++ | ++ | - |
| **BPB-PP1000** | - | -+ | ++ | ++ | ++ | ++ | ++ | ++ | ++ | - |

**-,** Insoluble; -+, Partial soluble; +, Soluble on heating; ++, Soluble

[a] 10 mg sample was dissolved in 2 ml of a solvent

All heterocycles were soluble in THF, DMF, DMSO and MeOH but partially soluble in *n*-hexane and toluene. Both PF and NF were soluble in THF, DMF, DMSO and MeOH but partially soluble in *n*-hexane, toluene, diethyl ether, $CHCl_3$, $CH_2Cl_2$ and water. BPB were soluble in diethyl ether, THF, $CH_2Cl_2$, DMF, DMSO, MeOH and water but partially soluble in *n*-hexane, toluene and $CHCl_3$. Among all heterocycles, the order of solubility was BPB > NF > PF.

All heterocyclic polyureas, polyurethanes and polyurethane-ureas were soluble in DMSO but insoluble in *n*-hexane and water. Within the same series of both PF and NF, the solubility of polyureas was less than that of polyurethane-ureas. This is because polyurethane-ureas were synthesized from PB900 and PP1000, which contain flexible aliphatic ether units. The heterocyclic polyurethane-ureas with good solubility, namely PF-PB900, NF-PB900 and NF-PP1000, except PF-PP1000, were also soluble in various solvents such as diethyl ether, THF, $CHCl_3$, $CH_2Cl_2$, DMF and DMSO but partially soluble in toluene. PF-PP1000 was soluble in DMF and DMSO but partially soluble in toluene, diethyl ether, THF, $CHCl_3$, $CH_2Cl_2$ and MeOH. For heterocyclic polyureas in the same series of both PF and NF, the solubility of the MDI-based polyureas was less than that of the IPI-based polyureas because of the presence of aromatic rings in the main chain of the polyurea-based MDI. The MDI-based polyureas, namely PF-MDI and NF-MDI were soluble in DMSO but partially soluble in toluene, diethyl ether, THF, $CHCl_3$, $CH_2Cl_2$, MeOH and DMF. The IPI-based polyureas, namely PF-IPI and NF-IPI were soluble in DMF and DMSO but partially soluble in toluene, diethyl ether, THF, $CHCl_3$, $CH_2Cl_2$, MeOH. For heterocyclic polyurethanes based on bromphenol blue, the order of solubility was the MDI-based polyurethanes < IPI-based polyurethanes < prepolymer-based polyurethanes. This result could be explained using the same reason as described above. Among all polymers, the order of solubility was BPB series > NF series > PF series.

From these results, which the polymer can soluble in non polar sovent, it concluded that the obtained polymer may be the mixture of heterocycles, oligomer and polymer.

### 3.3.6 Inherent viscosity

Inherent viscosity of heterocyclic polyureas, polyurethanes and polyurethane-ureas was measured at 40°C in DMSO. The viscosity data of all polymers are given in Table 3.9. Inherent viscosity value of the polymers was in the range 0.09-0.35. From the work of Liu and Ma [21], the viscosity of polyurethane-imide copolymers with multiple hard segments (MHPUI) was found to be in the range between 0.34-0.63 dL/g. To compare with heterocyclic polyureas, polyurethanes and polyurethane-ureas which higher than those of the heterocyclic polyureas, polyurethanes and polyurethane-ureas.

In comparison between the polymer obtained from different heterocycles, the inherent viscosity increases in the order NF > PF > BPB.

#### 3.3.6.1 Inherent viscosity of polyureas and polyurethane-ureas containing proflavine units

The inherent viscosity value of polyureas and polyurethane-ureas containing heterocycle from proflavine and diisocyanates is shown in Table 3.9. The diisocyanates used were IPI, MDI, PB900 and PP1000. The inherent viscosity value of the polymers depend on molecular weight and steric effect. If the molecular weight of diisocyanate increased, the inherent viscosity of polymers would also increase. It was found that the order of inherent viscosity value of polyureas and polyurethane-ureas containing heterocycle from proflavine and diisocyanates based on IPI, MDI, PB900 and PP1000 is PP1000 > PB900 > MDI > IPI. The inherent viscosity of propylene glycol prepolymer-based polymers was higher than that of 1,4-butanediol prepolymer-based polymers. The higher inherent viscosity was due to the propylene glycol prepolymer-based polymers had more steric effect than 1,4-butanediol prepolymer-based polymers. The polymers based on IPI show the lowest inherent viscosity value because of its low molecular weight.

### 3.3.6.2 Inherent viscosity of polyureas and polyurethane-ureas containing new fuchsin units

The inherent viscosity value of polyureas and polyurethane-ureas containing heterocycle from new fuchsin and diisocyanates is shown in Table 3.9. The diisocyanates used were IPI, MDI, PB900 and PP1000. The order of inherent viscosity value of polyureas and polyurethane-ureas containing heterocycle from new fuchsin and diisocyanates based on IPI, MDI, PB900 and PP1000 showed result in the same trend as in case of polyureas and polyurethane-ureas containing heterocycle from proflavine and diisocyanates as described in section 3.3.6.1.

### 3.3.6.3 Inherent viscosity of polyurethanes containing bromphenol blue units

The inherent viscosity value of polyurethanes containing heterocycle from bromphenol blue and diisocyanates is shown in Table 3.9. The diisocyanates used were IPI, MDI, PB900 and PP1000. The order of inherent viscosity value of polyurethanes containing heterocycle from bromphenol blue and diisocyanates based on IPI, MDI, PB900 and PP1000 followed the same trend as in case of polyureas and polyurethane-ureas containing heterocycle from proflavine and diisocyanates described in section 3.3.6.1.

**Table 3.9** Inherent viscosity of polyureas and polyurethanes containing heterocycles

| Polymers | $\eta_{inh}$(dL/g)[a] |
|---|---|
| PF-IPI | 0.1023 |
| PF-MDI | 0.2053 |
| PF-PB900 | 0.2057 |
| PF-PP1000 | 0.3508 |
| NF-IPI | 0.1291 |
| NF-MDI | 0.2956 |
| NF-PB900 | 0.3305 |
| NF-PP1000 | 0.2120 |
| BPB-IPI | 0.0974 |
| BPB-MDI | 0.1046 |
| BPB-PB900 | 0.1795 |
| BPB-PP1000 | 0.1950 |

[a] determined at a concentration of 0.5 g/100 ml in DMSO at 40°C

### 3.3.7 Flame retardancy

Flame retardancy property of heterocyclic polyureas, polyurethanes and polyurethane-ureas was investigated by measuring their limiting oxygen index (LOI) values as shown in Table 3.10. A polymer having an LOI greater than 21 does not burn in atmosphere since the oxygen content in atmosphere is 21%. The polymer with higher LOI is more flame retardant. LOI value of the polymers were in the range of 21-26. In comparison to the work reported by Modesti and coworkers [15], which described thermally stable hybrid foams based on cyclophosphazenes and polyurethanes, the obtained polymers exhibited higher LOI values in the range between 21 to 31.

It was found that the order of flame retardancy of polymers based on PF, NF and BPB is PF > NF = BPB. The polymers based on PF show slightly higher flame retardancy than polymers based on NF and BPB which might be due to the more stable aromatic system of PF.

**Table 3.10** Limiting oxygen index (LOI) value of heterocyclic polyureas, polyurethanes and polyurethane-ureas

| Polymers | LOI |
|---|---|
| PF-IPI | 21 |
| PF-MDI | 23.5 |
| PF-PB900 | 23.4 |
| PF-PP1000 | 22.3 |
| NF-IPI | 21 |
| NF-MDI | 21 |
| NF-PB900 | 22.1 |
| NF-PP1000 | 21 |
| BPB-IPI | 21 |
| BPB-MDI | 21 |
| BPB-PB900 | 22 |
| BPB-PP1000 | 21 |

# CHAPTER IV

# CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

## 4.1 Conclusion

The synthesis of heterocyclic polyureas, polyurethanes and polyurethane-ureas was done by the polymerization reactions of various heterocycles, namely proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB), with different diisocyanate compounds, namely isophorone diisocyanate (IPI), 4,4′-methylenebis (phenyl isocyanate) (MDI), tolylene 2,4-diisocynate terminated prepolymers (PB900 and PP1000). The mole ratio of heterocycles:diisocyanate used was 1:1 to avoid crosslinking of the polymers.

The reaction of isophorone diisocyanate (IPI) with various heterocycles, namely proflavine (PF), new fuchsin (NF) and bromphenol blue (BPB), have been investigated in order to obtain the information on the reactivity of diamine group or diol group in heterocyclic compounds towards diisocyanate group in the polymerization reaction. Their completeness of polymerization reaction was observed from the disappearance of isocyanate peak at 2275 cm$^{-1}$ by infrared spectroscopy. The obtained information in this step was utilized for the synthesis of heterocyclic polyureas, polyurethanes and polyurethane-ureas in the next step. The polymerization was done using DMSO as a solvent at 90°C in the presence of dibutyltin dilaurate as a catalyst.

The structure of polymers was characterized by IR, NMR and UV-visible spectroscopy. Physical properties of polymers investigated were inherent viscosity and solubility. It was found that all polymers were soluble in DMSO and the inherent viscosity of the polymers was found to be in the range 0.09-0.35 dL/g. Thermal and flame retardant properties of polymers were investigated by using thermogravimetric analysis and measuring limit oxygen index, respectively. Among all of polymers, heterocyclic polyureas showed the highest thermal stability. The MDI-based polyureas, namely PF-MDI and NF-MDI gave the best thermal stability with the char yield at 600°C of 59 and 62%, respectively. The polymers based on PF showed slightly higher flame retardancy than the polymers based on NF and BPB.

## 4.2 Suggestions for future work

The obtained polymers contained the mixture of the heterocyclic starting material, oligomer and polymer. Therefore, the suggestion for future work is to purify the polymers to remove the starting material and oligomer. The purification could be done by extraction of the product in refluxing organic solvents such as chloroform and methanol. It was found that the polyureas showed good thermal stability but poor solubility. The solubility of polyureas in organic solvents should be improved by the synthesis of copolymer from the reaction between diisocyanates, heterocycles and aromatic or aliphatic diol.

# REFERENCES

1. Jiang, B.; Hao, J.; Wang, W.; Jiang, L.; and Cai, X. Synthesis and thermal properties of poly(urethane-imide). J. Appl. Polym. Sci. 81 (2001); 773-781.
2. Sendijarevic, A.; Sendijarevic,V.; Frisch, K. C.; Korugalzarevic, B.; and Sodaso, E. T. Synthesis and properties of urethane-modified polyimides. J. Polym. Sci. A.: Polym. Chem. 25 (1990): 3603-3615.
3. Mallakpour, S.; and Khoee, S. Synthesis and characterization of new optically active poly(amide-imide-urethane) thermoplastic elastomers, derived from 4,4′-(hexafluoroisopropylidene)-*N*,*N*′-bis(phthaloyl-L-leucine-*p*-aminobenzoic acid) and PEG-MDI. J. Appl. Polym. Sci. 91 (2004): 2288-2294.
4. Zuo, M.; and Takeichi, T. Novel method for the preparation of poly(urethane-imide)s and their properties. J. Polym. Sci. A.: Polym. Chem. 35 (1997): 3745-3753.
5. Gnanarajan, T. P.; Nasar, A. S.; Iyer, N. P.; and Radhakrishnan, G. Synthesis of poly(urethane-imide) using aromatic secondary amine blocked polyurethane prepolymers. J. Polym. Sci. A.: Polym. Chem. 38 (2000); 4032-4037.
6. Masiulanis, B.; and Zielinski, R. Mechanical, thermal and electrical properties of polyurethaneimide elastomers. J. Appl. Polym. Sci. 30 (1985): 2731-2741.
7. Abu-Zeid, M. E.; Nofal, E. E.; Abdul-Rasoul, F. A.; Mahmoud, G. S.; and Ledwith, A. Photoacoustic study of thermal degradation of polyurethane. J. Appl. Polym. Sci. 28 (1983): 2317-2324.
8. Mehdipour-Ataei, S.; and Keshavarz, S. Use of diimide-dinaphthols in preparation of novel thermally stable poly(ester-imide)s. J. Appl. Polym. Sci. 88 (2003): 2168-2172.

9. Mehdipour-Ataei, S.; and Keshavarz, S. Use of new diimide-dinaphthols in preparation of novel thermally stable poly(ester-imide)s. J. Appl. Polym. Sci. 89 (2003): 2567-2572.

10. Pielichowski, K.; Slotwinska D.; and Dziwinski, E. Segmented MDI/HMDI-based polyurethanes with lowered flammibility. J. Appl. Polym. Sci. 91 (2004): 3214-3224.

11. Mehdipour-Ataei, S.; and Heidari, H. Preparation of novel pyridine-based, thermally stable poly(ether-imide)s. J. Appl. Polym. Sci. 91 (2004): 22-26.

12. Behniafar, H.; Haghighat, S.; and Farzaneh, S. Direct synthesis of soluble and thermally stable poly(urethane-imide)s from a new triimide-dicarbonylazide. Polymer 46 (2005): 4627-4634.

13. Mehdipour-Ataei, S.; and Amirshaghaghi, A. Novel poly(amide-imide)s from 2,6-bis(5-amino-1-naphtoxy) pyridine. Eur. Polym. J. 40 (2004): 503-507.

14. Mehdipour-Ataei, S.; and Hatami, M. Synthesis and characterization of novel heat resistant poly(amide-imide)s. Eur. Polym. J. 41 (2005): 2010-2015.

15. Modesti, M.; Zanella, L.; Lorenzetti, A.; Bertani, R.; and Gleria, M. Thermally stable hybrid foams based on cyclophosphazenes and polyurethanes. Polym. Degrad. Stab. 87 (2005): 287-292.

16. Behniafar, H.; and Banihashemi, A. Synthesis and charaterization of new soluble and thermally stable aromatic poly(amide-imide)s based on *N*-[3,5-bis(*N*-trimellitoyl)phenyl]phthalimide. Eur. Polym. J. 40 (2004): 1409-1415.

17. Nair, P. R. K.; Nair, C. P.; and Francis, D. J. Imide-modified polyurethanes, syntheses, thermal and mechanical characteristic. J. Appl. Polym. Sci. 70 (1998): 1483-1491.

18. Nair, P. R. K.; Nair, C. P.; and Francis, D. J. Effect of imide-oxazolidinone modification on the thermal and mechanical properties of HTPB-polyurethanes. J. Appl. Polym. Sci. 71 (1999): 1731-1738.

19. Gajiwala, H. M.; and Zand, R. Synthesis and characterization of 3,6-diaminoacridine (proflavine) containing polyimides. Macromolecules 28 (1995): 481-485.

20. Patil, R. D.; and Gajiwala, H. M. Thermally stable imide oligomers from acridine yellow. Polymer 38 (1997): 4557-4562.

21. Liu, J.; and Ma, D. Study on synthesis and thermal properties of polyurethane-imide copolymers with multiple hard segments. J. Appl. Polym. Sci. 84 (2002): 2206-2215.

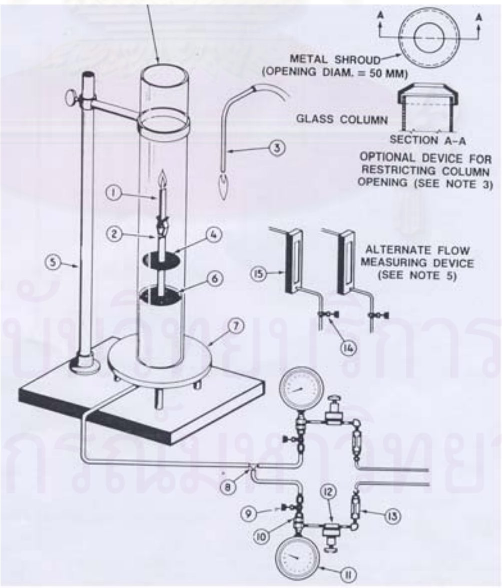
# APPENDICES

# APPENDIX A

## A-1 Limiting Oxygen Index (LOI)

**ASTM D2863-70:** the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature. The LOI method used for self-supporting samples has been modified as described below to accommodate the viscous of the powdery samples. The measurement was carried out as follows. About 1 g. of the polymer sample was placed in a glass cup (diameter 20 mm, height 10 mm) fitted to the specimen holder. An external flame of 20 mm length was maintained in contact, for 10 s, with the polymer. The LOI value was taken as the minimum percentages of oxygen required in a nitrogen-oxygen atmosphere, surrounding the sample, to maintain its combustion for at least 30 s after ignition. The LOI value was taken as the average of five experiments each.

### Apparatus



11. Burning Specimen
12. Clamp with Rod Support
13. Igniter
14. Wire Screen
15. Ring Stand

6. Glass Beads in a Bed
7. Brass Base
8. Tee
9. Cut-off valve
10. Orifice in Holder

1. Pressure Gage
2. Precision Pressure Regulator
3. Filter
4. Needle Valve
5. Rotameter

**Figure A.1** LOI apparatus

**Procedure**

1. Calibrate the flow-measuring system using a water-sealed rotalin drummter in accordance with Method D 1071.
2. The test shall be conducted at room temperature condition in accordance with Practice D 618.
3. Clamp the specimen vertically in the approximate center of the column.
4. Select the desired initial concentration of oxygen. If the specimen burns rapidly, start at a concentration of about 18 %.
5. Set the flow valves so that desired initial concentration of oxygen in flowing through the column.
6. Allow the gas to flow for 30 s to purge the system.
7. Ignition the entire top of the specimen with the ignition flame so that the specimen is well lighted. Remove the ignition flame and start the timer.
8. Do not adjust the oxygen concentration after ignition the specimen.
9. The concentration of oxygen must be raised if the flaming of the specimen extinguishes before meeting.
10. Perform the test at least three times.
11. Adjust the oxygen concentration, insert a new specimen.

# APPENDIX B

# B-1 DETERMINATION OF INHERENT VISCOSITY

**Inherent viscosity [$\eta_{inh}$] ASTM D2270:** Inherent viscosity is calculated from the dilute solution (1% or less) relative viscosity of the polymer. The inherent viscosity is calculated as:

The relative viscosity is given by:

$$\eta_{rel} = \frac{\text{solution flow time (t), sec}}{\text{solvent flow time } (t_0)\text{, sec}}$$

The inherent viscosity is calculated as:

$$\eta_{inh} = \ln \eta_{rel}/C$$

where

C = concentration of the polymer in grams per 100 ml of solvent; usually, C = 0.5 g/100 mL

$\ln\eta_{rel}$ = natural logarithm of the relative viscosity of the dilute polymer solution

K = 0.01431, $t_0$ = 98.97 sec, $Kt_0$ = 1.4163 sec

Relative viscosity can be taken as the ratio of the flow times of a polymer solution and the pure solvent in the same viscometer and at the same temperature. Relative viscosity values generally are used for calculating the intrinsic or inherent viscosity of a polymer. The solvent to be used will depend on the polymer solubility. In general, the solvent should completely dissolve the sample in less than 30 minutes. It is desirable that the polymer be dissolved at room temperature although, heating is permissible if no degradation occurs. Select the viscometer through which the solvent will flow in not less than 100 seconds and not more than 200 seconds.

# VITAE

Miss Nipaporn Suparattadet was born on May 26, 1980 in Nakornsawan, Thailand. She received the Bachelor Degree of Science majoring in Chemistry from Srinakarinwirot University in 2003. Then, she has been a graduate student studying in the field of Petrochemistry and Polymer Science at Chulalongkorn University and become a member of the Supramolecular Chemistry Research Unit under supervision of Associate Professor Dr. Nuanphun Chantarasiri. She graduated with a Master Degree of Science in Petrochemistry and Polymer Science in 2005.