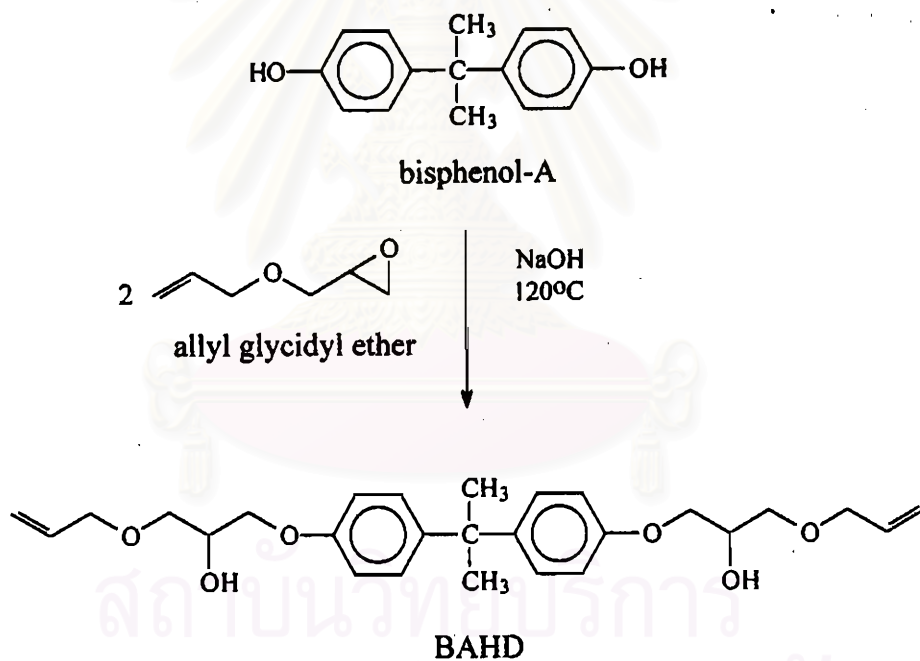


CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of BAPD

The synthesis of BAPD was carried out according to the procedure described in the literature[26-27]. The reaction involves the epoxide ring opening by a nucleophile as shown in Scheme 3.1. The structure of BAPD was characterized by ^1H NMR spectroscopy.



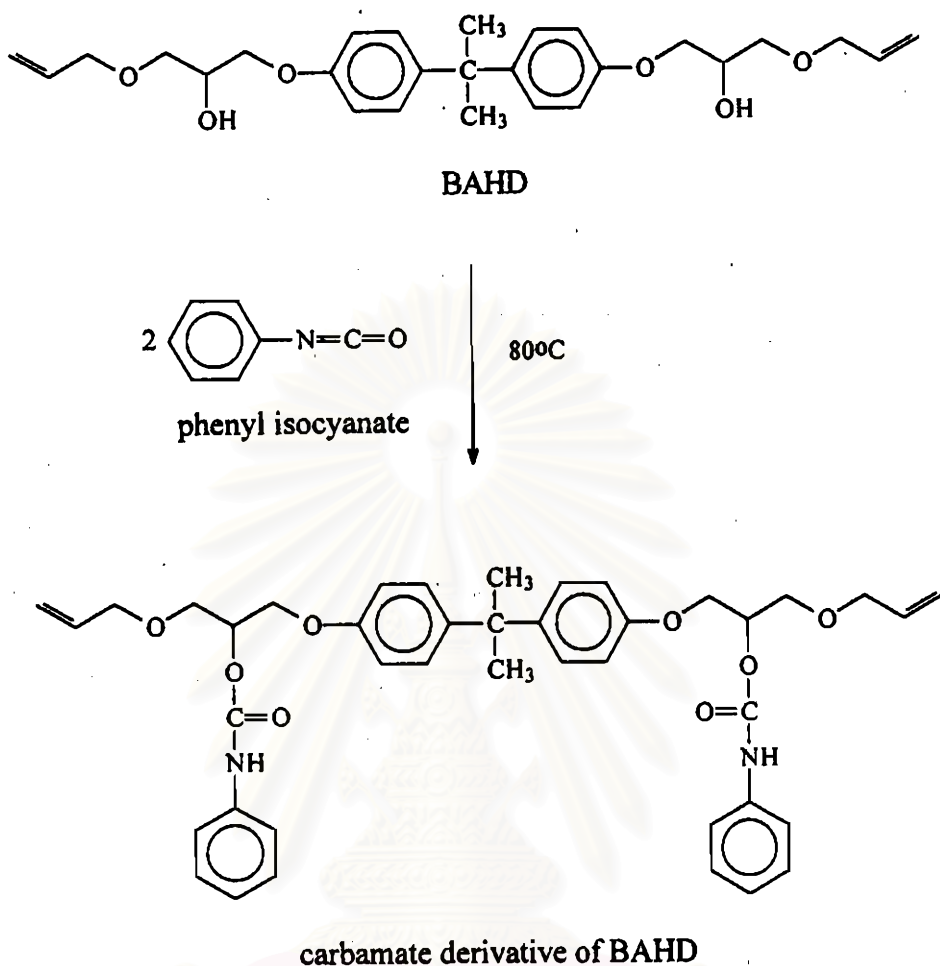
Scheme 3.1 Synthesis of Bis-(3-allyloxy-2-propanol) diphenylolpropane (BAPD)

The potential application of BAPD as a crosslinking agent for PU elastomer was also investigated[28-29]. The expected reactions were those of the hydroxyl groups with the isocyanate groups to create urethane linkages and free radical polymerization of vinyl groups to give polyvinyl linkages.

It was found that both hydroxyl groups in BAPD underwent a reaction with the isocyanate group in phenyl isocyanate to yield carbamate derivative of BAPD (Scheme 3.2). ^1H NMR spectrum of the carbamate derivative indicated that both hydroxyl groups were converted to carbamates. The presence of carbamate groups was also confirmed by ^{13}C NMR chemical shift at 152.7 ppm (C=O). In addition, the IR spectrum showed a characteristic absorption at 3295 and 1729 cm^{-1} associated with N-H stretching and C=O stretching, respectively.

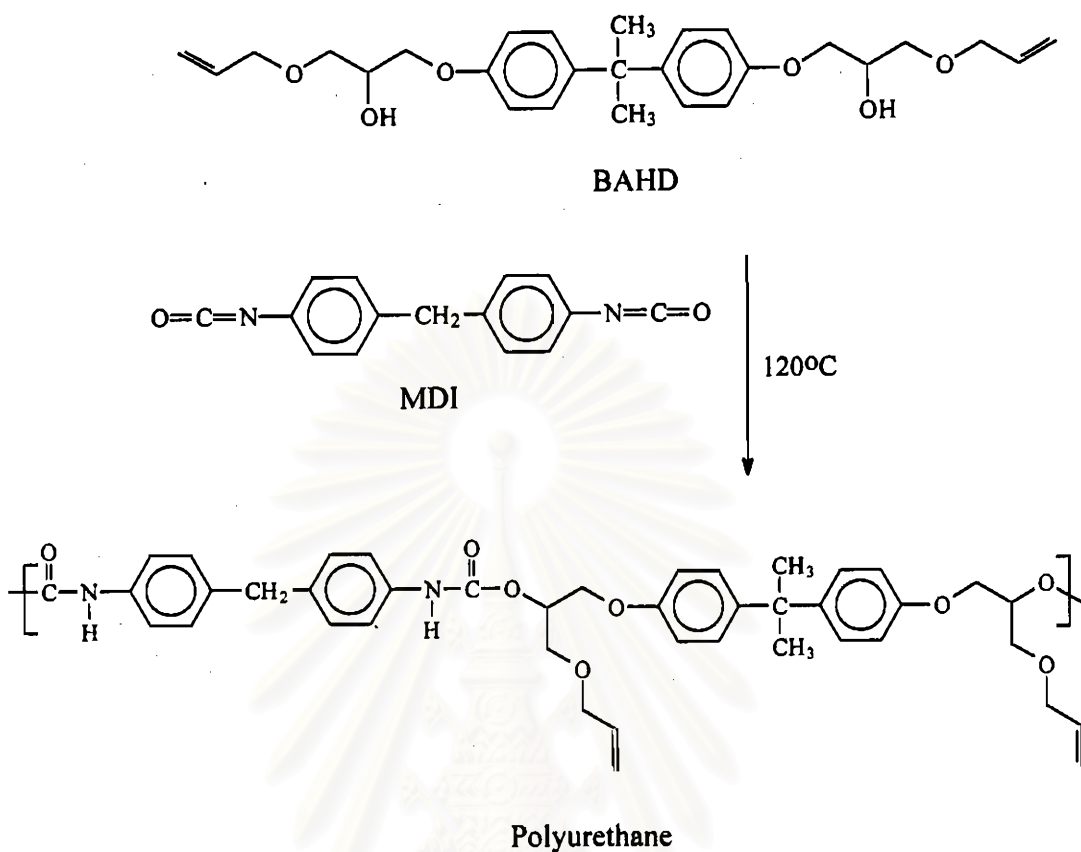


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Scheme 3.2 Reaction between BAPD and phenyl isocyanate [27]

Reaction between BAPD and MDI yielded polyurethane as shown in Scheme 3.3. The IR spectrum of the resulting polyurethane showed carbonyl stretching vibrations and N-H stretching vibrations of a urethane linkage at 1734 and 3402 cm^{-1} , respectively.



Scheme 3.3 Reaction between BAPD and MDI [27]

The reactivity of vinyl groups in BAPD was studied employing a reaction between BAPD and 5 mole % of benzoyl peroxide in the absence of solvent at 80°C. The progress of reaction was observed by comparison of the integration ratio of aromatic protons : olefinic protons in the ^1H NMR spectrum. It was found that as the reaction time increased, the integration ratio of aromatic proton:olefinic protons increased which indicated that the free radical reaction occurred at the vinyl groups of BAPD. Furthermore, the integration of allylic protons also decreased as the reaction time increased. This data suggested that the free radical reaction also occurred at the allylic carbon. Therefore, BAPD is expected to be suitable as a crosslinking agent for the

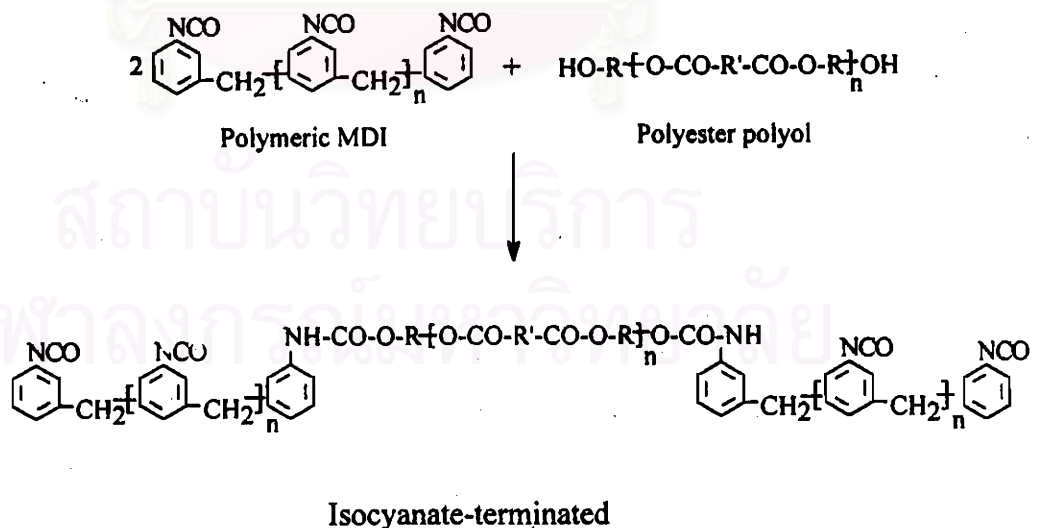
preparation of PU and PU/PS elastomers. The hydroxyl groups in BAPD should be able to react with isocyanate groups in MDI or polyurethane prepolymer, while the vinyl groups are expected to undergo free radical polymerization in the presence of a free radical initiator to give the elastomer with two phases, i.e. polyurethane and polyvinyl phases.

3.2 Preparation of PU Elastomers

In our study, PU elastomers were prepared from MDI and polyol by use of BAPD as a crosslinking agent in the presence of peroxide initiator. The reactions expected to occur during polymerization are shown as follows:

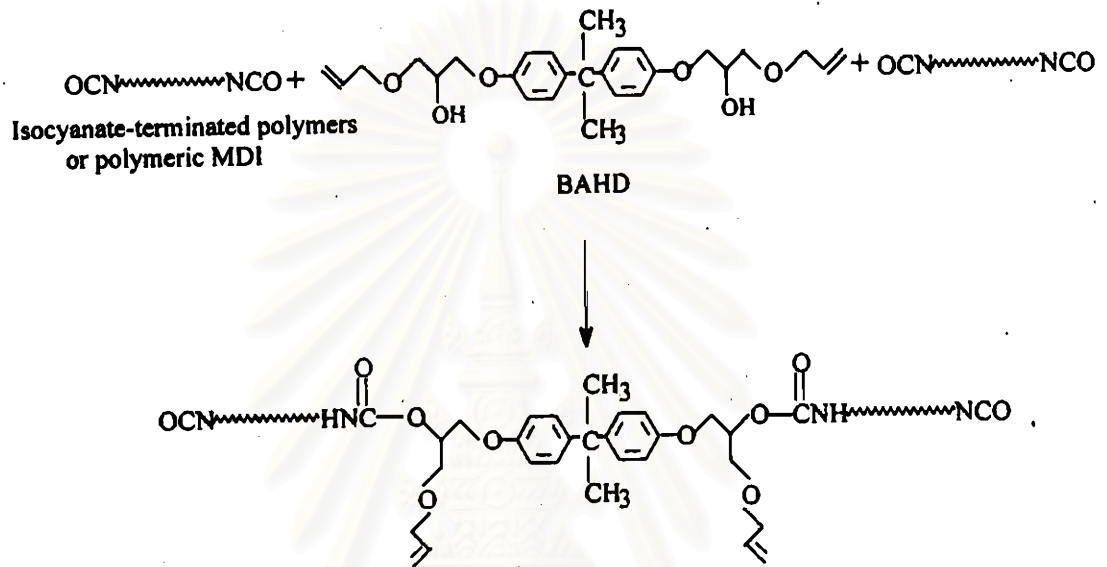
1. Reaction between hydroxyl groups in BAPD or polyol and isocyanate groups in MDI or isocyanated terminated polymers to give urethane linkages.

1.1 Reaction between polymeric MDI and polyol to give isocyanate-terminated polymers.



Scheme 3.4 Reaction between polymeric MDI and polyol

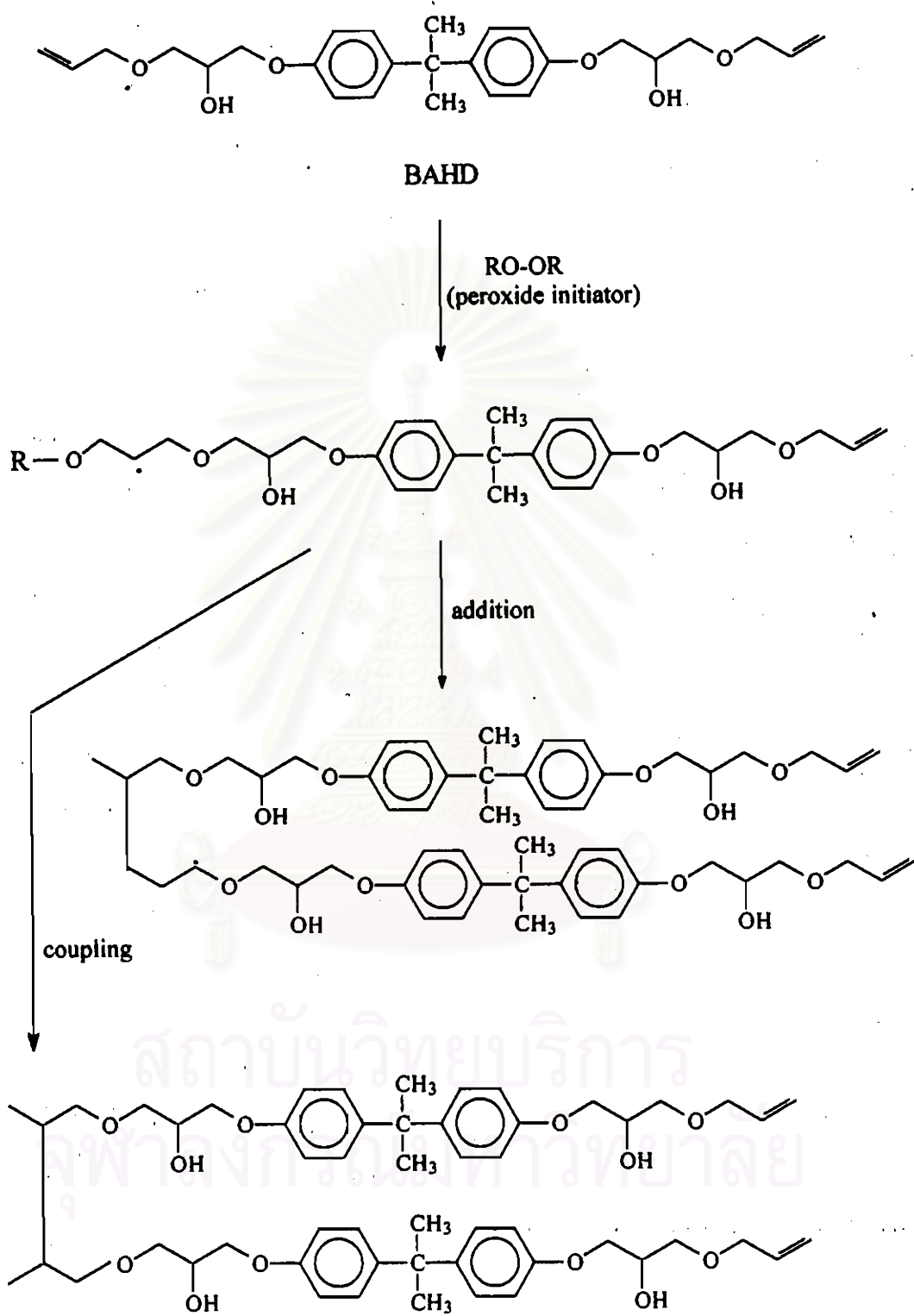
1.2 Reaction between BAPD and polymeric MDI or isocyanate-terminated polymers to give urethane linkage.



Scheme 3.5 Reaction between BAPD and polymeric MDI

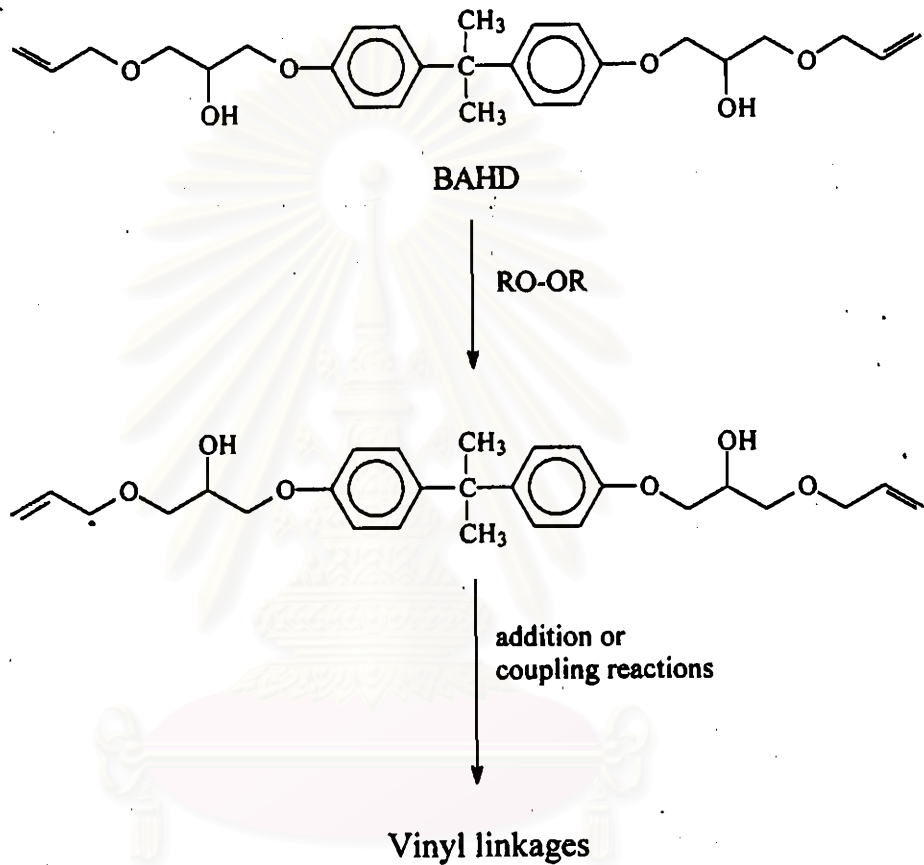
2. Free radical reaction of vinyl groups in BAPD in the presence of peroxide initiator to give polyvinyl linkages.

2.1 Free radical reaction at the double bonds



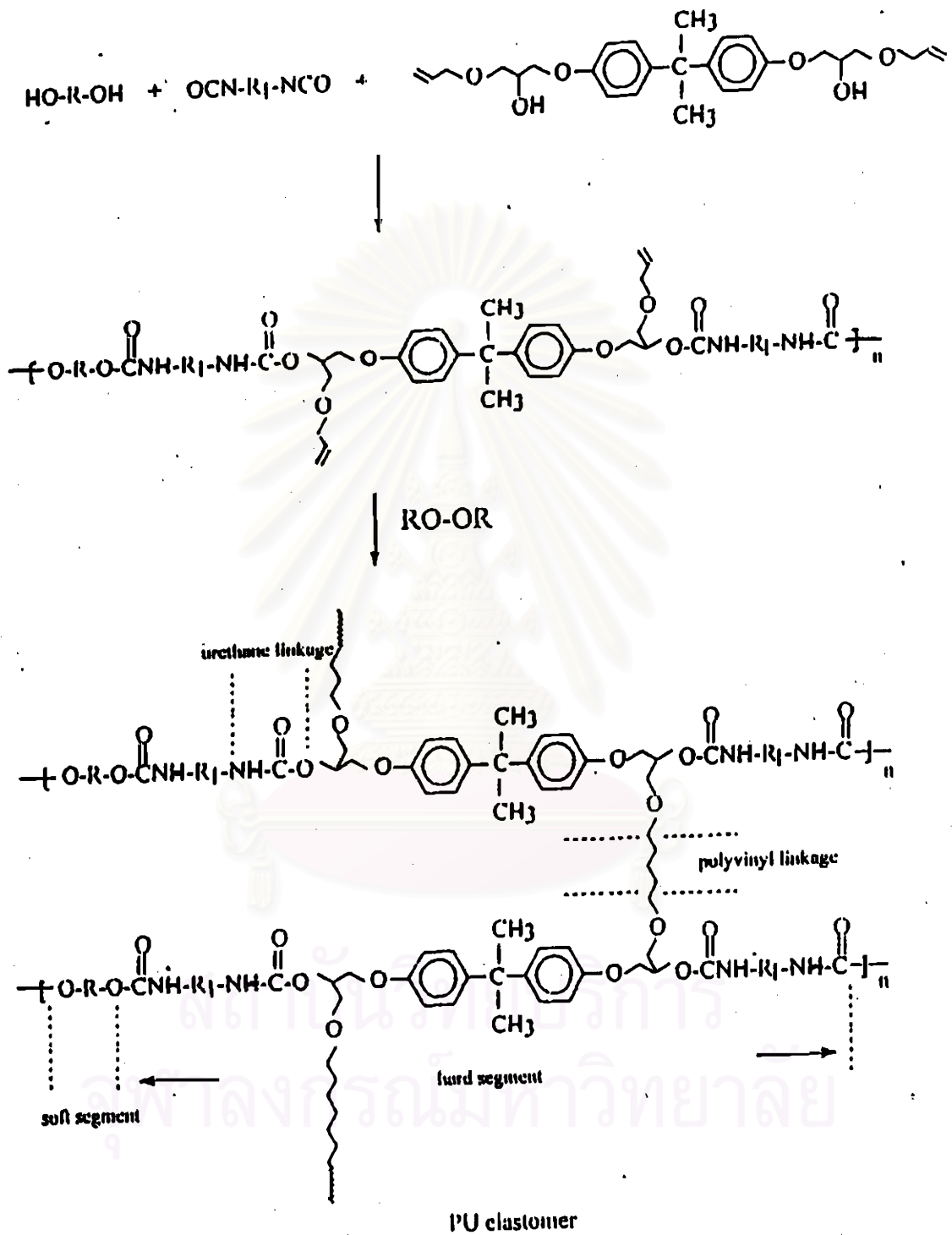
Scheme 3.6 Free radical reaction at the double bonds

2.2 Free radical reaction at the allylic carbon



Scheme 3.7 Free radical reaction at the allylic carbon

The overall reaction in the preparation of PU elastomer from MDI and polyol by using BAPD as a crosslinking agent in the presence of peroxide initiator was shown in Scheme 3.8. The structure of the PU elastomer should be a crosslinked network.



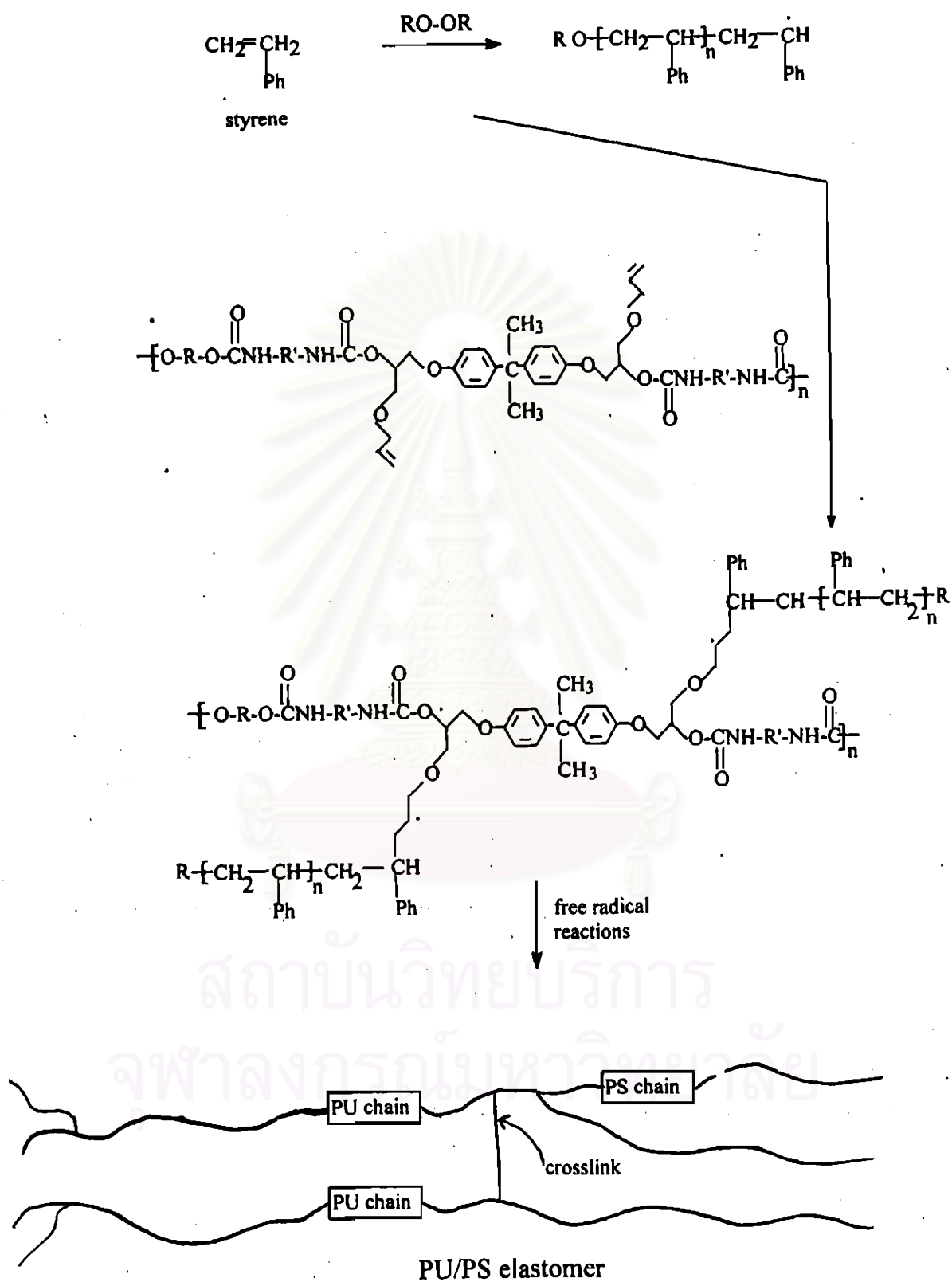
Scheme 3.8 Reactions occurred during the formation of PU elastomers

3.3 Preparation of PU/PS Elastomers

In this work, PU/PS elastomers were prepared from MDI, polyol, BAPD and peroxide initiator in the presence of styrene monomer. The reactions occurred during the polymerization are the same as in the case of PU elastomers as previously described in Schemes 3.4 to 3.8. An additional reaction expected was the free radical reaction between the double bonds in BAPD and styrene monomer. This would lead to the grafting of polystyrene onto the polyurethane. The structure of the obtained PU/PS elastomer should consist of the polyvinyl phase dispersed in the polyurethane phase. A possible route that leads to the formation of PU/PS elastomer as shown in Scheme 3.9.



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Scheme 3.9 Possible route to the formation of PU/PS elastomers

3.4 Mechanical Properties of PU and PU/PS Elastomers

The objective in this work was to prepare PU and PU/PS elastomers by using BAPD as a crosslinking agent. The variables studied were the contents of rigid and flexible segment contents, type of initiator, amount of initiator and amount of styrene monomer. The mechanical properties of the PU and PU/PS elastomers obtained from different formulations were then investigated.

3.4.1. Preparation of PU Elastomers from MDI:Polyol:BAPD Formulation in the Absence of Free Radical Initiator

When BAPD was employed as a crosslinking agent in the absence of free radical initiator, only hydroxyl groups underwent a reaction with isocyanate groups in MDI as discussed in Scheme 3.5. The free radical reaction at the vinyl groups in BAPD did not occur. For a comparison 1,4-BD was also employed as a crosslinking agent in stead of BAPD. The purpose of this experiment was to study the change in the mechanical properties of PU elastomers as the polyol content (flexible segment) is decreased and the isocyanate content (or rigid segment) is increased.

The equivalent weight ratios of MDI:Polyol:BAPD employed were 2:1.8:0.2, 2:1.4:0.6, 2:1.0:1.0 and 2:0.6:1.4. Table 3.1 shows the mechanical properties of the PU elastomers.

Table 3.1 Mechanical properties of the PU elastomers at different equivalent weight ratios of MDI:Polyol:BAPD and MDI:Polyol:1,4-BD

Property	MDI:Polyol:BAPD				MDI:Polyol:1,4-BD			
	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:0.6:1.4	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:0.6:1.4
Tensile strength (kg/cm ²)	12.85	15.20	17.65	39.78	9.59	10.81	13.87	39.78
Elongation at break (%)	138.5	106.21	110.1	110.18	100.16	57.55	71.97	85.9

It was found that tensile strength of the PU elastomer obtained from BAPD increases as the diisocyanate content is increased and the maximum value obtained was 39.78 kg/cm² at the ratio of 2:0.6:1.4. The elongation at break, on the other hands, decreases with increasing diisocyanate content and the maximum value obtained was 138.5 at the ratio of 2:1.8:0.2. In comparison to the PU elastomers obtained from 1,4- BD, the PU elastomers obtained from BAPD have slightly higher tensile strength and elongation at break.

3.4.2 Preparation of PU Elastomers from MDI:Polyol:BAPD Formulation in the Presence of Free Radical Initiators

The goal of this experimental to study the effect of free radical initiator. When a free radical initiator was employed in the preparation of PU elastomer, the vinyl groups in BAPD underwent free radical reaction (Scheme 3.6 and 3.7) which resulted in the crosslinked polyurethane (Scheme 3.8). The purpose of this experiment was to study the effect of the amount of free radical initiator employed on the mechanical properties of PU elastomer. The free radical initiators used in this study were MEKP-Co and BP. MEKP-Co decomposes to

give free radical at room temperature while BP starts to decompose at 100°C. The amount of the free radical employed were 1.0, 2.0 and 5.0 wt% of PU.

Mechanical properties of the PU elastomers obtained from MEKP-Co were shown in Table 3.2. When the amount of free radical initiator is increased from 0 wt% to 1 wt%, a small increase in tensile strength could be observed. It could be seen that larger increase in tensile strength was obtained with increasing of the amount of free radical initiator from 1 wt% to 2 wt%. This should be due to the increase of crosslinking in PU elastomer. Further increase of MEKP-Co from 2 wt% to 5 wt% resulted in the decrease of elongation at break since the PU elastomer reached the gel point rapidly and therefore the polymer was not homogeneous. The mechanical properties of the PU elastomers obtained from BP (Table 3.3) showed a similar trend to those obtained from MEKP-Co. From this experiment, the optimum amount of free radical initiator employed was found to be 2 wt%.

Table 3.2 Mechanical properties of the PU elastomers obtained from MDI:Polyol:BAPD at different wt% of MEKP-Co

Amount of MEKP-Co (wt %)	MDI : Polyol: BAPD							
	Tensile strength (kg/cm ²)				Elongation at break (%)			
	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:0.6:1.4	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:0.6:1.4
1.0	14.59	17.03	19.18	39.98	143.83	105.65	104.02	121.30
2.0	26.42	28.07	32.54	42.02	146.56	152.90	118.28	112.92
5.0	11.53	12.85	16.93	-	149.55	124.35	138.8	-

Table 3.3 Mechanical properties of the PU elastomers obtained from MDI:Polyol:BAPD at different wt% of BP

Amount of BP (wt%)	MDI : Polyol : BAPD							
	Tensile strength (kg/cm ²)				Elongation at break (%)			
	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:0.6:1.4	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:0.6:1.4
1.0	15.30	16.73	18.67	25.91	205.33	177.75	210.56	155.83
2.0	34.88	38.25	39.27	40.19	217.92	185.87	180.77	146.65
5.0	12.34	12.85	14.59	-	152.77	115.19	102.85	-

3.4.3 Preparation of PU/PS Elastomers from MDI:Polyol:BAPD

Formulation in the Presence of Free Radical Initiators

As reported in the literature styrene monomer was used in the preparation of PU elastomer in order to improve the mechanical properties of PU. The reaction between hydroxyl groups in BAPD and isocyanate groups are the same as in the case of PU elastomer. In the presence of free radical initiator, another reaction expected to occur was a free radical reaction between the vinyl groups in BAPD and styrene monomer as mentioned before in Scheme 3.9. These reactions lead to the formation of PU/PS elastomer. Since PU is elastomeric in nature, it is flexible and has high elongation at break. Polystyrene is a rigid thermoplastic[30]. Therefore, PU/PS elastomers obtained should have higher tensile strength and still shows good elongation at break since the properties of PU/PS elastomers result from the combination of the properties of PU and PS. The amount of styrene monomer employed in the

preparation of PU/PS elastomers were 5, 10, 15 and 20 wt%. The phase separation of PU/PS elastomers could be observed when the amount of styrene monomer was greater than 20 wt%.

MEKP-Co and BP were used as free radical initiators at the amount of 2 wt% since the maximum tensile strength was achieved when 2 wt% of these initiators were used in the preparation of PU-elastomers.

Table 3.4 shows the mechanical properties of PU/PS elastomers obtained from MDI:Polyol:BAPD:MEKP-Co and using different wt% of styrene monomer. The maximum tensile strength was obtained at 10 wt% and 15 wt% of styrene monomer at the MDI:Polyol:BAPD ratio of 2:1.8:0.2. Good elongation at break was maintained since at MDI:Polyol:BAPD ratio of 2:1.8:0.2, the content of soft segment was high. Further increase of styrene monomer to 20 wt% resulted in the decrease of both tensile strength and elongation at break.

Thus, the optimum amount of styrene monomer used in the preparation of PU/PS elastomer was 10-15 wt%.

Table 3.4 Mechanical properties of the PU/PS elastomers obtained from MDI:Polyol:BAPD:MEKP-Co^a at different wt% of styrene monomer

Amount of styrene monomer (wt%)	MDI:Polyol:BAPD					
	Tensile strength (kg/cm ²)			Elongation at break (%)		
	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0
5.0	51.08	36.72	31.72	119.19	115.12	114.73
10.0	77.01	29.27	26.93	262.25	101.18	92.81
15.0	70.79	48.25	28.25	224.37	170.43	111.47
20.0	53.65	31.21	29.68	187.33	170.38	153.83

^a 2 wt% of MEKP-Co was used

The mechanical properties of PU/PS elastomers obtained from MDI:Polyol:BAPD:BP at different wt% of styrene monomer were shown in Table 3.5. The PU/PS elastomers had low tensile strength. However, good elongation at break was obtained at 10 wt% and 15 wt% of styrene monomer at the MDI:Polyol:BAPD ratio of 2:1.8:0.2.

Table 3.5 Mechanical properties of the PU/PS elastomers obtained from MDI:Polyol:BAPD:BP^a at different wt% of styrene monomer

Amount of styrene monomer (wt%)	MDI:Polyol:BAPD					
	Tensile strength (kg/cm ²)			Elongation at break (%)		
	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0	2:1.8:0.2	2:1.4:0.6	2:1.0:1.0
5.0	18.56	19.38	31.52	224.40	179.45	169.23
10.0	46.21	32.33	34.99	294.57	233.10	164.70
15.0	34.07	39.47	42.13	294.40	168.13	148.90
20.0	35.80	47.02	53.86	271.88	231.53	163.28

^a 2 wt% of BP was used

It could be seen from Tables 3.4 and 3.5 that most of the PU/PS elastomers obtained by use of MEKP-Co as a free radical initiator have higher tensile strength than those obtained from BP initiator. On the other hand, the elastomers obtained from BP initiator give better elongation at break than those obtained from MEKP-Co.

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Figure 4.1 SEM micrograph of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 0 wt% of styrene monomer, and 2 wt% of MEKP-Co

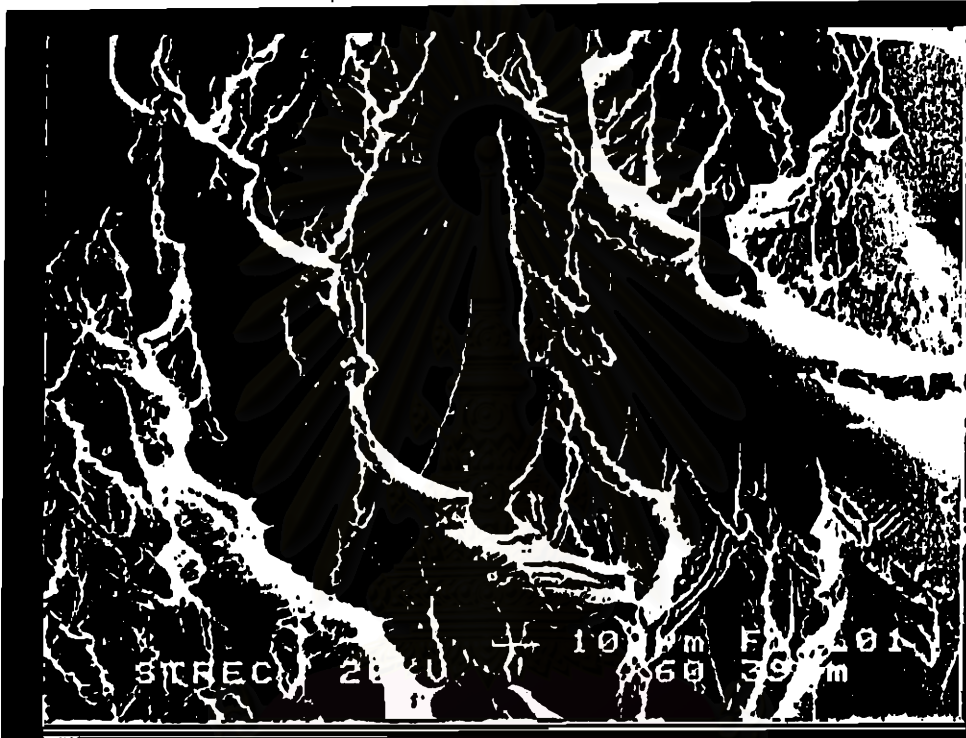


Figure 4.2 SEM micrograph of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 10 wt% of styrene monomer, and 2 wt% of MEKP-Co

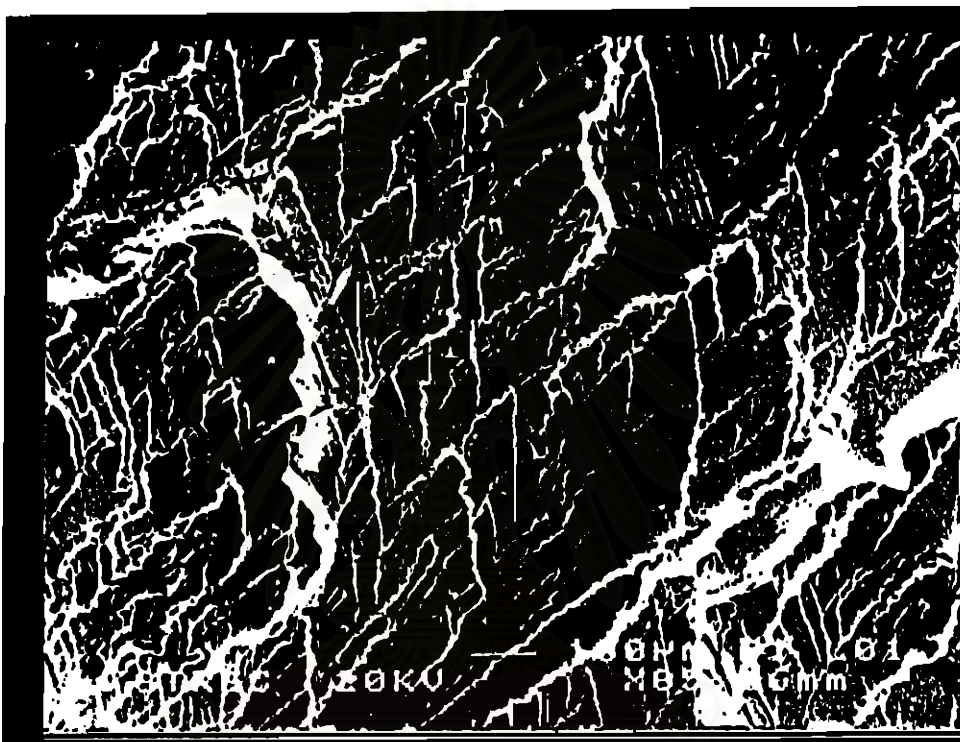


Figure 4.3 SEM micrograph of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 15 wt% of styrene monomer, and 2 wt% of MEKP-Co

3.5 Morphology of PU/PS Elastomers

The SEM of PU/PS elastomers in the present investigation are shown in Figures 4.1, 4.2 and 4.3. The white particles associated to PS phase which dispersed in the black PU matrix was observed. It was also evident that the PS phase can be well dispersed in the PU phase. The morphology of these elastomers indicated that there were two phases due to individual component network.

3.6 Thermal Analysis of PU/PS Elastomers

DMA thermograms of PU/PS elastomers at various formulations show two $\tan \delta$ peaks at -15.7 to -16.7°C and 130 - 135°C which result from PU and PS components, respectively (Figures A2-A5).

TGA thermograms of the PU/PS elastomers was obtained (Figures A6 and A7). The elastomers show 10 and 50 % weight loss at the temperature 80 and 310°C , respectively. Another weight loss 10 and 50 % could be observed at the temperature 180 and 340°C , respectively.

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