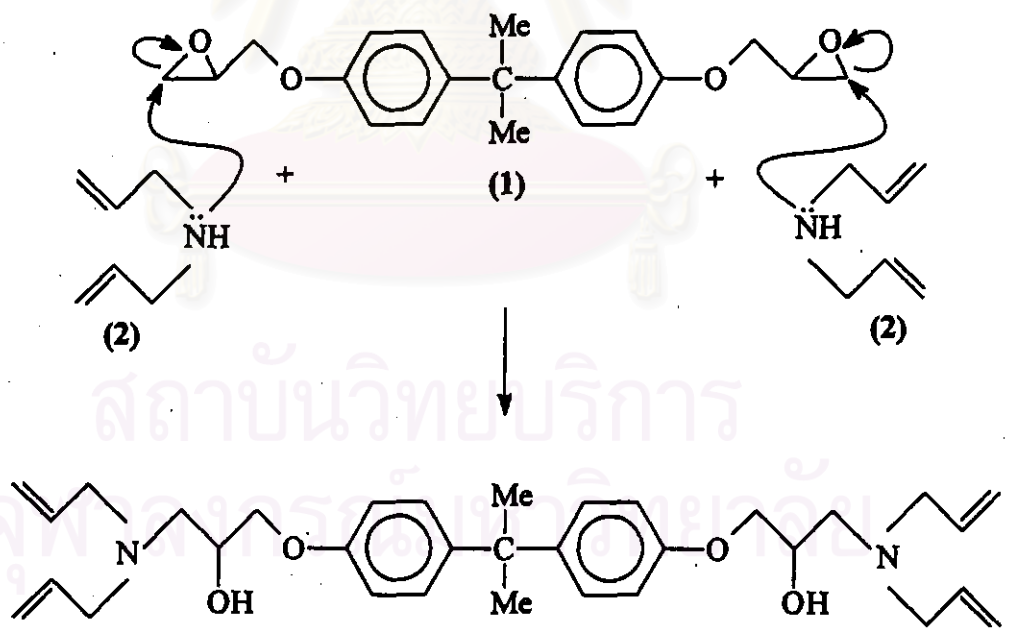
CHAPTER IV

RESULTS AND DISCUSSION

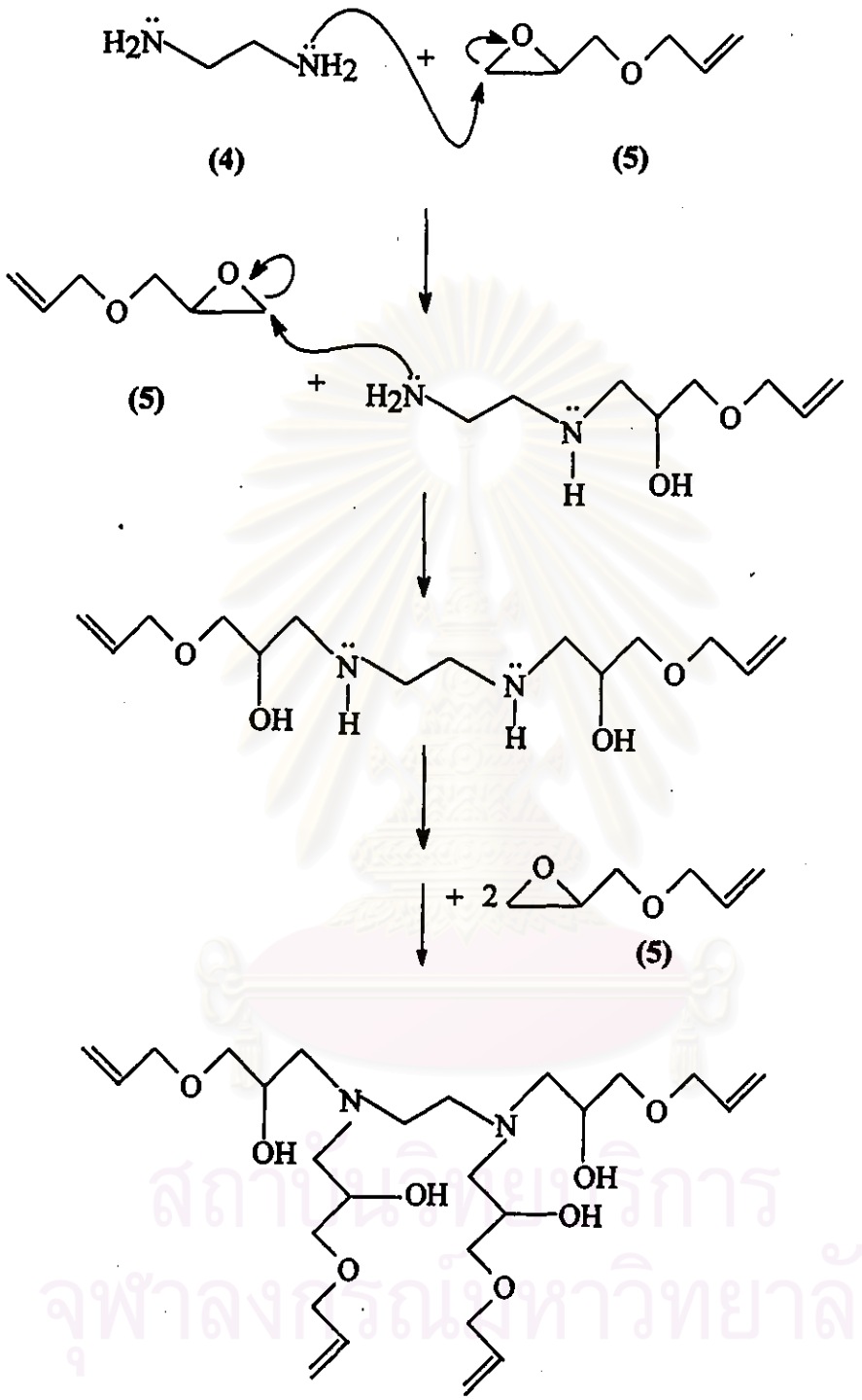
4.1 Synthesis of Crosslinking Agents [5,12]

In this research, crosslinking agents BDPD (**3**) and TAPE (**6**) were synthesized by ring opening reaction of epoxy compounds (**1** and **5**) with amines (**2** and **4**) as shown in Scheme 4.1 and 4.2 . The structure of BDPD and TAPE were characterized by ^{1}H NMR spectroscopy.



(3)
BDPD

Scheme 4.1 Synthesis of Bis-(3-N,N'-diallylamino-2-propanol) diphenylolpropane (BDPD, **3**)



(6)

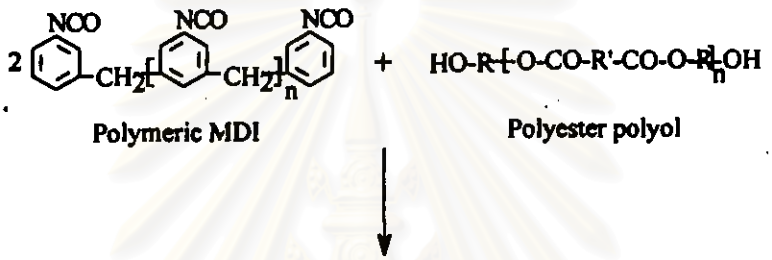
TAPE

Scheme 4.2 Synthesis of N,N,N',N',-tetrakis-(3-allyloxy-2-propanol) ethylenediamine (TAPE, 6)

When BDPD was used as a crosslinking agent in the preparation of polyurethane elastomer, the reactions expected to occur during polymerization were shown as follows

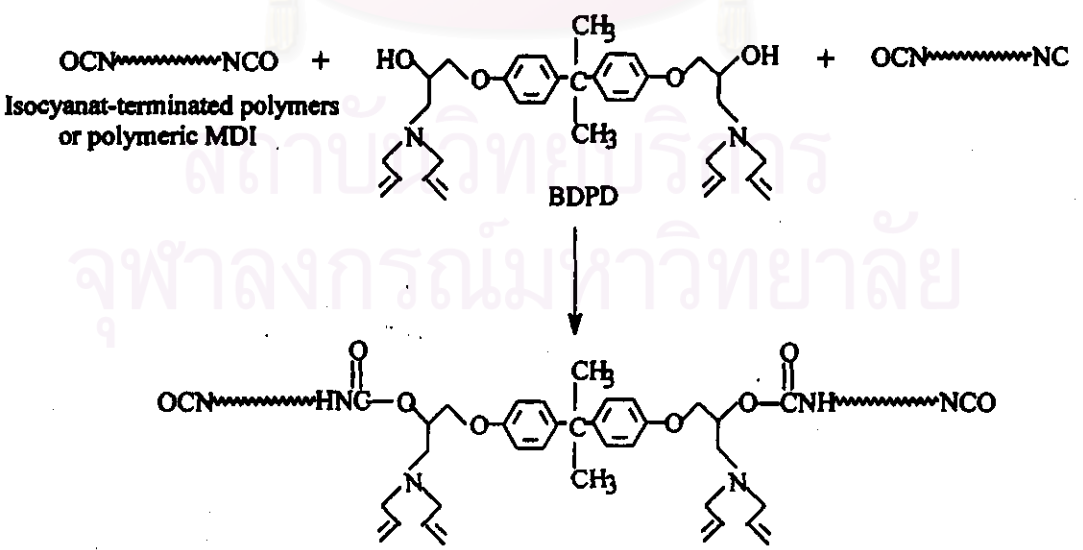
1. Addition of hydroxyl groups to isocyanate groups

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

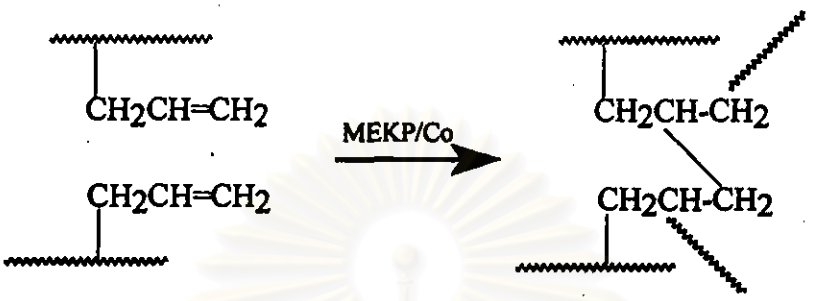


Isocyanate-terminated polymers

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

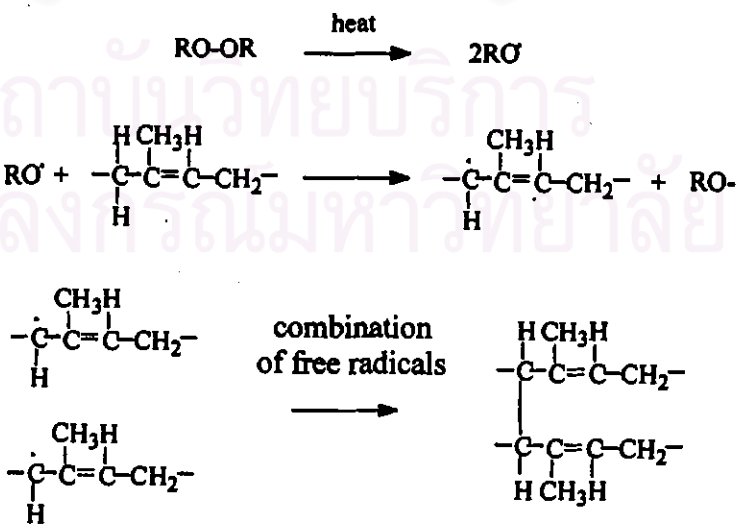


2. Free radical polymerization of terminal double bonds in BDPD to give polyvinyl linkage



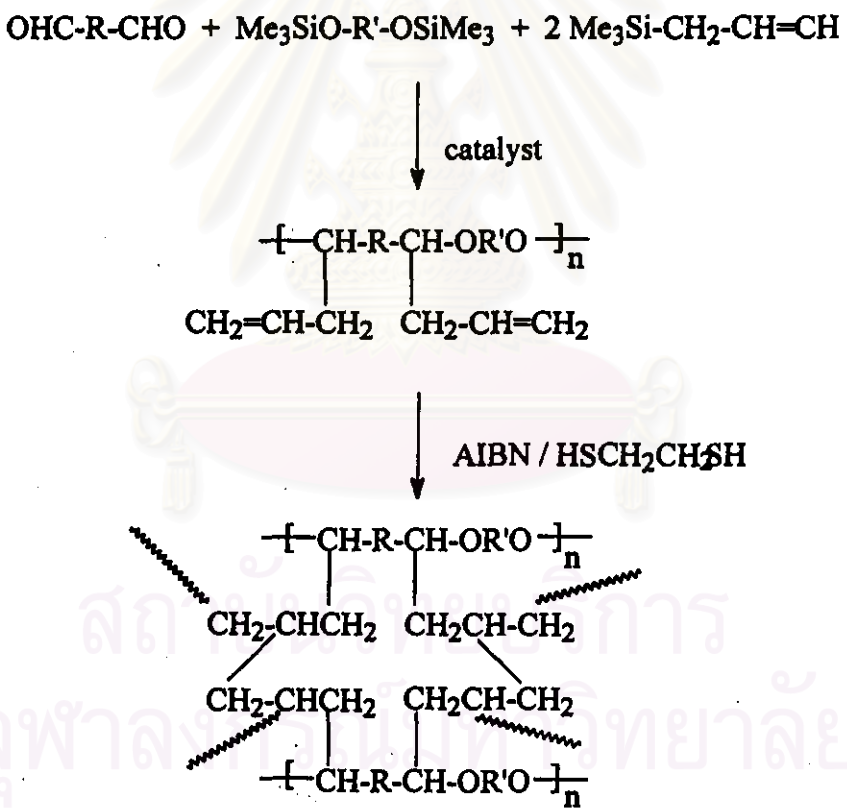
Peroxide curing is a univesal method of crosslinking most elastomers when the reaction mechanism is free radical. This gives carbon-carbon crosslinks between the polymer chains. The mechanism of peroxide crosslinking of an elastomer was shown in Scheme 4.3 .[1]

In neutral and alkaline media, the peroxide decomposes to give free radical which can abstract a hydrogen atom to form an allylic free radical on the polymer chain. Combination of these two allylic free radicals results in a crosslinked polymer network.



Scheme 4.3

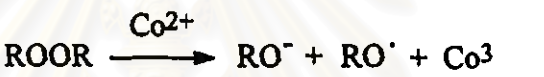
An example that demonstrated free radical crosslinking reaction of allyl groups was done by Yokozawa and Takenoya. They synthesized polyethers which contained allyl groups in the side chains. When polyether with functional side chain was heated in the presence of azobis(isobutyronitrile) (AIBN) and ethanedithiol, the crosslinked polymer was obtained. The reaction occured was the radical addition to the allyl groups since the absorption of a carbon-carbon bouble bond of the crosslinked polymer at 1641 cm^{-1} became weaker in the IR Spectrum.[13-14]

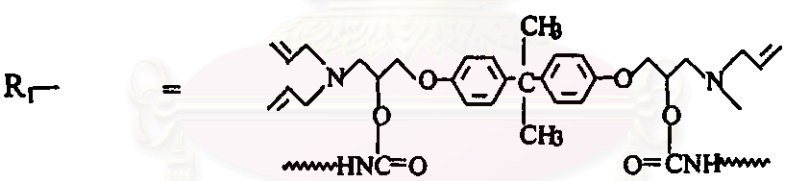


Since BDPD also contained allylic double bonds, reaction in the presence radical initiator should be the mechanism of free radical reaction at the allylic double bonds of BDPD was proposed as follows.

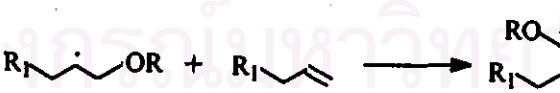
Initiation

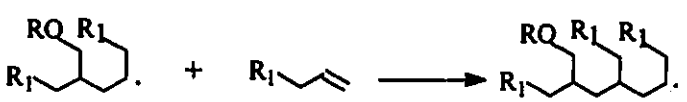
Initiation system which are effective at room temperature normally consist of mixtures of a peroxy compound and an accelerator. In the presence of the accelerator, the peroxy compound rapidly decomposes without the application of heat into free radicals. The most common accelarators for methyl ethyl ketone peroxide is salt of which exhibit more thane one valency. The most wildly used metal of this kind is cobolt and the most commonly used salts are naphthenates, which are readily soluble. The decomposition of the peroxide by a metal salt such as cobolt naphthenate to give free radical species.

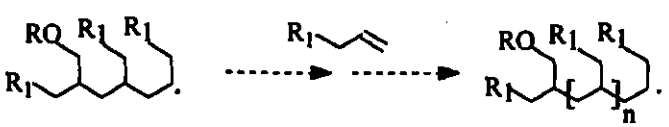


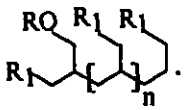


Propagation

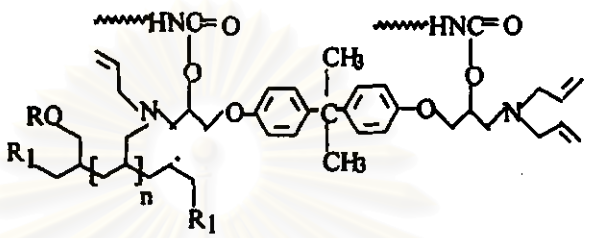






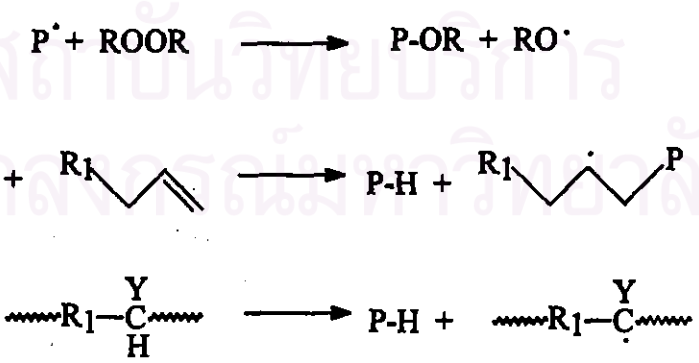


III



Chain transfer

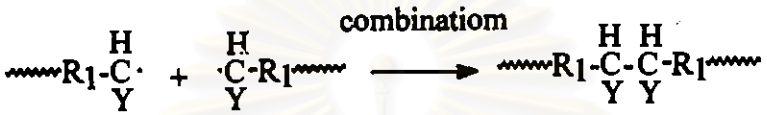
Chain transfer was a chain-breaking reaction which caused in a decrease in the size of the propagation polymer chain to give the small-sized polymer chain (telomer). There were three possible ways of chain transfers in this case, i.e. chain transfer to initiator, chain transfer to crosslinking agents, and chain transfer to polymer.



P· = propagating polymer chain

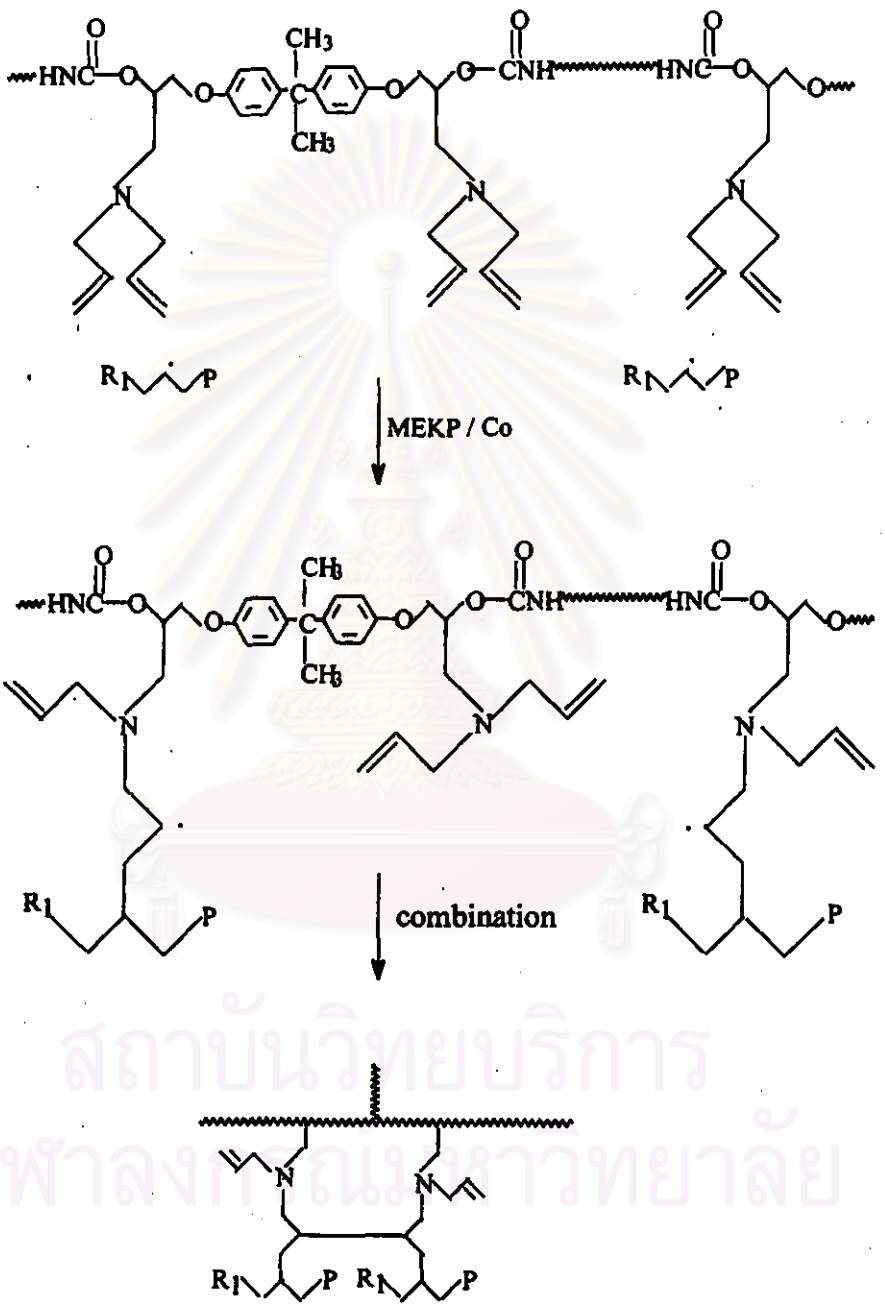
Termination

In this step, the propagating polymer chains stopped growing and terminated by combination and disproportionation.[36]

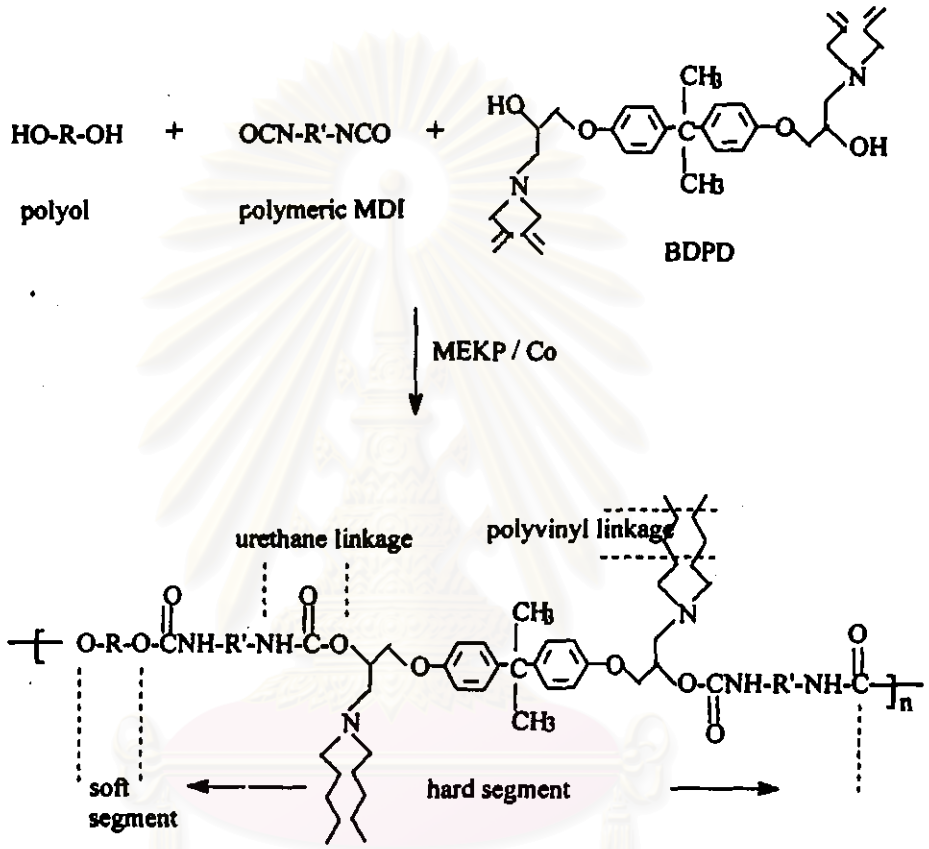


Other possible reaction was cyclization reaction which involed intramolecular free radical coupling (Scheme 4.4).

When BDPD was used in the preparation of polyurethane elastomer, reaction between hydroxyl and isocyanate groups resulted in linear polyurethane. Free radical reaction of double bonds in BDPD yielded crosslinked network. Scheme 4.5 illustrated the structure of polyurethane elastomer obtained by use of BDPD as a crosslinking agent. The obtained polyurethane should have polyvinyl phase dispersed in polyurethane phase.

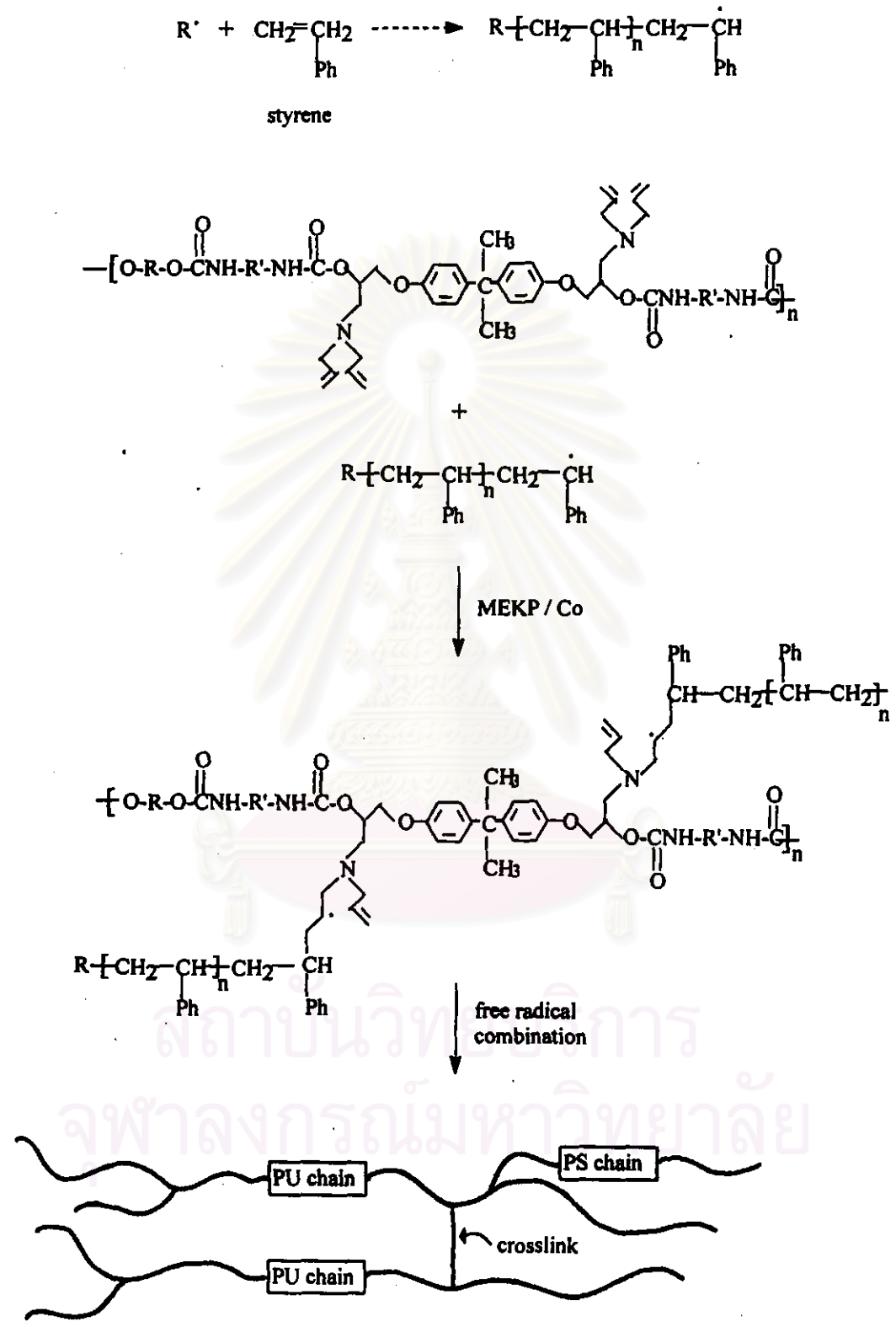


Scheme 4.4



Scheme 4.5 Possible structure of the crosslinked polyurethane

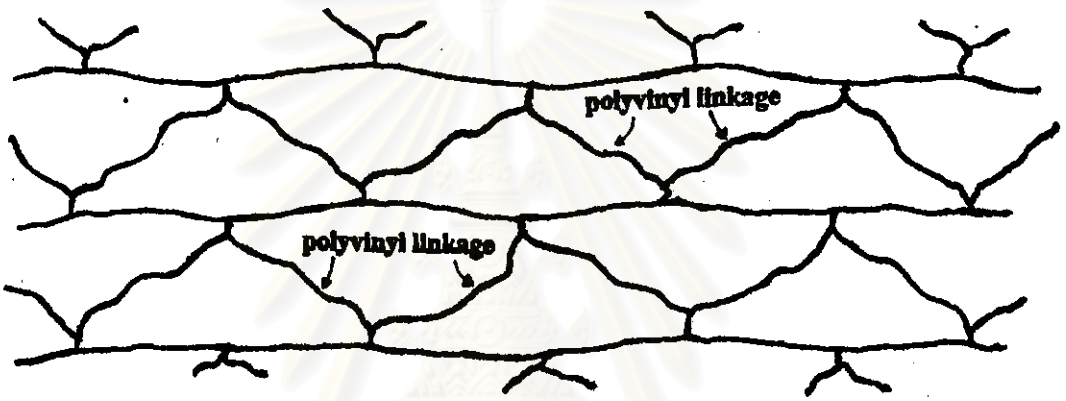
Free radical reaction between the double bond in BDPD with styrene monomer by use of free radical initiator was also possible. In this case, the polymer obtained would be a crosslinked PU/PS elastomer. This free radical reaction could occur via many routes since the reaction invilved many types of free radicals. One possible mechanism that leaded to the formation of PU/PS elastomer was shown in Scheme 4.6.



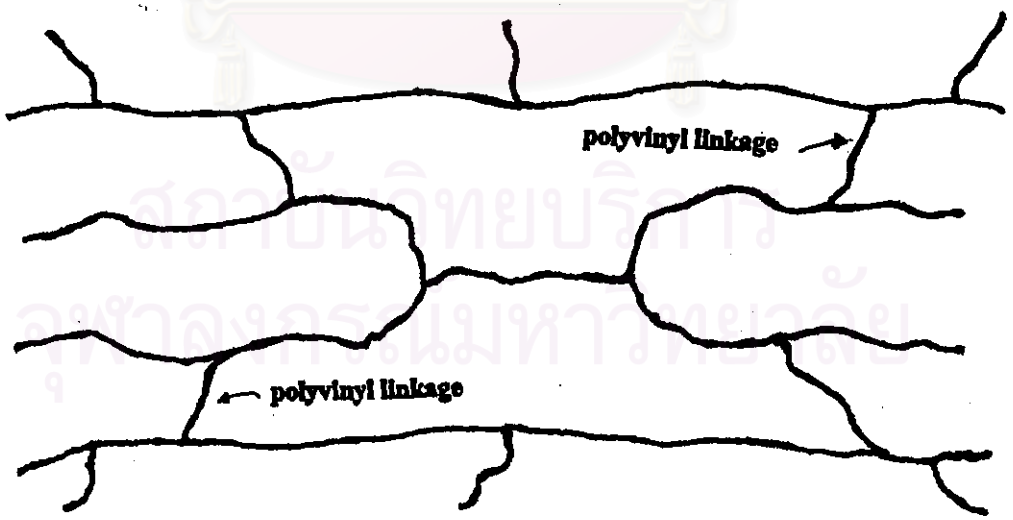
Scheme 4.6 Possible of PU/PS elastomer

When TAPE was used as a crosslinking agent in preparation of PU and PU/PS elastomer , the reaction were expect to be the same as thoes of BDPD.

The PU and PU/PS elastomer obtained from the use of TAPE would have higher crosslink density since TAPE contained four hydroxy groups. Thus, the structure of the polyurethane phase would be crosslinked network. Possible structure of PU and PU/PS elastomers were shown in Scheme 4.7.



(a)



(b)

Scheme 4.7 Possible structure of PU and PU/PS elastomer (a) BDPD (b) TAPE

4.2 Preparation of PU Elastomer

In this study, the NCO/OH equivalent weight ratio was kept constant at 1.04 . When BDPD was employed as a crosslinking agent, the equivalent weight ratio of MDI:POLYOL:BDPD was at 2:1.8:0.2 . In the case of TAPE, MDI:POLYOL:TAPE equivalent weight ratio were 2:1.8:0.2, 2:1.6:0.4 and 2:1.4:0.6 . Both BDPD and TAPE contained tertiary amine in their molecules which accelerate the reaction of isocyanates and polyol. The mechanism of catalysis by tertiary amine involes the donation of electrons by the tertiary nitogen to the carbonyl carbon of the isocyanate group to form an intermediate. The reactivity of BDPD was higher than TAPE because of the catalytic effect of tertiary amine in TAPE was reduced by steric hindrance. Therefore, in the case of BDPD only one formulation at the equivalent weight ratio of MDI:POLYOL:BDPD = 2:1.8:0.2 could be used in the preparation of polyurethane. For TAPE, three formulation at the equivalent weight ratio of MDI:POLYOL:TAPE = 2:1.8:0.2, 2:1.6:0.4 and 2:1.4:0.6 could be employed. Increasing the amount of crosslinking agents more than the maximum amount in these ratios resulted in an increase of polymerization rate thus the polymer would reach the gel point very fast and the mixture of PU elastomer could not be casted. Since the polymerization was fast, dibutyltin dilaurate was not necessary in this preparation.

The optimum amount of MEKP/Co in the formulation of PU elastomer was 1 wt%. Increasing the amount of MEKP/Co gave the same result as increasing of crosslinking agents. Mechanical properties of PU elastomers prepared from BDPD and TAPE as crosslinking agents were shown in Table 4.1 . When 1 wt% of MEKP/Co was employed in the formulation, the PU elastomer obtained from MDI:POLYOL:BDPD at the equivalent weight ratio of 2:1.8:0.2 had the best properties.

In order to observe the effect of MEKP/Co on the mechanical properties, a PU elastomer was prepared from MDI:POLYOL:TAPE at the equivalent weight ratio of 2:1.4:0.6 without using MEKP/Co. Tensile strength decreased when MEKP/Co was not used which indicated that the use of MEKP/Co was necessary for the free radical reaction of double bond in the crosslinking agent. This free radical reaction gave rise to the higher crosslink density which, resulted in an increase of tensile strength.

In comparison to the PU elastomer obtained from using 1,4-butanediol as a crosslinking agent, the elastomer obtained from the use of BDPD and TAPE had slightly higher tensile strength.[15]

4.3 Preparation of PU/PS Elastomer

The PU/PS elastomer were prepared in order to investigate the effect of styrene monomer on the mechanical properties of the resulting PU/PS elastomer.

Following the formulation in the previous study, the NCO/OH equivalent weight ratio was kept constant at 1.04 . The equivalent weight ratio of MDI:POLYOL:BDPD was 2:1.8:0.2 and the MDI:POLYOL:TAPE equivalent weight ratio were 2:1.8:0.2, 2:1.6:0.4 and 2:1.4:0.6 . Table 4.2-4.5 showed the effect of upon the addition of styrene monomer and MEKP/Co on the mechanical properties of the PU/PS elastomers.

The polyurethane and the polystyrene networks were allowed to form *in situ* through the independent condensation and radical polymerization , respectively. In the presence of dibutyltin dilaurate, The isocyanate reaction could take place relatively fast at room temperature and the free radical polymerization of styrene with MEKP/Co initiator was also able to proceed at room temperature. Ultimately both reactions were run into completion after

transferring the reaction mixture near the gel point into a mold and heating it further at 100°C. It was found that the maximum amount of styrene monomer that could be in the formulation was 20 percentage by weight which the resulting PU/PS elastomer remained transparent. When more than 20 wt% of styrene monomer were added, phase seperation in PU/PS elastomer occurred.

The amount of MEKP/Co employed were at 1 and 2 wt%. When more than 2 wt% of MEKP/Co was used, the mixture reached the gel point very fast and could not be casted. TAPE showed better properties than BDPD at all formulations of PU/PS elastomers and the best properties was obtained at 2 wt% of MEKP/Co and 20 wt% of styrene.

In comparison with the PU elastomers, PU/PS elastomer showed better mechanical properties.

The properties of PU/PS elastomers were the combination of properties of polyurethane and polystyrene. Therefore, an increase in the amount of polystyrene phase in PU/PS elastomer resulted in the tensile strength, hardness and compression set while the materials still had high elongation at break.

4.4 Morphology of PU and PU/PS Elastomer

Figures A27-A32 showed DMA thermogram, the tan δ curve of PU and PU/PS at various formulation. The PU/PS elastomers exhibited two distinct glass transition temperatures, corresponding to the respective component networks.

Figures A21-A26 displayed SEM of PU and PU/PS elastomers taken at different formulations. For PU/PS elastomers, the white particles associated to PS phase which dispersed in the dark PU matrix was observed. When the weight percentage of styrene in PU/PS elastomers was increased, the larger

white particles could be observed, indicating that the polystyrene phase could not be well dispersed in the PU matrix.

4.5 Thermogravimetric Analysis of PU and PU/PS Elastomer

TGA is usually employed to study materials compositions. When they are subjected to thermal treatment, the certain temperature destroyed their molecules or atoms, resulting in weight reduction from the original mass. In these studies, PU and PU/PS elastomers were subjected to the thermal treatment and their TGA thermograms were shown in Figures A37-A42 . The thermograms of the PU and PU/PS elastomers showed the same pattern of weight loss. Table 4.6 presented the thermal stability of the PU and PU/PS elastomers via TGA measurements.

From the data discussed above, it is believed at this stage that the structure of PU/PS elastomer may be grafted IPN or pseudo IPN. However, more experimental data will be needed for the further study.

Table 4.1 Mechanical properties of PU elastomers at different equivalent weight ratios of MDI:POLYOL:Crosslinking agents and 1 wt% of MEKP/Co

Property	MDI:POLYOL:BDPD	MDI:POLYOL:TAPE		
	2:1.8:0.2	2:1.8:0.2	2:1.6:0.4	2:1.4:0.6
Tensile strength (MPa)	1.35	1.02	1.29	1.39
		(0.94)[b]		(0.99)[a]
				(1.06)[b]
Elongation at break (%)	150.88	80.67	94.49	78.52
				(77.30)[a]
		(110.16)[b]		(57.55)[b]
Hardness (shore A)	51.4	50.6	52.0	59.6
				(40.83)[a]
Compression set 24 h at 70°C (%)	3.54	3.46	2.04	1.82
				(3.28)[a]

[a] MEKP/Co was not used in the formulatiom

[b] 1,4-butanediol was used as a crosslinking agent [15]

Table 4.2 Effect of the amount of styrene monomer and MEKP/Co on the mechanical properties of PU/PS elastomer : 10 wt% of styrene and 1 wt% of MEKP/Co.

Property	MDI:POLYOL:BDPD	MDI:POLYOL:TAPE		
	2:1.8:0.2	2:1.8:0.2	2:1.6:0.4	2:1.4:0.6
Tensile strength (MPa)	1.11	1.68	1.60	1.88
Elongation at break (%)	167.63	167.53	130.38	114.93
Hardness (shore A)	38.9	47.2	48.0	55.6
Compression set 24 h at 70°C (%)	10.21	7.26	7.86	8.26

Table 4.3 Effect of the amount of styrene monomer and MEKP/Co on the mechanical properties of PU/PS elastomer : 10 wt% of styrene and 2 wt% of MEKP/Co.

Property	MDI:POLYOL:BDPD	MDI:POLYOL:TAPE		
	2:1.8:0.2	2:1.8:0.2	2:1.6:0.4	2:1.4:0.6
Tensile strength (MPa)	1.32	1.73	2.13	2.08
Elongation at break (%)	155.38	146.78	124.50	85.69
Hardness (shore A)	50.0	56.2	56.8	62.4
Compression set 24 h at 70°C (%)	8.09	6.07	6.51	8.90

Table 4.4 Effect of the amount of styrene monomer and MEKP/Co on the mechanical properties of PU/PS elastomer : 20 wt% of styrene and 1 wt% of MEKP/Co.

Property	MDI:POLYOL:BDPD	MDI:POLYOL:TAPE		
	2:1.8:0.2	2:1.8:0.2	2:1.6:0.4	2:1.4:0.6
Tensile strength (MPa)	0.96	1.82	1.64	2.43
Elongation at break (%)	167.30	170.70	144.72	123.17
Hardness (shore A)	40.2	42.4	52.2	56.2
Compression set 24 h at 70°C (%)	17.09	13.29	10.33	12.36

Table 4.5 Effect of the amount of styrene monomer and MEKP/Co on the mechanical property of PU/PS elastomer : 20 wt% of styrene and 2 wt% of MEKP/Co.

Property	MDI:POLYOL:BDPD	MDI:POLYOL:TAPE		
	2:1.8:0.2	2:1.8:0.2	2:1.6:0.4	2:1.4:0.6
Tensile strength (MPa)	0.91	1.91	2.53	2.60
Elongation at break (%)	127.01	150.35	122.83	98.72
Hardness (shore A)	47.7	52.3	57.3	61.0
Compression set 24 h at 70°C (%)	11.29	9.38	10.23	10.95

Table 4.6 Properties of PU and PU/PS elastomer

Type	Styrene (wt%)	MEKP/Co (wt%)	Thermal Stability	
			10% wt Loss (°C)	50% wt Loss (°C)
MDI:POLYOL:BDPD				
2:1.8:0.2	-	1.0	350	420
2:1.8:0.2	20.0	1.0	360	420
2:1.8:0.2	20.0	2.0	350	410
MDI:POLYOL:TAPE				
2:1.4:0.6	-	1.0	350	420
2:1.4:0.6	20.0	1.0	350	420
2:1.4:0.6	20.0	2.0	360	420