

CHAPTER III

RESULTS AND DISCUSSION

Synthesis of Crosslinking Agents

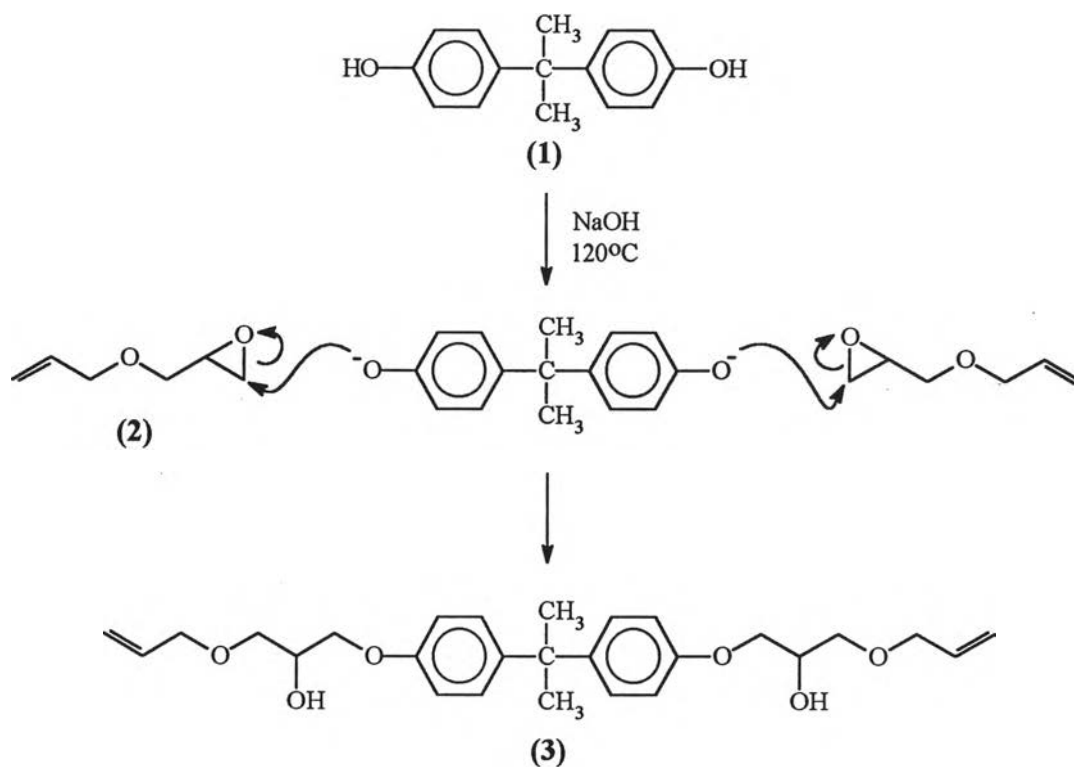
General Discussion

The synthetic approach employed in the synthesis of the crosslinking agents was a one-step reaction involving epoxide ring opening by nucleophiles. This type of reaction was chosen since it occurs easily and the starting materials are readily available. The reaction can give mono and di substitution products, and, in some cases tri and tetra substituted products. This was determined by comparison of the ^1H NMR integral of the olefinic protons, which come from the epoxide, and aryl protons which come from the nucleophiles. The crosslinking agents were characterized by IR, ^1H and ^{13}C NMR, MS and elemental analysis.

Synthesis of bis-(3-allyloxy-2-hydroxy-1-propoxy)diphenoxypropane (3)

Scheme 11 shows the preparation of bis-(3-allyloxy-2-hydroxy-1-propoxy) diphenoxypropane (3) which contains two hydroxyl and two vinyl groups. Starting from allyl glycidyl ether (2) and bisphenol-A (1), epoxide ring opening with two aromatic hydroxyl groups of (1), using sodium hydroxide as a base, was carried out in the absence of solvent at 120°C for 3 hours to obtain product (3) in 93% yield.

The spectroscopic data clearly confirm the structure of (3). The IR spectrum of (3) (Figure 4), showed absorption bands of a secondary alcohol at 3421 and 1040 cm^{-1} and bands of vinyl and aromatic C=C stretching vibrations at 1613, 1520, 1467, and 1419 cm^{-1} . The absorption bands at 932 cm^{-1} and 830 cm^{-1} coincided with the characteristic absorption peak of vinyl C=C bending vibrations and aromatic C-H bending of a 1,4-disubstituted benzene, respectively.

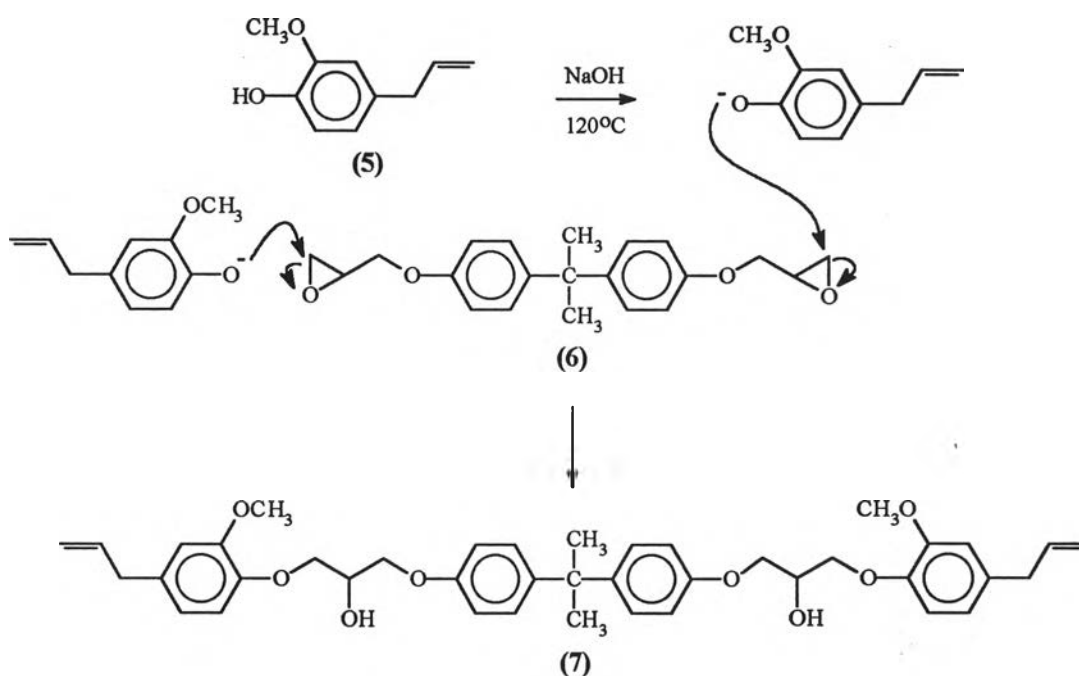


Scheme 11

If the reaction had resulted in monoalkylation, the ratio of H3 (olefinic protons) : H11 (aromatic protons) would be 1 : 4. Dialkylation would result in a ratio, H3 : H11 of 1 : 2. The ^1H NMR spectra of (3) (Figure 5), clearly showed a 1 : 2 ratio, which confirmed that both phenolic groups in (1) react with (2). The ^{13}C NMR spectrum (Figure 6) show the important carbon signals which could be assigned as follows : the signals at 134.3 ppm and 117.4 ppm were assigned to $-\text{CH}=\text{CH}_2$ of vinyl group. The signals of the benzene ring were at 156.3, 143.5, 127.7 and 113.9 ppm. MS (Figure 7) data gave m/e 456 which is M^+ for the molecular formula $\text{C}_{27}\text{H}_{36}\text{O}_6$. The fragmentation ion peak at m/e 441 (M^+-15), 399 (M^+-57) was due to the loss of methyl group and allyloxy group. The m/e 41 and 115 were identified as allyl group and 1-allyloxy-2-hydroxypropyl group, respectively. The m/e 327 and 213 indicated the elimination of methyl group with one molecule and two molecules of 3-allyloxy-2-hydroxy-1-propene.

Synthesis of Bis-[3-(4-allyloxy-2-methoxy)phenoxy-2-hydroxy-1-propoxy] diphenoxypropane (7)

The reaction between eugenol (5) and the diglycidyl ether of bisphenol A (6) in the presence of sodium hydroxide was carried out in the absence of solvent at 120°C for 5 hours (Scheme 12) to yield product (7), which contains two hydroxyl and two vinyl groups, in 62% yield.



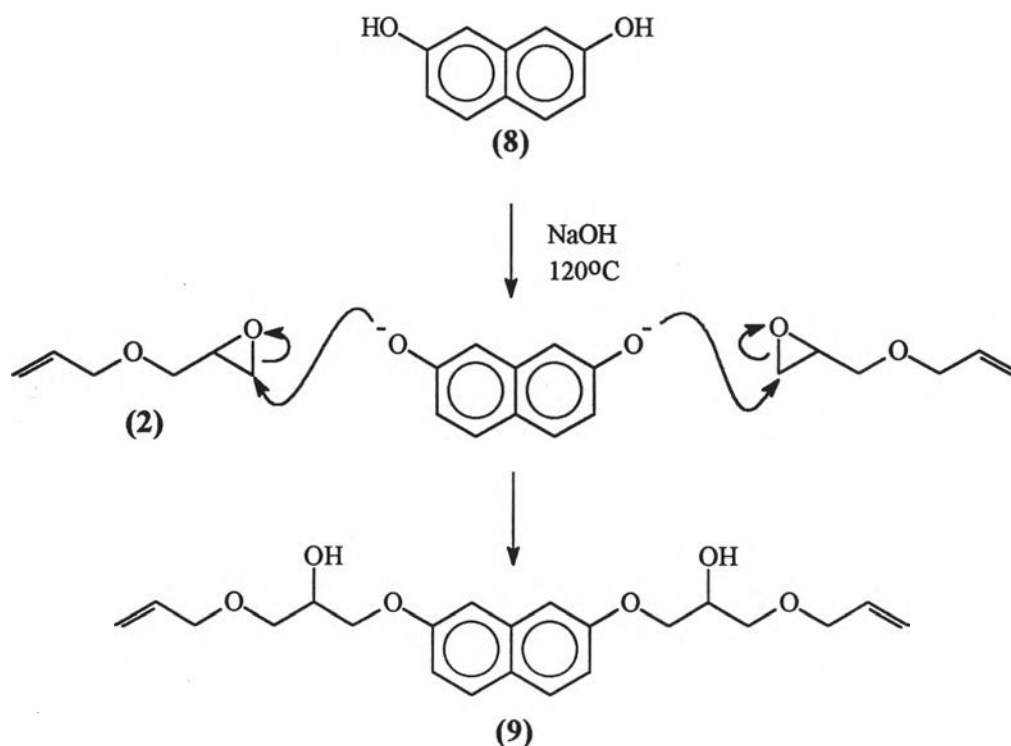
Scheme 12

The IR spectrum of (7) (Figure 8) showed the O-H absorption bands of a secondary alcohol at 3485 and 1034 cm^{-1} and bands of vinyl and aromatic C=C stretching vibrations at 1639, 1608, 1507, and 1470 cm^{-1} . The absorption band at 927 cm^{-1} was due to the C=C bending vibrations. If the reaction had resulted in monosubstituent, the ratio of H3 (olefinic protons) : H16 (aromatic protons) would be 1 : 4. Dialkylation would result in a ratio, H3 : H16, of 1 : 2. The ^1H NMR spectra of (7) (Figure 9), clearly showed a 1 : 2 ratio, which confirmed that both phenolic groups in (5) reacted with (6). The ^{13}C NMR spectrum (Figure 10) displayed signals at 137.5 ppm and 115.8 ppm which were assigned to vinyl carbons and 156.4, 143.6, 127.8, and 113.9 which were the signals of benzene ring carbons. The molecular ion could not

be found in the mass spectrum (Figure 11) due to instability. The fragmentation ion peaks at m/e 504 ($M^+ - 164$) and 340 indicated the elimination of one molecule and two molecules of eugenol, respectively. The m/e 489 ($M^+ - 179$) was due to loss of both eugenol and a methyl group and the m/e 41 was identified as allyl group. The m/e 164 was identified as eugenol.

Synthesis of 2,7-(Bis-3-allyloxy-2-hydroxy-1-propoxy)naphthalene (9)

2,7-Dihydroxy naphthalene (8) was used as a nucleophile (Scheme 13) in the presence of sodium hydroxide. The reaction was heated in the absence of solvent at 120°C for 5 hours. The product (9) was obtained in 77% yield.



Scheme 13

The IR spectrum of (9) (Figure 12), showed bands at 3474 and 1040 cm^{-1} assigned to O-H absorption bands of a secondary alcohol and at 1633, 1513, 1447, 1420 cm^{-1} assigned to be vinyl and aromatic C=C stretching vibrations. A band was observed at 938 cm^{-1} (C=C bending vibration). The ^1H NMR spectrum of (9)

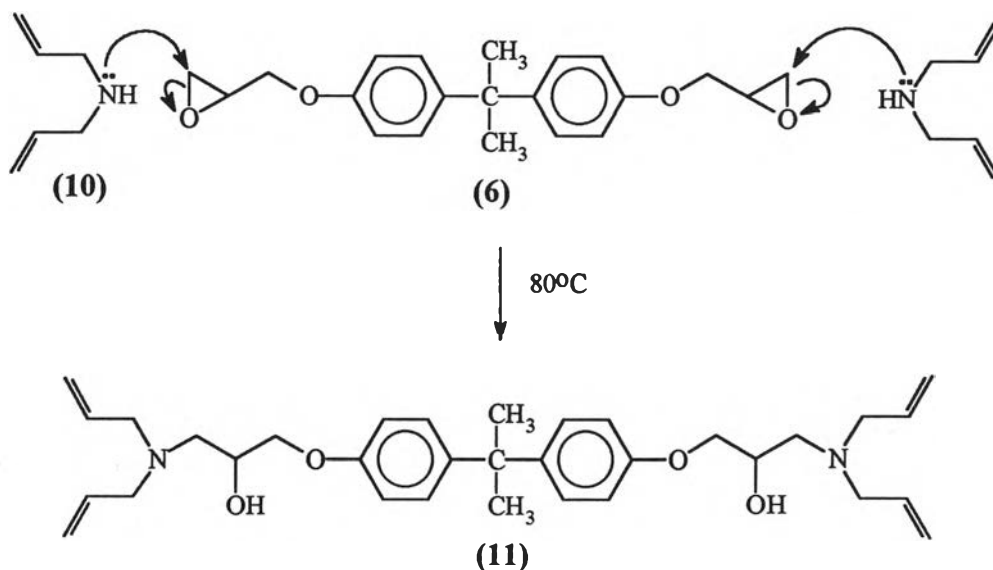
(Figure 13) showed that the ratio of H3 : H12 was 1 : 2, indicating that two phenolic groups of (8) reacted with (2). If only one had reacted it would have been 1 : 1. In the ^{13}C NMR spectrum (Figure 14) signals were observed at 134.4 ppm and 117.5 ppm, assigned to carbons of the vinyl groups. The signals of carbons of naphthalene were at 157.2, 135.7, 129.2, 124.6, 116.3 and 106.4 ppm. The mass spectrum (Figure 15) showed the molecular ion peak at m/e 388 consistent with a molecular formula $\text{C}_{22}\text{H}_{28}\text{O}_6$. The fragmentation ion peak at m/e 274 ($M^+ - 114$) and 160 was due to loss one molecule and two molecules of 3-allyloxy-2-hydroxy-1-propene. The m/e 115, 57, and 41 was identified as 1-allyloxy-2-hydroxypropyl group, allyloxy group and allyl group, respectively. The m/e 160 was 2,7-dihydroxynaphthalene.

Synthesis of Bis-(3-N,N-diallylamino-2-hydroxy-1-propoxy)diphenoxypropane (11)

This reaction was carried out by heating a mixture of (6) and (10) without base at 80°C for 3 hours (Scheme 14). The resulting adduct, which contains two hydroxyl groups and four vinyl groups, was obtained in 89% yield.

The IR spectrum of (11) is shown in Figure 16. The band assignments are 3424 and 1040 cm^{-1} (O-H stretching vibrations of a secondary alcohol), 1643 , 1614 , 1513 , and 1454 cm^{-1} (vinyl and aromatic C=C stretching vibrations), 921 cm^{-1} (vinyl C=C bending vibrations) and 830 cm^{-1} (1,4-disubstituted benzene). The ^1H NMR spectrum of (11) (Figure 17) showed that the ratio of H3 : H12 was 1 : 1, confirming that two molecules of (6) reacted with (10). If only one had reacted, the ratio would have been 1 : 2. The ^{13}C NMR spectrum (Figure 18) could be assigned as follow : the signals at 134.9 ppm and 118.3 ppm were assigned to vinyl carbons. The signals of the carbon of the benzene ring were at 156.6 , 143.4 , 127.7 and 113.9 ppm. In the mass spectrum (Figure 19), the m/e 534 was the molecular ion, consistent with a molecular formula $\text{C}_{33}\text{H}_{46}\text{N}_2\text{O}_4$. The fragmentation ion peak at m/e 493 ($M^+ - 41$) and 424 were due to loss of allyl group and the diallylaminomethyl group. The m/e 381, 228, and 213 indicated the elimination of one molecule, two molecules of 3-N,N-diallylamino-2-hydroxy-1-

propene and a methyl group, respectively. The m/e 154 was 3-N,N-diallylamino-2-hydroxypropyl fragment and m/e 41 was the allyl group.



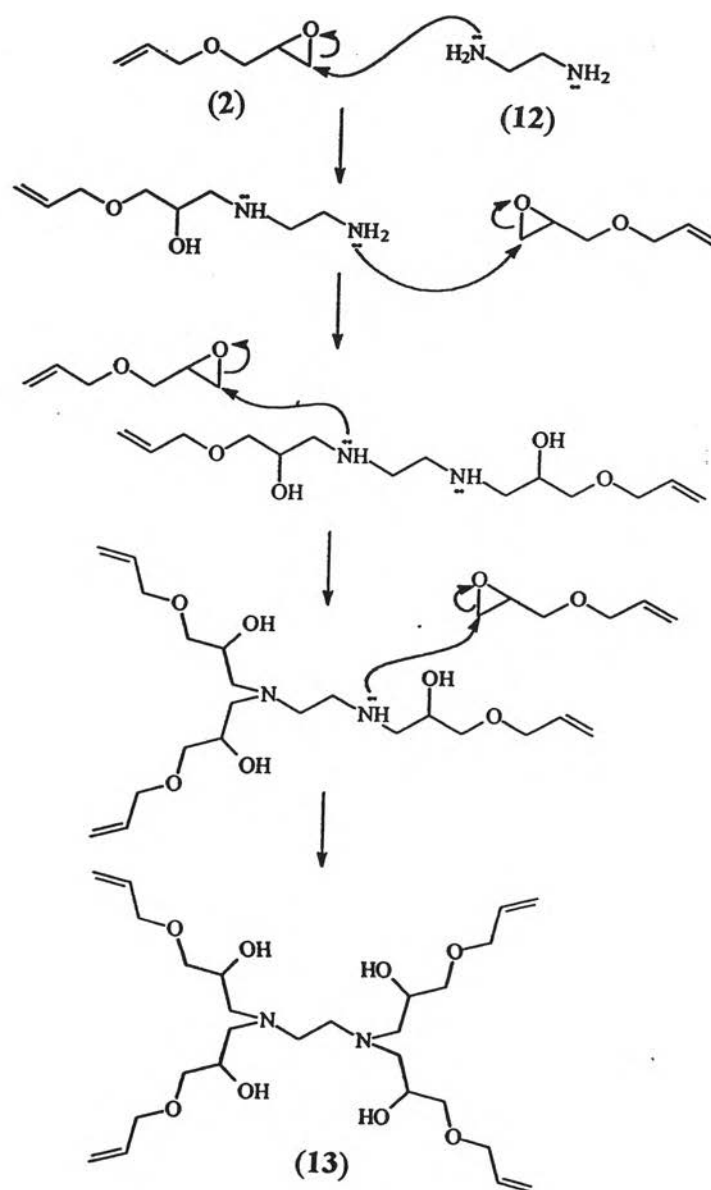
Scheme 14

In the synthesis of compounds (3), (7), and (9), it was necessary to use sodium hydroxide as a base since the nucleophiles used were phenolic oxygens. When diallylamine was employed as a nucleophile in the synthesis of (11), the use of sodium hydroxide was not necessary since an amine nitrogen is more nucleophilic than a phenolic hydroxyl group.

Synthesis of N,N,N',N'-tetrakis-(3-allyloxy-2-hydroxy-1-propoxy) ethylenediamine (13)

This reaction was carried out by heating a mixture of 2 and 12 at 80°C. The expected product 13 could not be obtained as a pure compound. This might be because the reaction gave a mixture of N-, N,N-, N,N', N,N,N', and N,N,N',N'-substituted products (Scheme 15). The ratio of olefinic protons (H1, H2, H3) : aliphatic protons (H4-H12, OH) of the trisubstituted product would be 1 : 3.11, but the tetrasubstituted product would display a ratio of 1:3. The ¹H NMR spectrum (Figure 20) of (13) showed that the ratio was 1 : 3.03, which indicated that the product may be a mixture of tri and tetrasubstituted compounds. As the product was a mixture, the ¹³C NMR

spectrum was more complicated. Nevertheless, the signals for the carbon atoms of the vinyl groups at 134.6 ppm and 117.2 ppm and the signals of aliphatic carbon of (13) at 72.4, 69.0, 67.9, 59.5, and 54.9 ppm were of higher intensity than the others. The IR spectrum of (13) (Figure 21) showed the O-H absorption bands of a secondary alcohol at 3403 and 1003 cm^{-1} .



Scheme 15

In the first stage of the reaction, epoxide ring-opening of (2) with the primary amine group in (12) would occur rapidly to give the N- and N,N'-substituted products which both contain secondary amine groups. Then the reaction would be slow due to steric hindrance from the allyloxypropanol group causing the secondary amine in the N,N'-substituted products to be less reactive than primary amine group in (12). When the product was mainly the N,N,N'-substituted compound, the reaction contained with difficulty and the reaction time required to obtain mainly product (13) was 15 hours.

Study of the Reactivity of Crosslinking Agents

The purpose of this study was to evaluate potential applications of compounds (3), (7), (9), (11), and (13) as crosslinking agents for polyurethane. The study focused on the reactivity of hydroxyl and vinyl groups. The expected reactions were those of the hydroxyl group with the isocyanate group to create urethane linkages and free radical polymerization of vinyl groups to give polyvinyl linkages.

Reactivity of the Hydroxyl Group

In the synthesis of polyurethanes, the formation of urethane linkages by reaction of isocyanates with hydroxyl groups is a very important reaction. This was investigated by studying the reaction between hydroxyl groups in the crosslinking agents and isocyanate compounds. The mono and diisocyanate compounds chosen for this study were phenyl isocyanate and 4,4'-diphenylmethane diisocyanate (MDI). The reaction of phenyl isocyanate with hydroxyl groups is particularly well adapted to a study of the reactivities of crosslinking agents. When a secondary hydroxyl group reacts with phenyl isocyanate to form carbamate derivatives, the result is that the hydroxyl nucleophile adds in a predictable manner to the polarized azomethine linkage of the isocyanate group. The carbamate derivatives were characterized by IR, ^1H and ^{13}C NMR spectroscopy. From IR and ^{13}C NMR spectra, it could be seen that a urethane linkage had formed. The reaction can give mono and di substitution products. This was determined by comparison of ^1H NMR integral of the olefinic protons, which came from the vinyl group of crosslinking agent, and aryl protons which came from

phenyl isocyanate. The reaction of crosslinking agents with 4,4'-diphenylmethane diisocyanate gave polyurethane polymers. The polyurethane polymers were insoluble in all solvents tried. The method used to determine structure was IR. The band at 3200-3400 cm^{-1} associated with O-H stretching vibrations in the starting secondary alcohol should disappear due to the reaction of the hydroxyl group of the crosslinking agents with the isocyanate group of MDI. The band at 2270 cm^{-1} would not be observed in the spectrum indicating that the MDI was consumed. And N-H band and C=O band appear. However, IR data can not give information about the structure of polyurethane polymers.

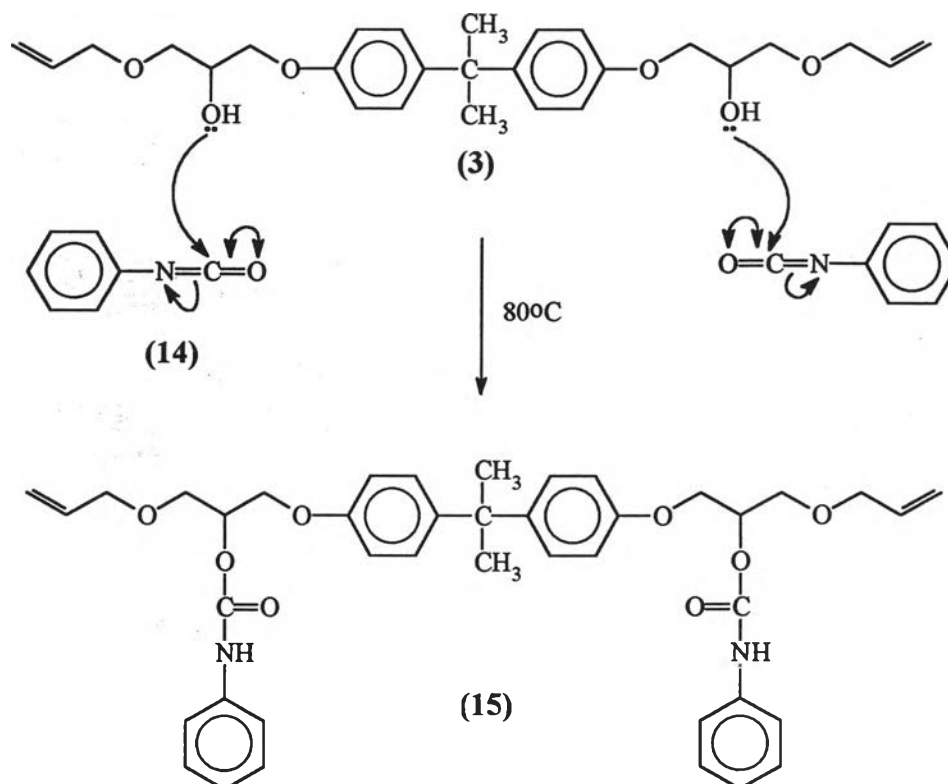
The objective of this study was to synthesize carbamate derivatives, by reaction between the crosslinking agent and phenyl isocyanate, which are of low molecular weight and can be characterized. Moreover, it is a model reaction for polyurethane preparation. For the reaction with MDI, we aimed to study the reactivity and suitability of the crosslinking agents for the preparation of polyurethanes suitable for engineering applications.

Reaction of (3) and Phenyl Isocyanate (14)

The reaction between crosslinking agent (3) and phenyl isocyanate (14) was carried out in the absence of solvent at 80°C for 4 hours. The reaction occurred by attack of hydroxyl groups in (3) on carbons of the isocyanate group in (14) to yield carbamate derivative (15) in 40% yield as shown in Scheme 16.

Spectral data of (15) indicated the presence of the aromatic ring from phenyl isocyanate. NMR aromatic signals could be observed in the ^1H and ^{13}C NMR spectra at δ 6.67-7.46 and δ 137.7, 129.1, 123.6 and 118.7 ppm, respectively. If only one equivalent of phenyl isocyanate reacted, the ratio of H3 : aryl protons would be 2 : 13 while if two equivalents reacted, the ratio would be 1 : 9. The ^1H NMR spectrum of (15) (Figure 22), showed a ratio of 1 : 9 indicating that both hydroxyl groups were converted to carbamates. They were confirmed by the disappearance of hydroxyl groups at 3421 cm^{-1} in the IR spectrum. The presence of carbamate groups was confirmed by ^{13}C NMR (Figure 23) chemical shift at 152.7 ppm (C=O). In addition the

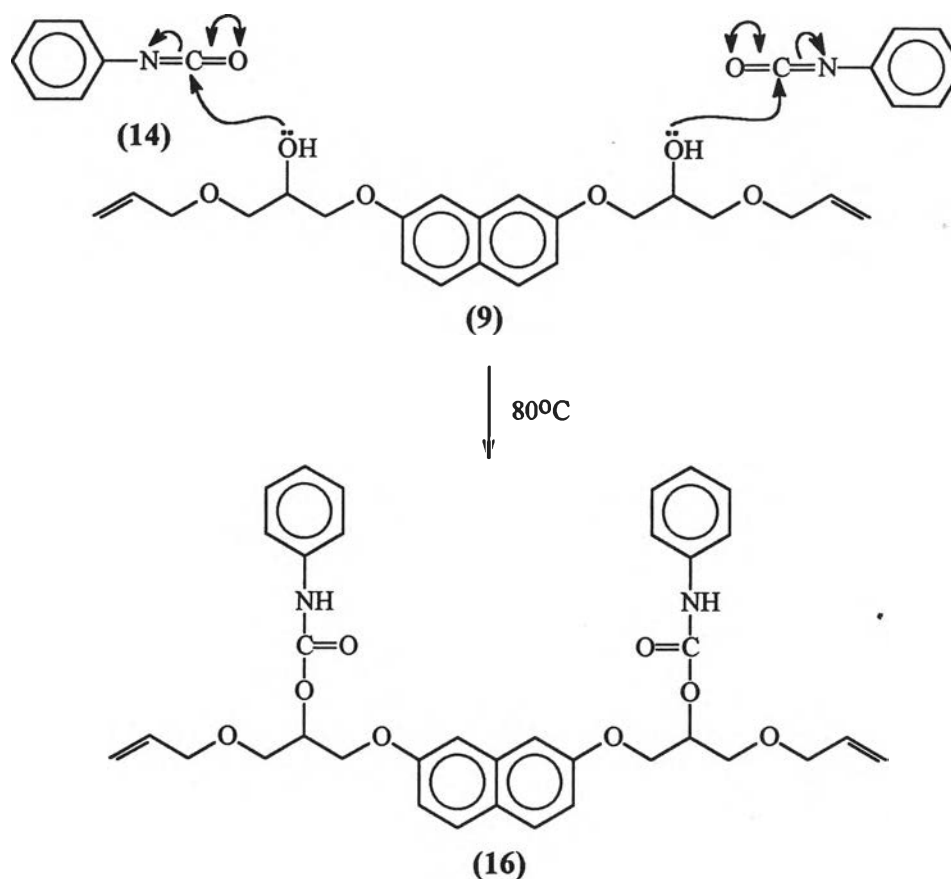
IR spectrum (Figure 24) showed a characteristic absorption at 3295 and 1729 cm^{-1} associated with N-H stretching and C=O stretching, respectively.



Scheme 16

Reaction of (9) and Phenyl Isocyanate (14)

The reaction between (9) and phenyl isocyanate (14) was carried out in the same manner as the reaction between (3) and (14). A mixture of (9) and (14) was heated in the absence of solvent at 80°C for 6 hours. The resulting carbamate derivative (16) was obtained in 74% yield (Scheme 17).

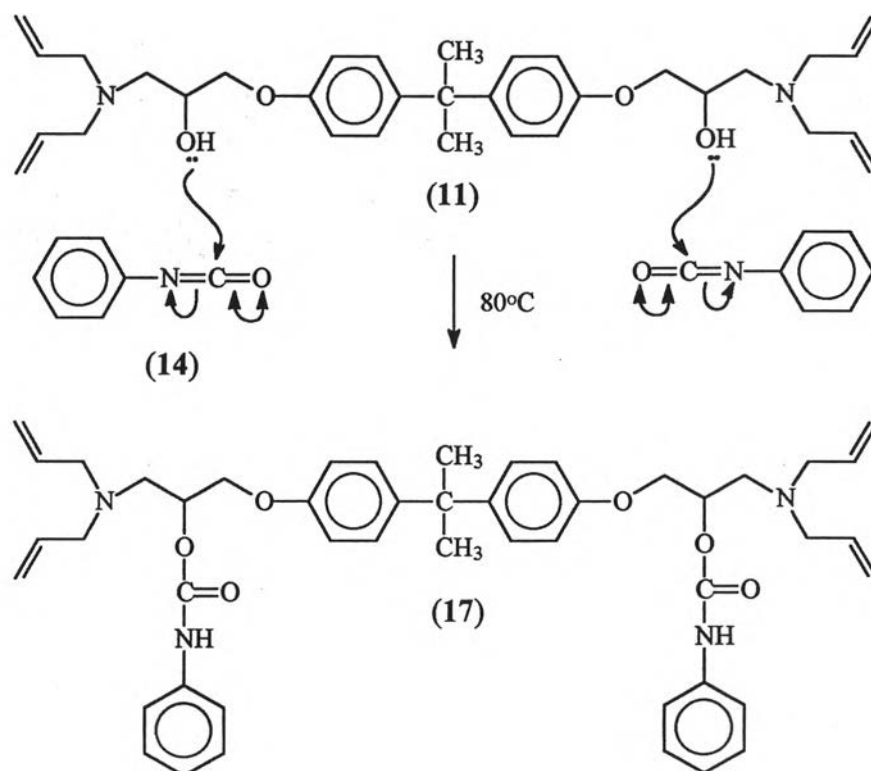


Scheme 17

The ^1H and ^{13}C NMR spectra of (16) showed aromatic signals at δ 6.78-7.85 ppm and δ 137.6, 129.0, 123.6 and 118.7 ppm. The absorption of the hydroxyl groups in the IR spectrum of (8) (Figure 25) at 3224 cm^{-1} disappeared completely. The integral of ^1H NMR spectrum (Figure 26) showed that the ratio of H3 : aryl protons was 1 : 9, which indicated that both hydroxyl groups in (8) reacted with phenyl isocyanate. If only one had reacted, the ratio would have been 1 : 12. The ^{13}C NMR spectrum (Figure 27) showed that (16) contained a carbamate group due to the presence of a signal at 152.7 ppm (C=O). It was also confirmed by the IR spectrum which showed bands at 1723 and 3332 cm^{-1} associated with C=O stretching and N-H stretching vibrations, respectively.

Reaction of (11) and Phenyl Isocyanate (14)

The reaction between (11) and phenyl isocyanate (14) was carried out in the same manner as the reaction between (3) and (14). A mixture of (11) and (14) was heated in the absence of solvent at 80°C for 24 hours. The resulting carbamate derivative (17) was obtained in 34% yield (Scheme 18)



Scheme 18

The ^1H and ^{13}C NMR spectra of (17) indicated the presence of the aromatic ring from phenyl isocyanate at δ 6.65-7.63 and δ 137.8, 129.0, 123.4 and 118.7 ppm, respectively. The absorption of the hydroxyl groups in the IR spectrum (Figure 28) at 3424 cm^{-1} disappeared completely. The integral of ^1H NMR spectrum (Figure 29) showed that the ratio of H3 : aryl proton was 2 : 9, which indicated that both hydroxyl groups in (11) reacted with phenyl isocyanate. If only one equivalent of phenyl isocyanate reacted, the ratio would be 4 : 13. The presence of carbamate groups was confirmed by ^{13}C NMR (Figure 30) chemical shift at 152.9 ppm (C=O). In addition, the

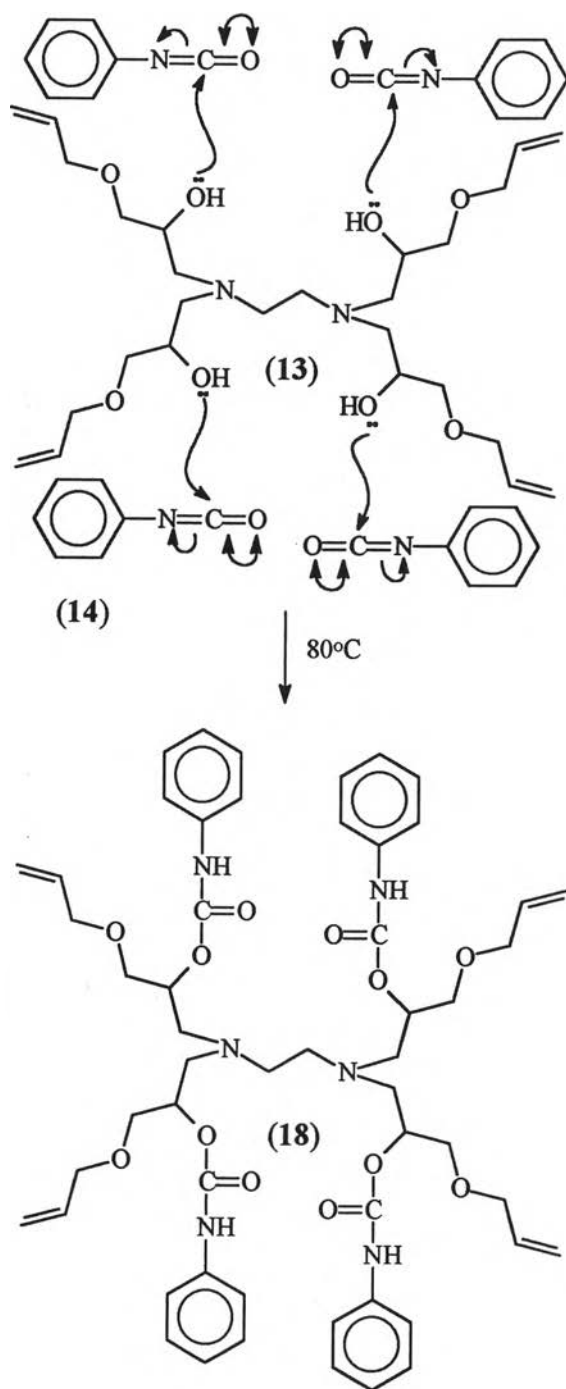
IR spectrum showed a characteristic absorption at 3316 and 1739 cm^{-1} associated with N-H stretching and C=O stretching, respectively.

Reaction of (13) and Phenyl Isocyanate (14)

The reaction between (13) and phenyl isocyanate (14) was carried out in the same manner as the reaction between (3) and (14). A mixture of (13) and (14) was heated in the absence of solvent at 80°C for 48 hours. The resulting carbamate derivative (18) was obtained in 20% yield (Scheme 19).

The ^1H and ^{13}C NMR spectra of (18) showed aromatic signals at δ 6.95-7.65 ppm and δ 138.1, 128.9, 123.2 and 118.7 ppm, respectively. The ^1H NMR spectrum of (18) (Figure 31), showed a ratio of 1 : 5 indicating that all of hydroxyl groups were converted to carbamates. If three equivalents of phenyl isocyanate reacted, the ratio of H3 : aryl protons would be 4 : 15 while if four equivalents reacted, the ratio would be 1 : 5. This was also confirmed by the disappearance of the IR absorbance of the hydroxyl groups at 3403 cm^{-1} in the IR spectrum. The presence of carbamate groups was confirmed the appearance of a peak at 153.4 ppm in the ^{13}C NMR spectrum (Figure 32) due to the carbonyl carbon. It was also confirmed by the IR spectrum (Figure 33) which showed bands at 1713 and 3338 cm^{-1} associated with C=O stretching and N-H stretching vibrations, respectively.

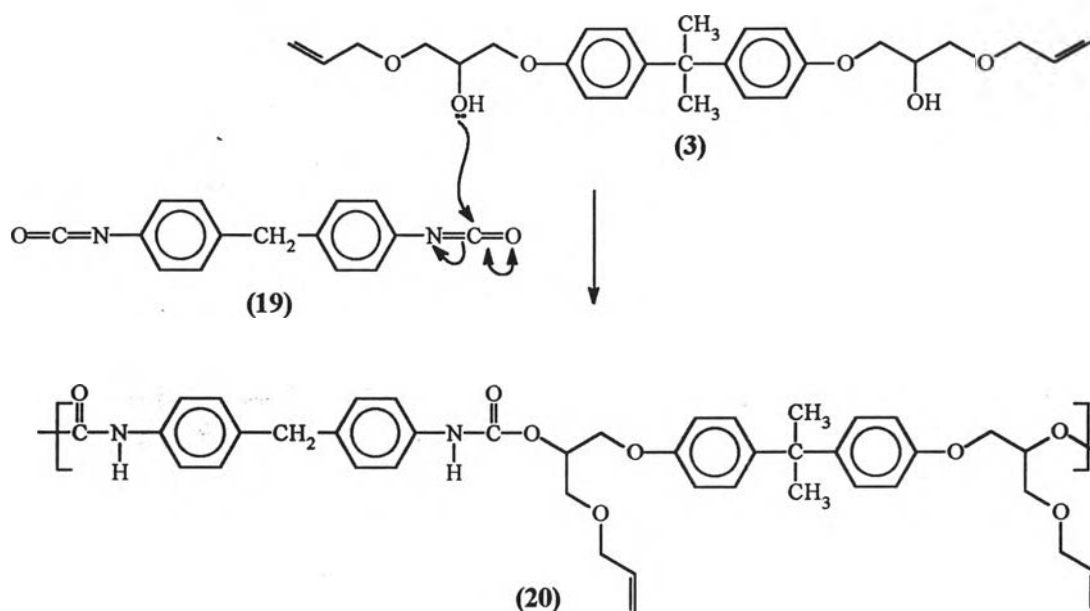
All of the crosslinking agents could react with phenyl isocyanate but the reaction between compound (7) and phenyl isocyanate was not done since (7) was very viscous and therefore could not be utilized in the preparation of polyurethane.



Scheme 19

Preparation of Polyurethane (20) from (3) and 4,4'-diphenylmethane diisocyanate (19)

The reaction between crosslinking agent (3) and 4,4'-diphenylmethane diisocyanate (19) was carried out by heating a mixture of (3) and (19) without solvent at 120°C for 18 hours. The resulting polyurethane (20) was obtained as a solid. The IR spectrum (KBr) of (20) (Figure 34) showed the urethane linkage in the structure of (20) : carbonyl stretching vibrations (C=O) and N-H stretching vibrations of a urethane linkage at 1734 and 3402 cm^{-1} , respectively. However, from IR the data, it could not be concluded whether the structure of (20) is linear or cyclic or even whether it is really a polymer. Scheme 20 shows the linear polyurethane (20).

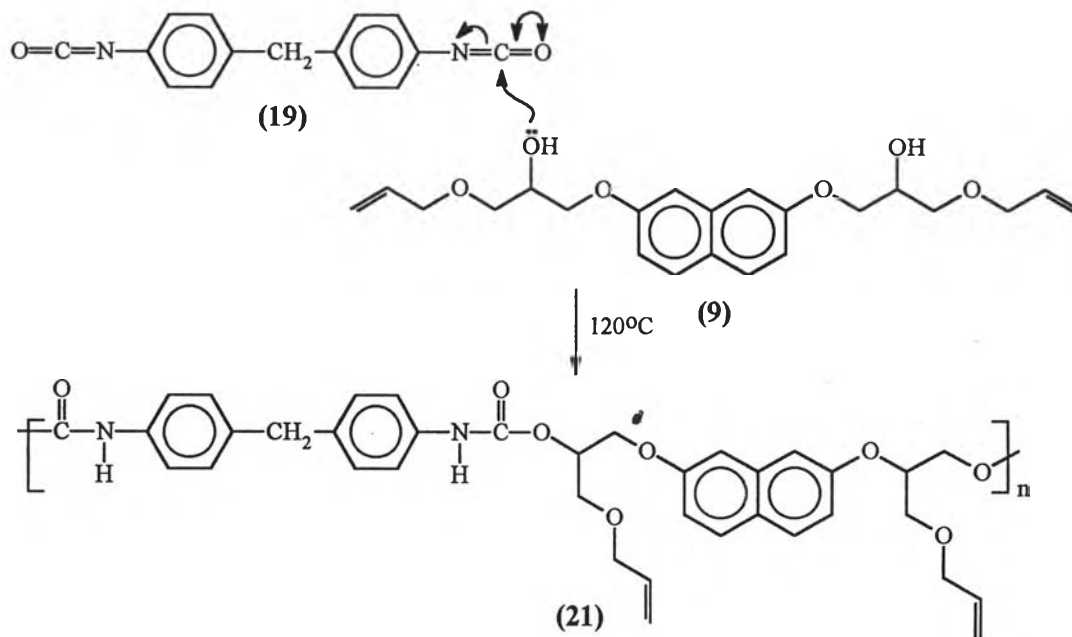


Scheme 20

Preparation of Polyurethane (21) from (9) and (19)

The polymerization reaction between crosslinking agents (9) and (19) was carried out in the absence of solvent at 120°C for 15 hours, which is the time taken for the reaction to be complete. The resulting polyurethane (21) was obtained as a solid. The IR spectrum (KBr) of (21) (Figure 35), gave the absorption band of a urethane linkage at 1720 cm^{-1} (C=O stretching vibrations) and 3400 cm^{-1} (N-H stretching

vibrations). From the IR data, it can be concluded that the structure of (21) contains a urethane linkage. The linear polyurethane (19) is proposed in Scheme 21.



Scheme 21

Preparation of Polyurethane (22) from (11) and (19)

The reaction between (11) and (19) occurred rapidly at room temperature to give the product as solid 5 minutes after mixing. The IR spectrum showed an isocyanate band at 2270 cm^{-1} , indicating that the reaction was incomplete. The reaction was then carried out in the absence of solvent at 120°C . The polymerization was complete in 30 mins. This might be because the tertiary amine group in (11) can serve as a catalyst for the reaction between the hydroxy group and isocyanate group. Baker and Holdsworth explained the mechanism of catalysis as involving donation of electrons from the amine nitrogen to the carbonyl carbon of isocyanate group to form a complex intermediate (Figure 36) which is more reactive towards nucleophilic attack (Scheme 22)³⁰. Alternatively, the amine nitrogen may just be acting as a basic catalyst (Scheme 23).

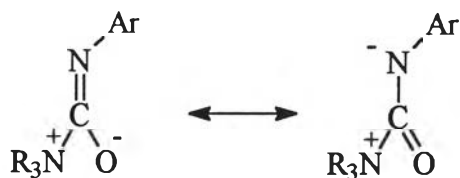
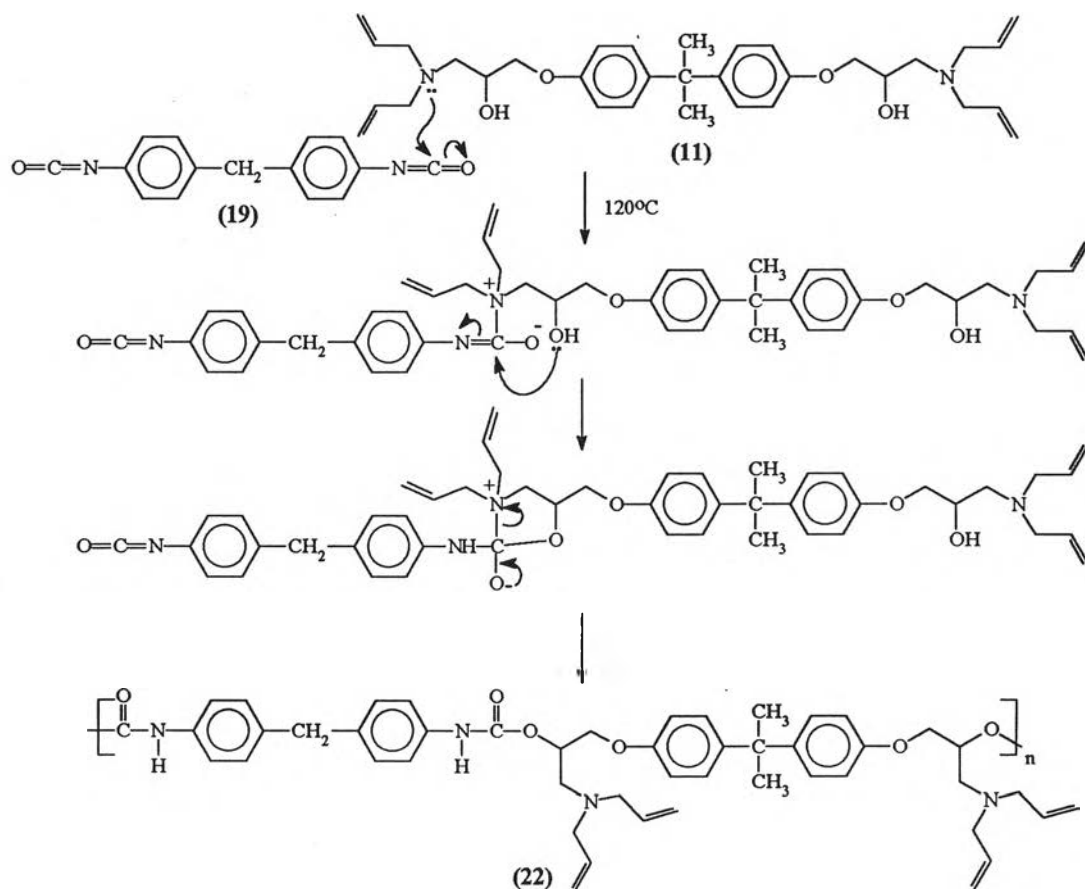
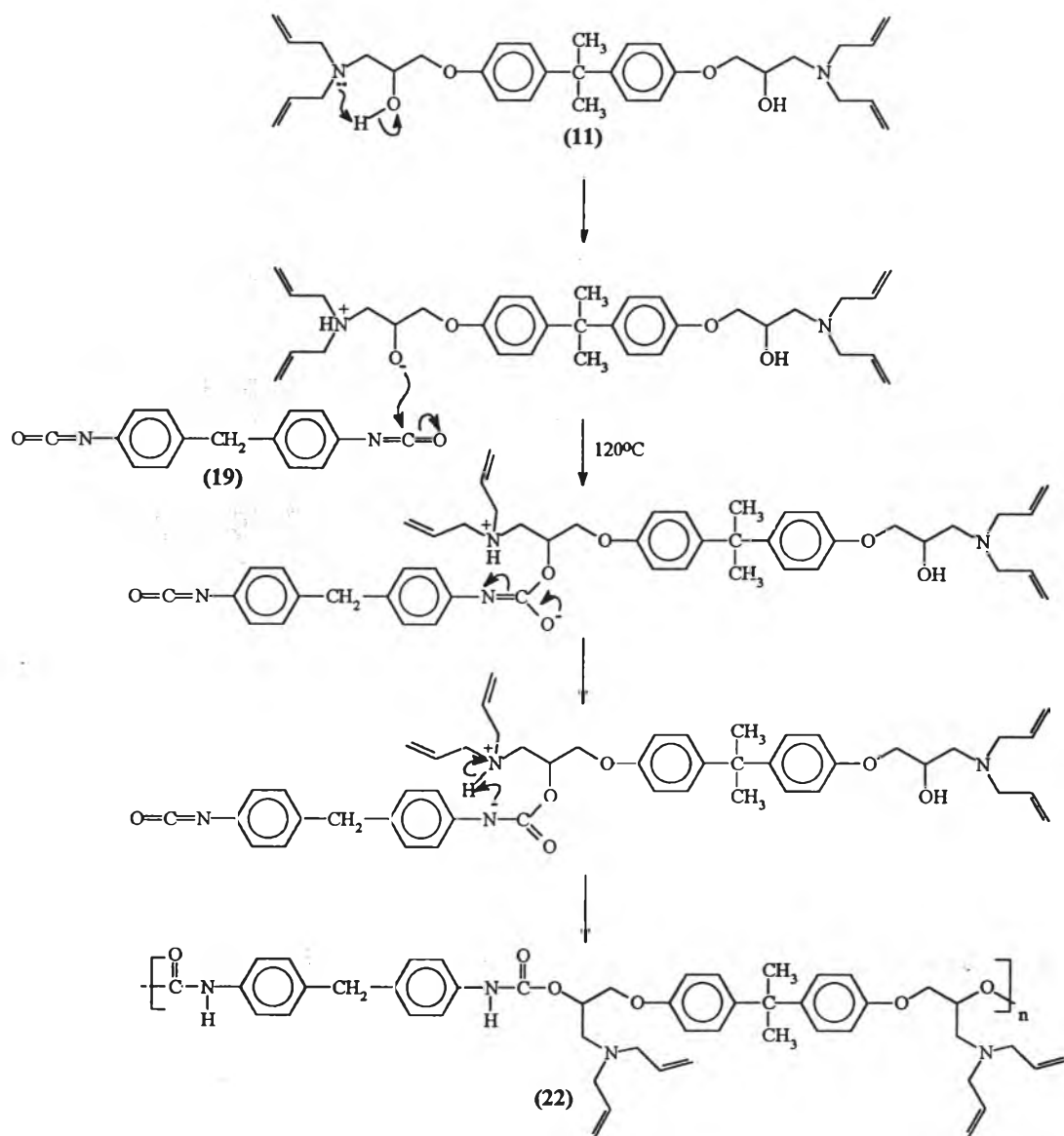


Figure 36



Scheme 22

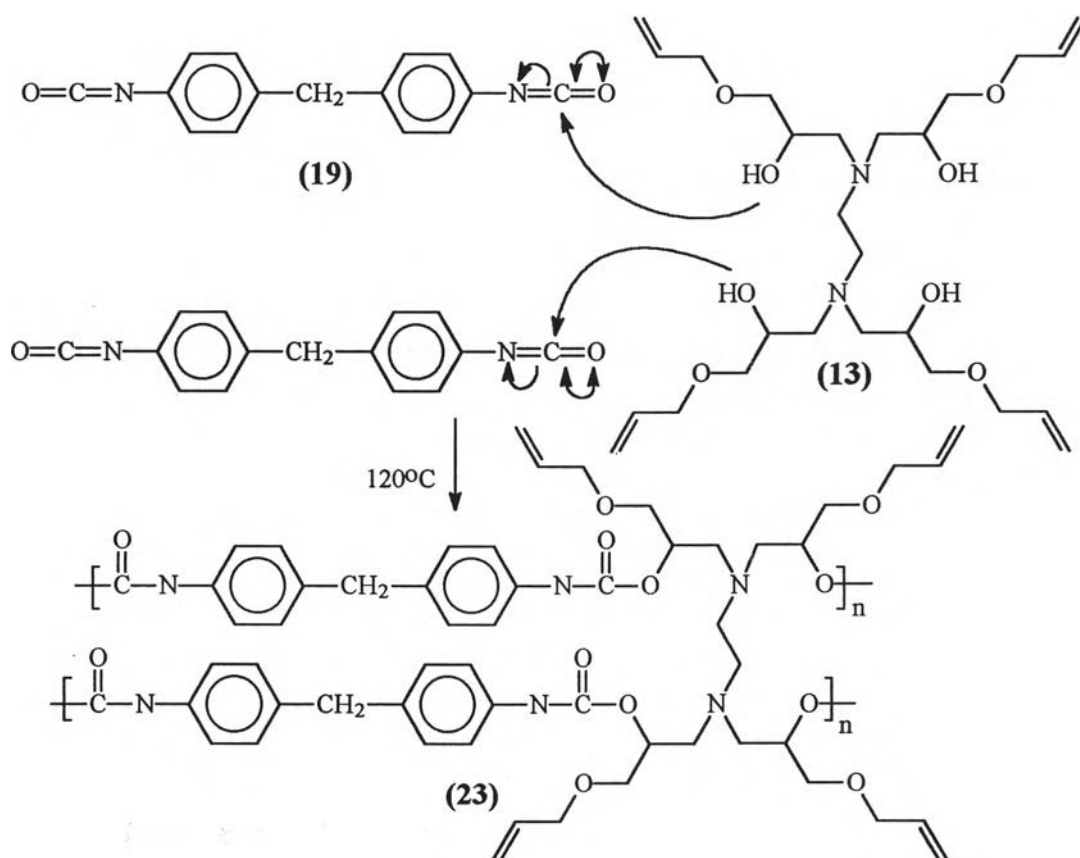
Polyurethane (**22**) was obtained as a solid. The IR spectrum of (**20**) (Figure 37) showed bands at 3360 cm^{-1} (N-H stretching vibrations) and 1713 cm^{-1} (C=O stretching vibrations) for the urethane linkage. However, from the IR data, it could not be concluded whether the structure of (**22**) is linear or cyclic, or even whether it is really a polymer. Schemes 22 and 23 shows the linear polyurethane (**22**).



Scheme 23

Preparation of Polyurethane (23) from (13) and (19)

The reaction between (13) and (19) was carried out in the absence of solvent at 120°C. The reaction occurred slowly and it took 24 hours to reach completion. Polyurethane (23) was obtained as a yellow solid. The obtained polymer (23) should have a network structure while (20), (21), and (22) would be linear or cyclic polymers. The reaction took a long time since (13) had four hydroxy groups. The IR spectrum of (23) (Figure 38) show the absorption band of carbonyl (C=O) stretching vibrations and N-H stretching vibrations of urethane linkage at 1725 and 3390 cm^{-1} , respectively. The IR data indicated that a urethane linkage was present in the structure of (23). A possible structure of (23) is shown in Scheme 24.



Scheme 24

A TGA thermogram of polyurethane (20-23) obtained from the reaction between crosslinking agents and MDI was obtained. Their weight loss data is shown in Table 1. Polyurethane (20) showed 27.3% weight loss at the temperature range 280-380°C which is due to decomposition of polymer chain (Figure 39). TGA thermograms of polyurethanes (21), (22), and (23) gave similar results (Figures 40-42).

Table 1. Weight loss of polyurethane from TGA

Polyurethane	Beginning temperature (°C)	Temperature at which weight loss occurs (°C)			
		5%	10%	20%	30%
Polyurethane (20)	180	280	320	350	380
Polyurethane (21)	180	280	310	340	380
Polyurethane (22)	170	250	270	330	390
Polyurethane (23)	170	220	240	270	340

In this work, the secondary hydroxyl groups of various crosslinking agents can be reacted with isocyanate groups of MDI. The reactivity of them will depend upon two factors : (1) whether the structure can allow them to serve as a catalyst for this reaction, and (2) steric hindrance. All of the compounds are feasible as crosslinking agents for the preparation of polyurethane.

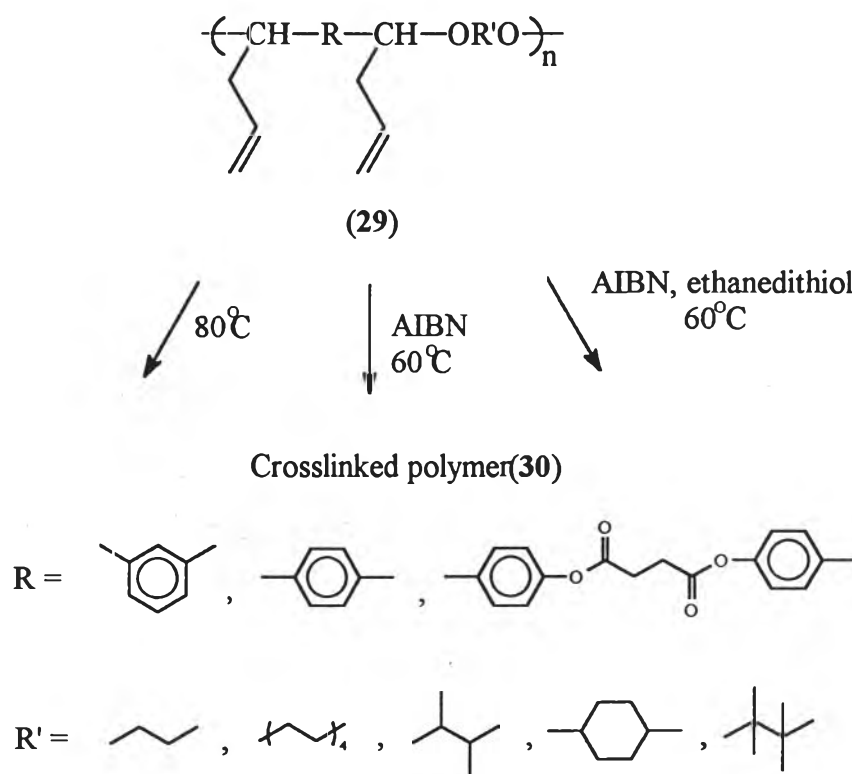
Reactivity of Vinyl Group

The other expected reaction of crosslinking agents (3), (9), (11), and (13) is free radical reaction of vinyl groups. The most important synthetic reactions that organic radicals undergo are addition to multiple bonds and abstractions. This investigation was based on the free radical reaction of vinyl groups in crosslinking agents since the expected reaction was free radical addition to give a polyvinyl system.

Many initiators can be employed such as AIBN, benzoyl peroxide and dicumyl peroxide. Benzoyl peroxide was chosen since it is comparatively stable at room

temperature but rapidly decomposes at 100°C. AIBN decomposes into radicals very rapidly (65-85°C) which can be attributed to the formation of a very stable product (N₂). The decomposition of dicumyl peroxide is much slower than benzoyl peroxide. The free radical initiator that was chosen in this study was benzoyl peroxide, which could undergo homolytic cleavage at 80°C to give two benzoyl radicals. When benzoyl radical are generated in the presence of crosslinking agents, the benzoyl radical may add to the double bonds of vinyl groups on crosslinking agents to form new free radicals in the initiation step. The new free radical may add to the vinyl group of another molecule in a manner similar to the initiation step. The reaction would continue until the supply of vinyl groups was exhausted, i.e. the starting material (crosslinking agents) and benzoyl peroxide disappeared. The product would be characterized by IR and ¹H NMR. The IR spectra were expected to show the ester group, and the band at 900-940 cm⁻¹ (vinyl C=C bending vibration) should disappear. In the ¹H NMR spectrum, the reaction could be observed by comparison of integral of the vinyl groups (CH₂=CH-) at 4.50-6.20 ppm and aryl protons at 6.80-7.20ppm.

Yokozawa and Takenoya^{31, 32} synthesized polyether (29) which had allyl groups in the side chains. Crosslinking of the polymer (29) using AIBN as an initiator gave crosslinked polymer (30) in 33% yield (Scheme 25). Furthermore, when the polymer (29) was treated with AIBN and ethanedithiol, the crosslinked polymer was obtained in 95% yield. The radical addition of the thiol groups in ethanedithiol to the allyl groups in the polymer (29) took place since the absorption of a carbon-carbon double bond of the polymer became weak in the IR spectrum.



Scheme 25

Reaction of (3) and Benzoyl Peroxide (24)

The reaction between crosslinking agent (3) and 5 mole % of benzoyl peroxide (24) was carried out in the absence of solvent at 80°C and the reaction was monitored by ^1H NMR. This reaction temperature was chosen to avoid the loss of benzoyl peroxide from the reaction mixture by sublimation. The progress of the reaction was observed by comparison of the integration ratio of H3 (olefinic protons) : H11 (aromatic protons) in the ^1H NMR spectrum. At the beginning of the reaction, the integration ratio of H3 : H11 was 0.5. As the reaction time increased, the integration ratio of H3 : H11 decreased which indicated that the free radical reaction occurred at the vinyl groups of crosslinking agent (3) (Figures 43-46). The reaction was slow after a reaction time of 6 hours and the reaction was still incomplete after 24 hours. The ^1H NMR obtained after 24 hours showed that the ratio H3 : H11 was 0.31, which implied that the reaction was a partial addition reaction at the double bond. Appearance of the signal at 3.45-3.62 ppm, the integration ratio of H1 + H2 : H3 from 2 was 2.37 at

24 hours, indicating the formation of alkyl groups which resulted from the free radical reaction. The relationship between the decrease integration ratio of H3 (olefinic protons) : H11 (aromatic protons) and reaction time is shown in Figure 47.

Furthermore, the integration ratio of H11 (aromatic protons) : H4 + H5 + H8 + H9 + H10 (allylic protons + H8 + H9 + H10) in (3) was also observed. The integration of H4 + H5 + H8 + H9 + H10 also decreased as the reaction time increased. This suggests that the free radical reaction also occurred at the allylic carbon which bears H4, H5. The relationship between the decrease integration ratio of H4 + H5 + H8 + H9 + H10 (allylic proton + H8 + H9 + H10) : H11 (aromatic protons) and reaction time is shown in Figure 48.

Further study of the reaction between (3) and 5 mole % of (24) was done using differential scanning calorimetry (DSC). The DSC experiment was performed by heating a mixture of (3) and (24) in a DSC cell using an aluminum pan under nitrogen. An exothermic peak between 90°C and 175°C could be observed (Figure 49). This also indicated that the free radical reaction of (3) took place. By use of a DSC kinetic program, the selected reaction temperature was 80°C, 100°C, 130°C, and 150°C. It could be observed that the shortest reaction time was 20 min which was obtained at 150°C (Figure 50).

The IR spectrum (KBr) of the product (25) after a reaction time of 24 hours (Figure 51) showed an absorption band of carbonyl stretching vibration at 1725 cm^{-1} . This absorption came from the ester group derived from benzoyl peroxide. Since the spot of benzoyl peroxide was not observed on the TLC of product (25), the carbonyl absorption should be the ester group on the product (25) resulted from reaction between (3) and benzoyl peroxide. Other IR absorption observed were bands of vinyl and aromatic C=C stretching vibration at 1605, 1508, 1465, and 1422 cm^{-1} . However, it exhibited the absorption bands at 910 cm^{-1} associated to C=C bending vibration which indicated that the free radical reaction at the double bond was incomplete.

Reaction between (9) and Benzoyl Peroxide (24)

The reaction between (9) and (24) was carried out in the same manner as the reaction between (3) and (24). The ^1H spectra at different reaction times showed the same trend as in the case of reaction between (3) and (24). A mixture of (3) and (24) was heated in the absence of solvent at 80°C . At the beginning of the reaction, the integration ratio of H3 (olefinic protons) : H11 + H12 (aromatic protons) was 0.48 and the integration ratio of H4 + H5 + H8 + H9 + H10 (allylic protons + H8 + H9 + H10) : H11 + H12 (aromatic protons) was 2.46. As the reaction time increased, the integration of H3 decreased which indicated that the free radical reaction occurred at the vinyl groups of crosslinking agent (9) (Figure 52-55). The relationship between the integration ratio of H3 (olefinic protons) : H11 + H12 (aromatic protons) and reaction time is shown in Figure 56.

While the reaction time increased, the integration ratio of H11 + H12 (aromatic protons) : H4 + H5 + H8 + H9 + H10 (allylic protons + H8 + H9 + H10) was not changed. This indicated that the free radical reaction did not occur at the allylic position of crosslinking agent (9)

DSC study of the reaction between (9) and 5 mole % of (24) was done in the same manner as the reaction between (3) and (24) and a similar result was obtained. The exothermic peak between 68°C and 147°C could be observed (Figure 57). This also indicated that the free radical reaction of (24) took place. By use of the DSC kinetic program, it could be observed that the shortest reaction time was 5 min which was obtained at 150°C (Figure 58).

The IR spectrum (KBr) of the product (26) obtained after a reaction time of 24 hours (Figure 59) showed the absorption band of a carbonyl stretching vibrations at 1723 cm^{-1} , which indicates the presence of benzoate groups in the product. Other IR absorption observed were bands of vinyl and aromatic C=C stretching vibrations at 1632, 1573, 1465, and 1438 cm^{-1} . However, the IR spectrum displayed a significant band at 927 cm^{-1} (C=C bending vibrations) indicating that the vinyl groups exist in the product

Reaction between (11) and Benzoyl Peroxide (24)

The reaction between (11) and (24) was carried out in the same manner as the reaction between (3) and (22). A mixture of (11) and (22) was heated in the absence of solvent at 80°C. The ^1H NMR spectra at different reaction times showed the same trend as in the case of reaction between (3) and (22). At the beginning of the reaction, the integration ratio of H3 (olefinic protons) : H11 (aromatic protons) was 1 and the integration ratio of H4 + H5 (allylic protons) : H11 (aromatic protons) was 2. As the reaction time increased, the integration ratio of H3 (olefinic protons) : H11 (aromatic protons) and H4 + H5 (allylic protons) : H11 (aromatic protons) decreased which indicated that the free radical reaction occurred at the vinyl groups of crosslinking agent (11) (Figures 60-63). The relationship between the integration ratio of H3 (olefinic protons) : H11 (aromatic protons) and reaction time is shown in Figure 64. Figure 65 shows the relationship between the integration ratio of H4 + H5 (allylic protons) : H11 (aromatic protons) and reaction time.

A DSC study of the reaction between (11) and (24) could not be done since the mixture of (11) and (24) was not homogeneous and therefore the exothermic peak was not observed in DSC thermogram.

The IR spectrum (KBr) of the product (27) obtained after a reaction time of 24 hours (Figure 66) showed the absorption bands at 1720 cm^{-1} (C=O stretching vibration). The carbonyl absorption should be the ester group of the product (27) resulting from the reaction between (11) and benzoyl peroxide. However, the IR spectrum showed the absorption bands at 921 cm^{-1} (C=C bending vibrations) which indicated that the free radical reaction at the double bond was incomplete.

Reaction between (13) and Benzoyl Peroxide (24)

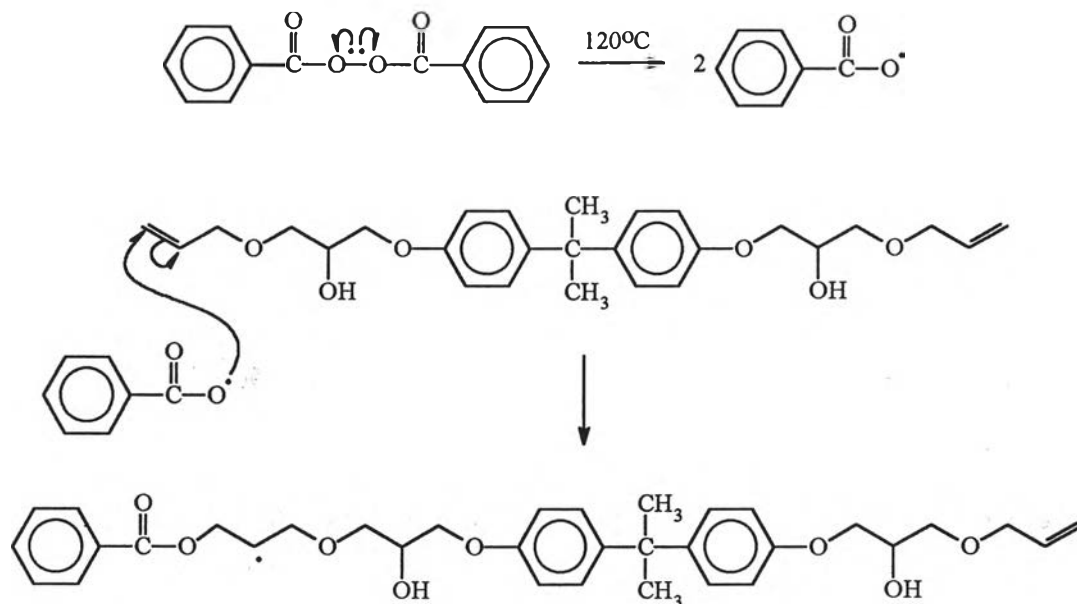
This reaction was carried out in the absence of solvent at 80°C. In the ^1H NMR spectrum, olefinic protons of the crosslinking agent (13) were observed at δ 5.88 ppm and alkyl protons at δ 2.05-3.02 ppm. Comparison of the ^1H NMR integrals of these proton indicated that the free radical reaction occurred. The integration ratio of H3 (olefinic protons) : H9 - H12 (aliphatic protons) was 0.3 and the ratio of H4 + H5 + H8 (allylic protons + H8) : H9 - H12 (aliphatic protons) was 1.05 at the beginning of

the reaction. The ratio of the integration of H3 (olefinic protons) : H9 - H12 (aliphatic protons) decreased as the reaction time increased which indicated that the free radical reaction occurred at the vinyl groups of crosslinking agent (13) (Figures 67-70). The relationship between the decrease integration ratio of H3 (olefinic protons) : H9 - H12 (aliphatic protons) and reaction time is shown in Figure 71. The integration of H4 + H5 + H8 (allylic protons + H8) : H9 - H12 (aliphatic protons) decreased as the reaction time increased. This suggested that the free radical reaction also occurred at the allylic position. The relationship between the decrease integration ratio of H4 + H5 + H8 (allylic proton + H8) : H9 - H12 (aliphatic protons) and reaction time is shown in Figure 72.

A DSC study of the reaction between (13) and (24) could not be done since (13) and (24) did not mix well and therefore the exothermic peak was not observed in the DSC thermogram.

The IR spectrum (KBr) of the product (28) obtained after a reaction time of 24 hour (Figure 73) showed an absorption band at 1739 cm^{-1} . This absorption came from ester group derived from benzoyl peroxide. The other IR absorptions observed were bands of vinyl and aromatic C=C stretching vibrations at 1648, 1603, 1454, and 1422 cm^{-1} . However, it also exhibited an absorption band at 927 cm^{-1} associated with the C=C bending vibration which indicated that the free radical reaction at the double bond was incomplete.

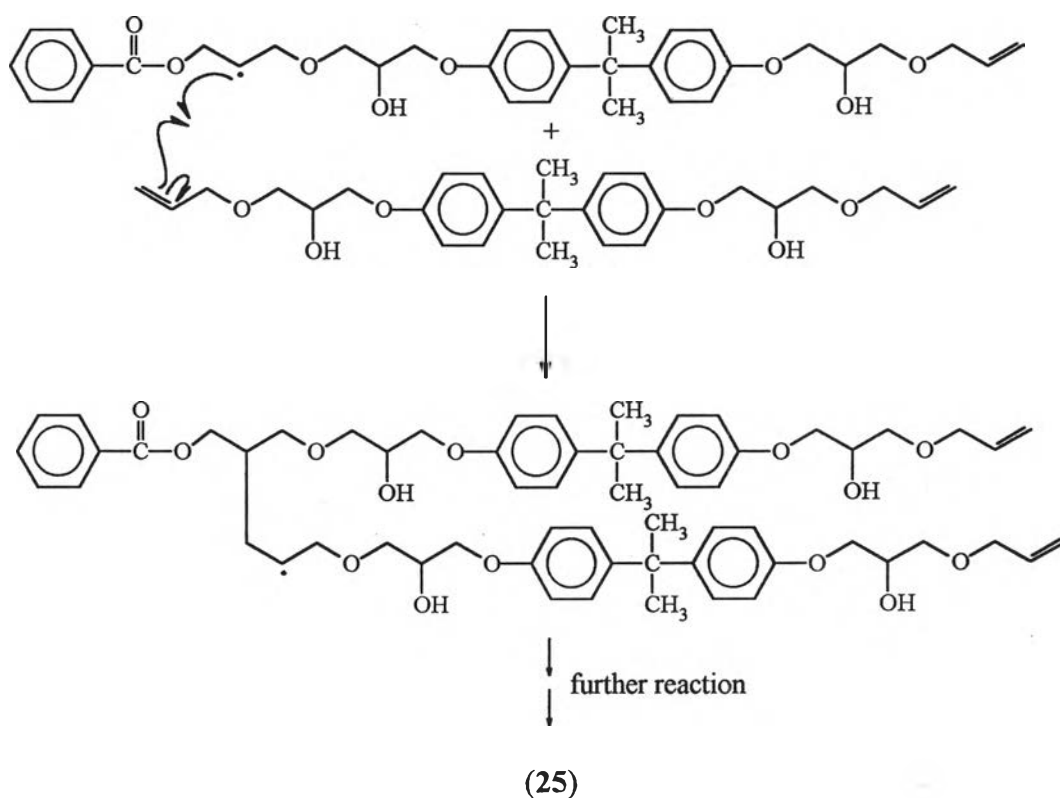
In this study, the crosslinking agents underwent a free radical reaction by the use of benzoyl peroxide as initiator. We could not confirm the structure of the product because the reaction can occur in a variety of ways. From the IR and ^1H NMR data discussed above, two mechanisms of initiation of crosslinking agents by benzoyl radical can be proposed. The first mechanism (Scheme 26) involves an attack of benzoyl free radical on double bond of a crosslinking agent such as (3) to generate a new alkyl free radical, which could then react with another double bond to give a polymer. However, there is no evidence to show that these products were polymers.



Scheme 26

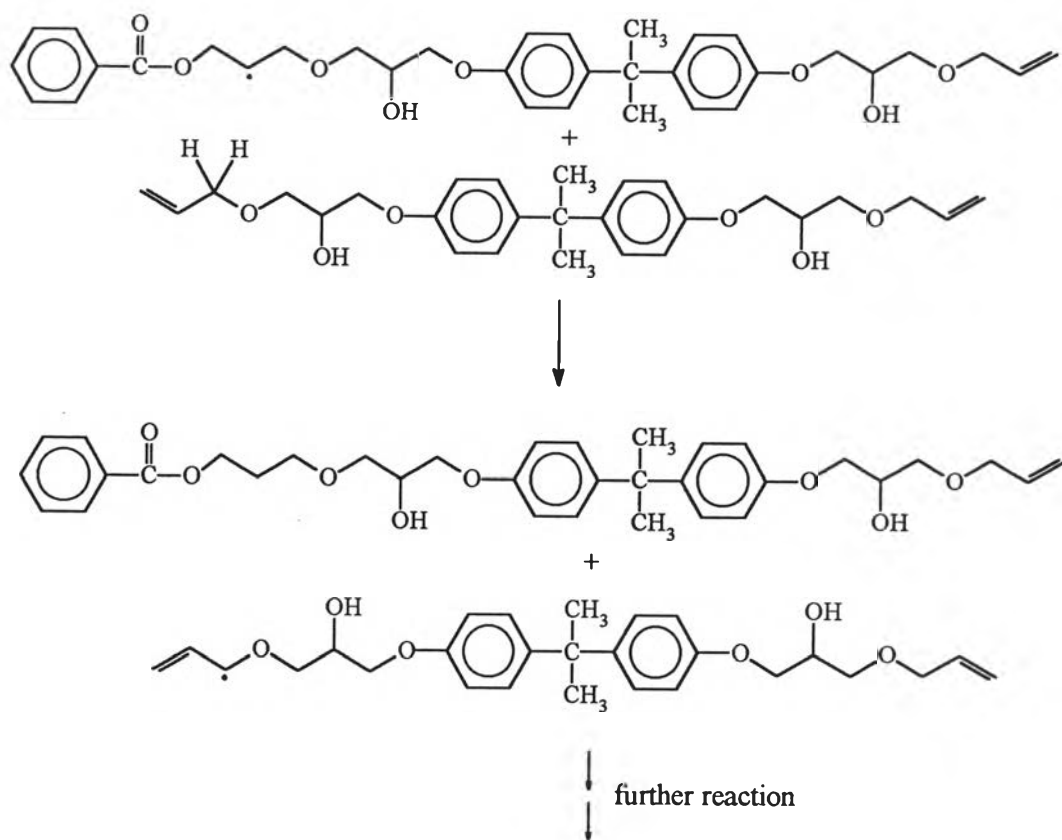
The second mechanism involves an abstraction of a hydrogen of benzoyl free radical at allylic position such as (3) to generate an allylic free radical (Scheme 27), which then coupled with another to give a low molecular weight polymer (Scheme 29). The IR and ^1H NMR data supported this mechanism too. For instance, for polymer (25), the IR spectrum displayed a significantly band at 927 cm^{-1} (C=C bending vibrations) and the ^1H NMR of polymer (25) signals at δ 5.82 ppm could be observed indicating that the vinyl groups exist in the product.

As discussed above, the interaction of free radicals with crosslinking agents (allylic compounds) is a competition between two fundamental reactions, addition and abstraction. Still another complication enters into the formation of the final products of such a reaction, and that is the relative reactivities of the two basically different free radicals formed in these two reactions. In general, the alkyl free radical formed in the addition reaction (Scheme 26) is very reactive because it is not stabilized by resonance. It is easily capable of increasing the chain length of the reaction by another addition (Scheme 28), or abstraction (Scheme 29) reaction.



Scheme 28

Either radical could also be subject to various termination reactions, such as radical coupling.



(25)

Scheme 29

Preparation of Polyurethane (29) from (3), MDI (19), and Benzoyl Peroxide (24)

The reaction between crosslinking agent (3), MDI (19), and 5 mole % of benzoyl peroxide (24) was carried out by heating a mixture of (3), (19), and (24) without solvent at 120°C under nitrogen atmosphere. The reaction took 24 hours to reach completion. The polyurethane (29) was obtained as a brown solid. The IR spectrum (KBr) of (29) (Figure 74), gave the absorption band of a urethane linkage at 3338 cm^{-1} (N-H stretching vibrations) and 1739 cm^{-1} (C=O stretching vibrations). However, IR data can not give information about the structure of the polyurethane polymer.

Preparation of Polyurethane (30) from (3), (19), and Benzoyl Peroxide (24)

The polymerization reaction between crosslinking agent (9), (19), and (24) was carried out in the absence of solvent at 120°C for 24 hours under nitrogen atmosphere, which is the time taken for the reaction to be complete. The resulting polyurethane (30) was obtained as a brown solid. The IR spectrum (KBr) of (30) (Figure 75) showed bands at 3338 cm^{-1} (N-H stretching vibrations) and 1718 cm^{-1} (C=O stretching vibrations) for the urethane linkage. However, from the IR data, the structure of polyurethane (30) could not be determined.

Preparation of Polyurethane (31) from (11), (19), and Benzoyl Peroxide (24)

The reaction between (11), (19), and (24) occurred rapidly at room temperature to give the product as solid 3 minutes after mixing. The reaction was then carried out in the absence of solvent at 120°C under nitrogen atmosphere for 24 hours. Polyurethane (31) was obtained as a yellow solid. The IR spectrum of (31) (Figure 76) showed bands at 3391 cm^{-1} (N-H stretching vibrations) and 1718 cm^{-1} (C=O stretching vibrations) for the urethane linkage. However, the IR data can not show the structure of polyurethane (31)

Preparation of Polyurethane (32) from (13), (19), and Benzoyl Peroxide (24)

The reaction between (13), (19), and (24) was carried out in the absence of solvent at 120°C for 24 hours under nitrogen atmosphere. Polyurethane (32) was obtained as a yellow solid. The IR spectrum of (32) (Figure 77) show the absorption band of carbonyl (C=O) stretching vibrations and N-H stretching vibrations of urethane linkage at 1713 and 3375 cm^{-1} , respectively. However, the IR data can not show the structure of polyurethane (32)

The TGA thermogram of the polyurethane (29-32) obtained from the reaction between crosslinking agents, MDI, and 5 mole % of benzoyl peroxide showed their weight loss (Table 2). TGA thermograms of polyurethane (29), (30), (31), and (32) gave similar results to polyurethane (20). (Figure 78-81)

Table 2. Weight loss of polyurethane from TGA

Polyurethane	Beginning temperature (°C)	Temperature at which weight loss occurs (°C)			
		5%	10%	20%	30%
Polyurethane (29)	250	300	340	360	400
Polyurethane (30)	210	310	320	340	390
Polyurethane (31)	180	250	280	360	400
Polyurethane (32)	210	225	250	290	350

In this work, vinyl groups of various crosslinking agents can be reacted by a free radical reaction using benzoyl peroxide as an initiator. The reactivity of (3) and (9) occurred rapidly within 6 hours. After 6 hours, the rate of reaction decreased as the reaction time increased. From the reactivity of hydroxyl and vinyl groups of various crosslinking agents, compound (3) was the most suitable one because both hydroxyl groups and vinyl groups of this compound could undergo reactions with MDI and benzoyl peroxide, respectively.

These crosslinking agents can be used to prepare polyurethane elastomers with MDI as one of the starting materials. These crosslinking agents containing multiple hydroxy and vinyl groups, can lead to improved properties of crosslinked polymers. The structure of the polymers should be IPN systems containing two phases, for example, the polyvinyl phase dispersed in the polyurethane phase.