

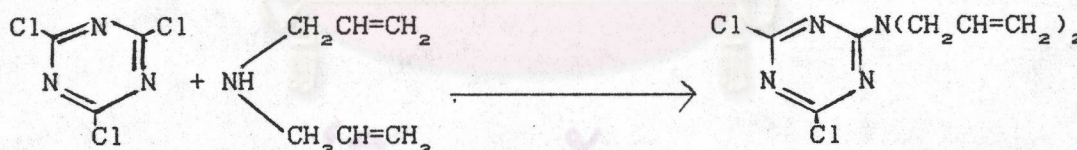


## CHAPTER III

## RESULTS AND DISCUSSION

3.1 Synthesis of the coupling agent

By using the Thurston method, the coupling agent was synthesized from the nucleophilic reaction of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) and diallylamine at low temperature. But the yield was unsatisfactory due to contamination of substantial amount of the unreacted starting material. When the reaction, however, was performed at ambient temperature by adding dropwise of the amine to the triazine, the product was obtained in 93% yield. It was found that the modified procedure led to the purer product which was easily isolated from the reaction mixture. The overall reaction can be shown by equation (3.1).

3.1.1 Infrared Spectroscopy (IR)

Infrared spectra of 2-diallylamino-4,6-dichloro-1,3,5-triazine and other starting materials, recorded on a Perkin-Elmer model 1720-X Infrared spectrometer using KBr disc technique, 1 scan,  $4 \text{ cm}^{-1}$  resolution were shown in Figure V. The peaks and the corresponding molecular vibrations are listed below.



wavenumber $\text{cm}^{-1}$	corresponding to
1644	C=C stretching
1586, 1476	C=N stretching of triazine ring
1339, 1232	C=N bending
1161	=C-N stretching
971, 940	-CH=CH <sub>2</sub> deformation
845, 785	C-Cl stretching

Figure VI shows the infrared spectrum of Cyanuric chloride. The peaks and the corresponding molecular vibration are listed below.

wavenumber $\text{cm}^{-1}$	corresponding to
1635	C=C stretching
1490	C=N stretching of triazine ring
1270	C=N bending
845, 785	C-Cl stretching

Figure VII shows the infrared spectrum of diallylamine. The peaks and the corresponding molecular vibration are listed below.

wavenumber $\text{cm}^{-1}$	corresponding to
3288	N-H stretching
3000-2800	C-H stretching
1644	C=C stretching
1455, 1417	CH <sub>2</sub> deformation
1105	C-N stretching
994, 918	CH <sub>2</sub> =CH deformation
756	N-H wagging

From evidences in the infrared spectrum, the product showed the C=C absorption band at  $1644 \text{ cm}^{-1}$  and the C=N absorption bands at  $1586 \text{ cm}^{-1}$  and  $1476 \text{ cm}^{-1}$  which were similar to those in the



spectra of the starting materials, cyanuric chloride and diallylamine. In addition, the product showed a new absorption band at  $1161\text{ cm}^{-1}$  which is the C-N stretching. It is clear that the product contains the diallylamino group and triazine ring. Subsequently, the chemical structure of the product may be designated as 2-diallylamino-4,6-dichloro-1,3,5-triazine.

### 3.1.2 Nuclear magnetic resonance (NMR)

$^{13}\text{C}$  Nuclear magnetic resonance studies of the product were performed on a JEOL Model FX 90Q (90MHz) using tetramethylsilane (TMS) as internal standard and deuteriochloroform as solvent. The NMR spectrum was shown in Figure VIII and the signals are listed below.

<u>Signal</u>	<u>Chemical shift (ppm)</u>	
1	170.27	(4-C,6-C of triazine ring)
2	164.74	(2-C of triazine ring)
3	131.31	(-N-CH-CH=CH <sub>2</sub> )
4	118.64	(-CH <sub>2</sub> -CH=CH <sub>2</sub> )
5	49.14	(-CH <sub>2</sub> -CH=CH <sub>2</sub> )

On the basis of  $^{13}\text{C}$  NMR spectroscopic data, the  $^{13}\text{C}$  NMR spectrum of the product contains only 5  $^{13}\text{C}$ -signals. The signal at 170.25 ppm indicated the overlapping of two symmetric  $^{13}\text{C}$  signals owing to the mono-substituted group at 2-C of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride).

### 3.1.3 Mass spectroscopy (MS)

Mass spectrum of the product recorded on a JEOL model JMS DX 300 Mass spectrometer with a 70 eV. impact source was shown in Figure IX.



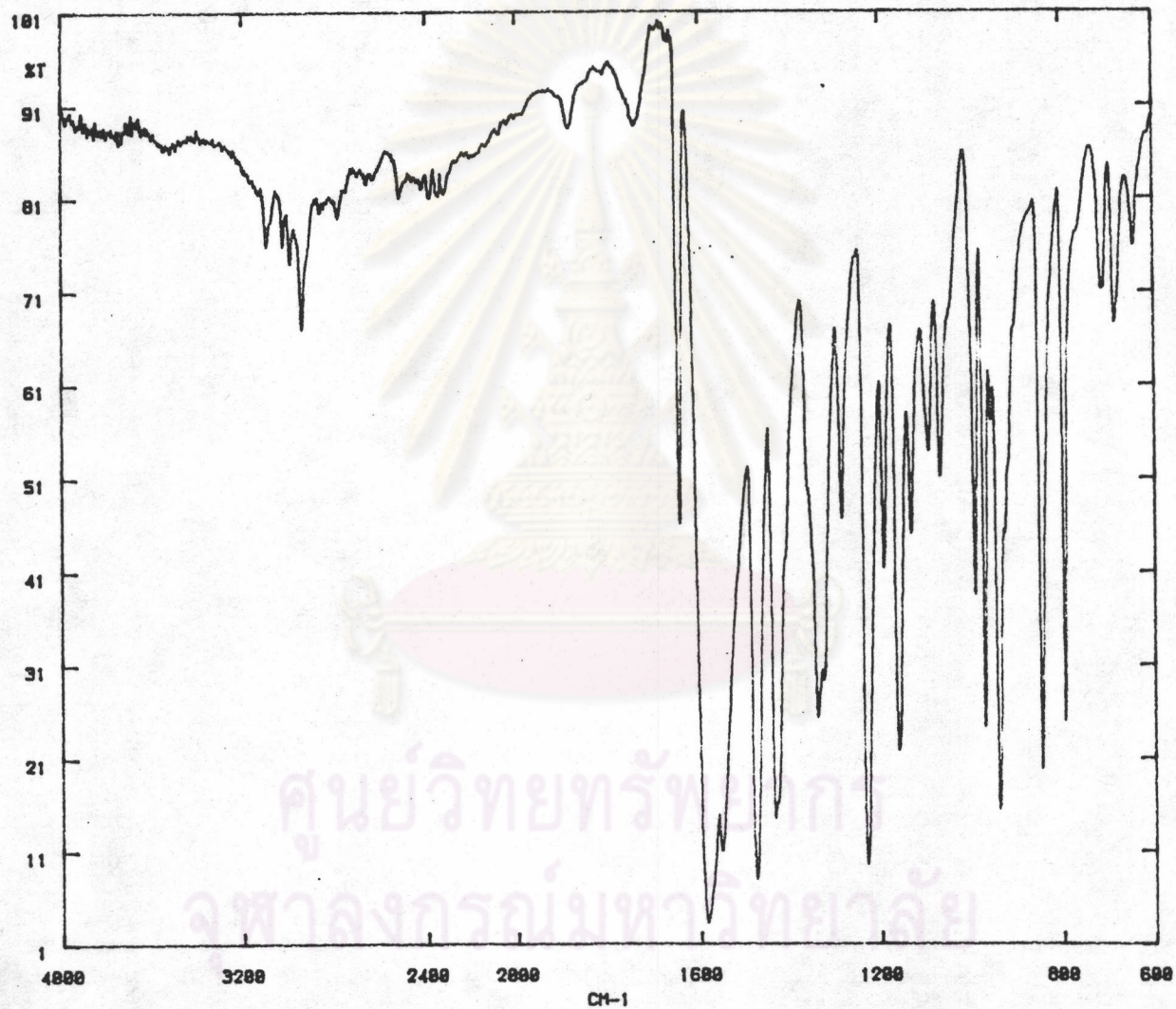


Figure V Infrared spectrum of 2-diallylamino-4,6-dichloro-1,3,5-triazine.



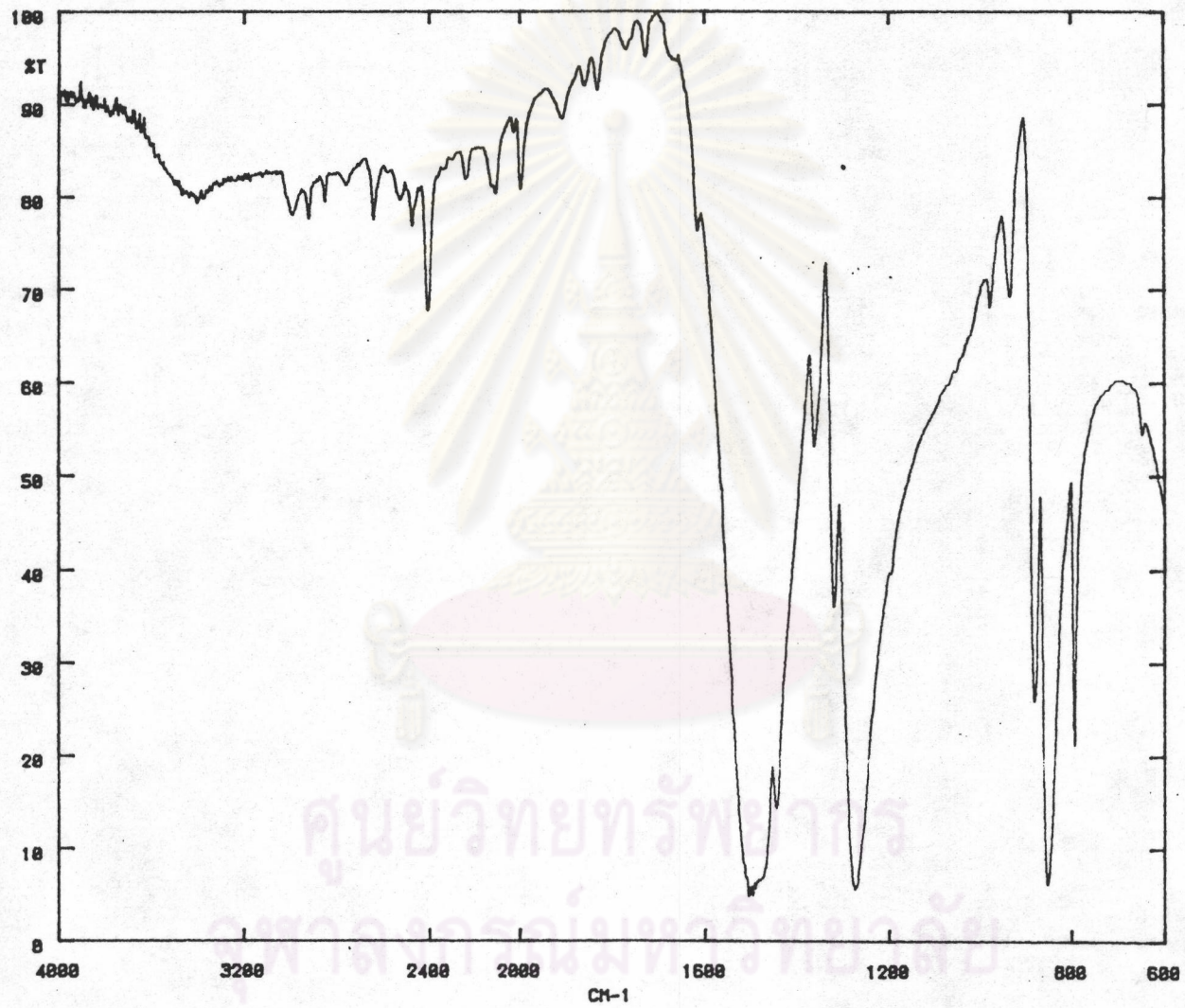


Figure VI Infrared spectrum of cyanuric chloride.



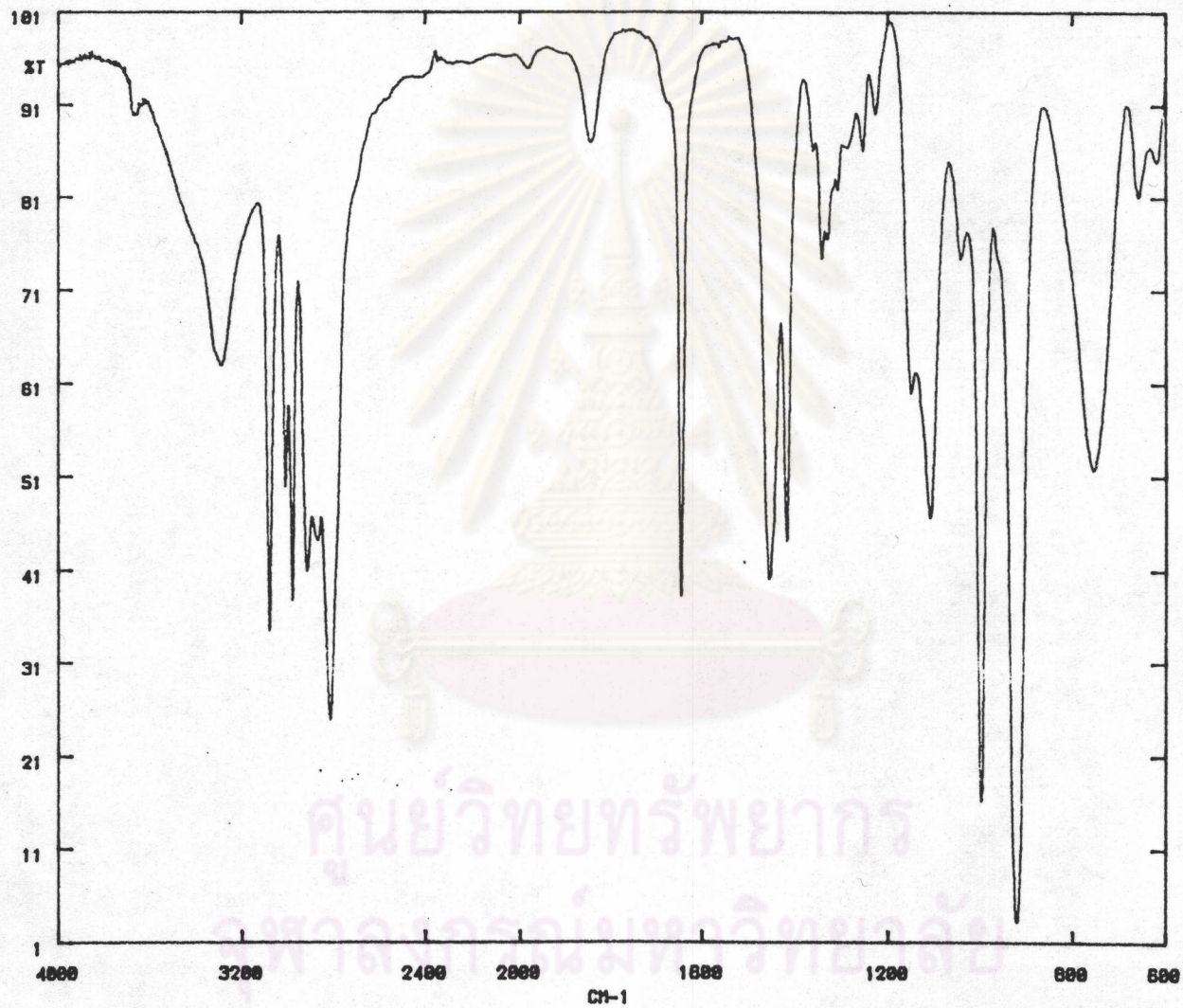


Figure VII Infrared spectrum of diallylamine.



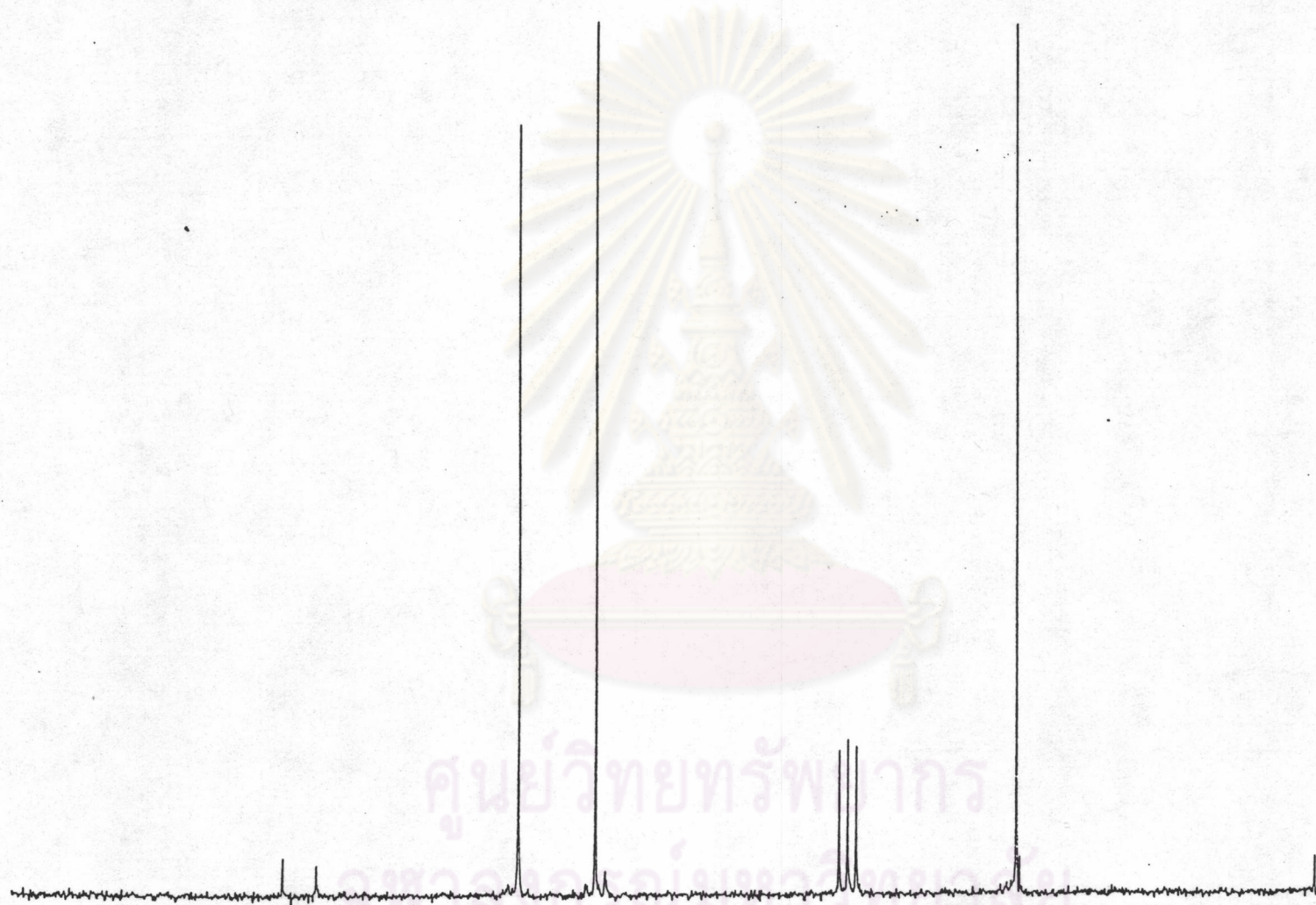


Figure VIII NMR spectrum of 2-diallylamino-4,6-dichloro-1,3,5-triazine.



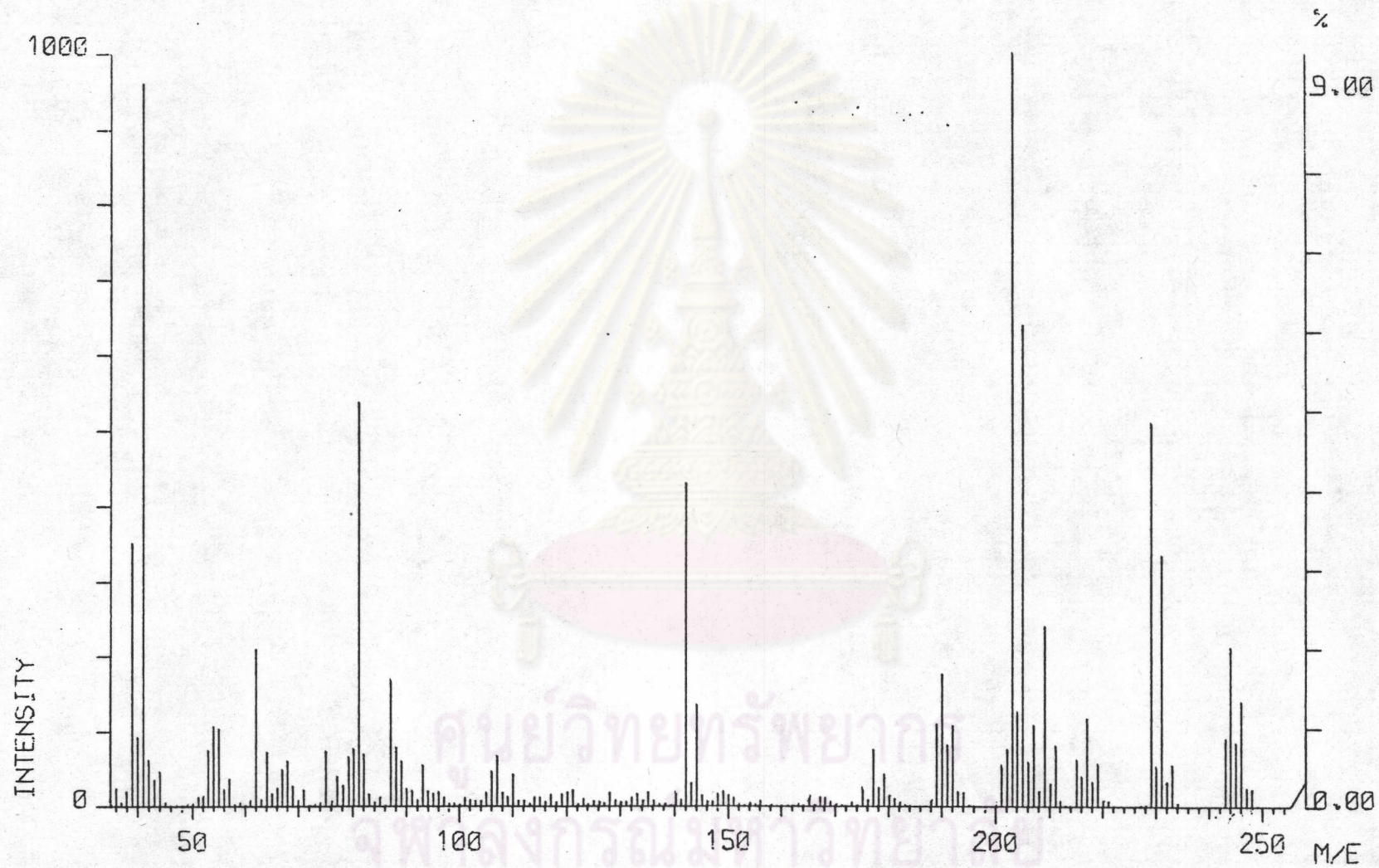


Figure IX Mass spectrum of 2-diallylamino-4,6-dichloro-1,3,5-triazine.









### 3.1.4 Elemental analysis

The coupling agent was analyzed by elemental analysis with a Perkin-Elmer Elemental Analyzer model 240 C. Analysis condition; combustion was temperature 950 °c, reduction temperature 650 °c, helium gas pressure 18.5 psi, oxygen gas pressure 17.5 psi. The result compared to the theoretical calculation was listed below.

	% N	% C	% H
Instrumental Analysis	23.22	44.70	4.17
Theoretical Calculation	22.86	44.08	4.08

From the results illustrated above, it was found that the percentages of the carbon, hydrogen, and nitrogen in the product as reported by Elemental Analyzer and those obtained from the calculation were slightly different.

By the evidences in infrared spectrum, <sup>13</sup>C NMR spectrum, mass spectrum and elemental analytical data, it was clear that the chemical structure of the product was designated as 2-diallylamino-4,6-dichloro-1,3,5-triazine with molecular weight 245, m.p. 42 °c, molecular structure, is as follows:

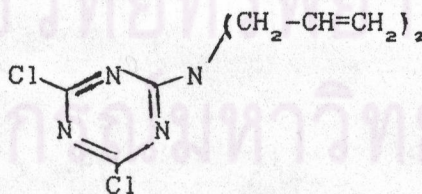


Figure XI Molecular structure of 2-diallylamino-4,6-dichloro-1,3,5-triazine.

### 3.2 Chemical Treatment of Coir Fibers

Treatment of the coir fiber is a two-step process. The first



step is the deposition of the reagent on the fibers and the other step involves the transfer of cellulosic hydroxyl groups as oxyanions induced by alkali to the coupling agent via the nucleophilic substitution reaction at the position bearing the chlorine atoms as shown Figure XII. However, the side reaction due to the interaction between the coupling agent and alkali lead to the compounds (II) and (V) which can be removed during the washing and the extraction of the fibers.

In addition, the coir fibers with the unsaturated active group (diallylamino group) can polymerize with unsaturated polyester which is a chemical modification on adhesion property of coir fiber for reinforced plastics.

### 3.3 Absorption of Water

The samples with unsealed edges were immersed in water at room temperature for 24 hrs. At saturation, the water uptake (Table IV) was dependent on the fiber treatment. The water uptake was decreased by surface treatments.

Table IV Effect of the Fiber Surface Treatment on the Water Uptake

Sample	Materials	Fiber treatment	Water Uptake (%)
1.	Unsaturated polyester	-	0.5
2.	30 % Coir fibers-polyester	none	16.5
3.	30 % Coir fibers-polyester	Coupling agent	10.7
4.	30 % fiber glass-polyester	none	0.4



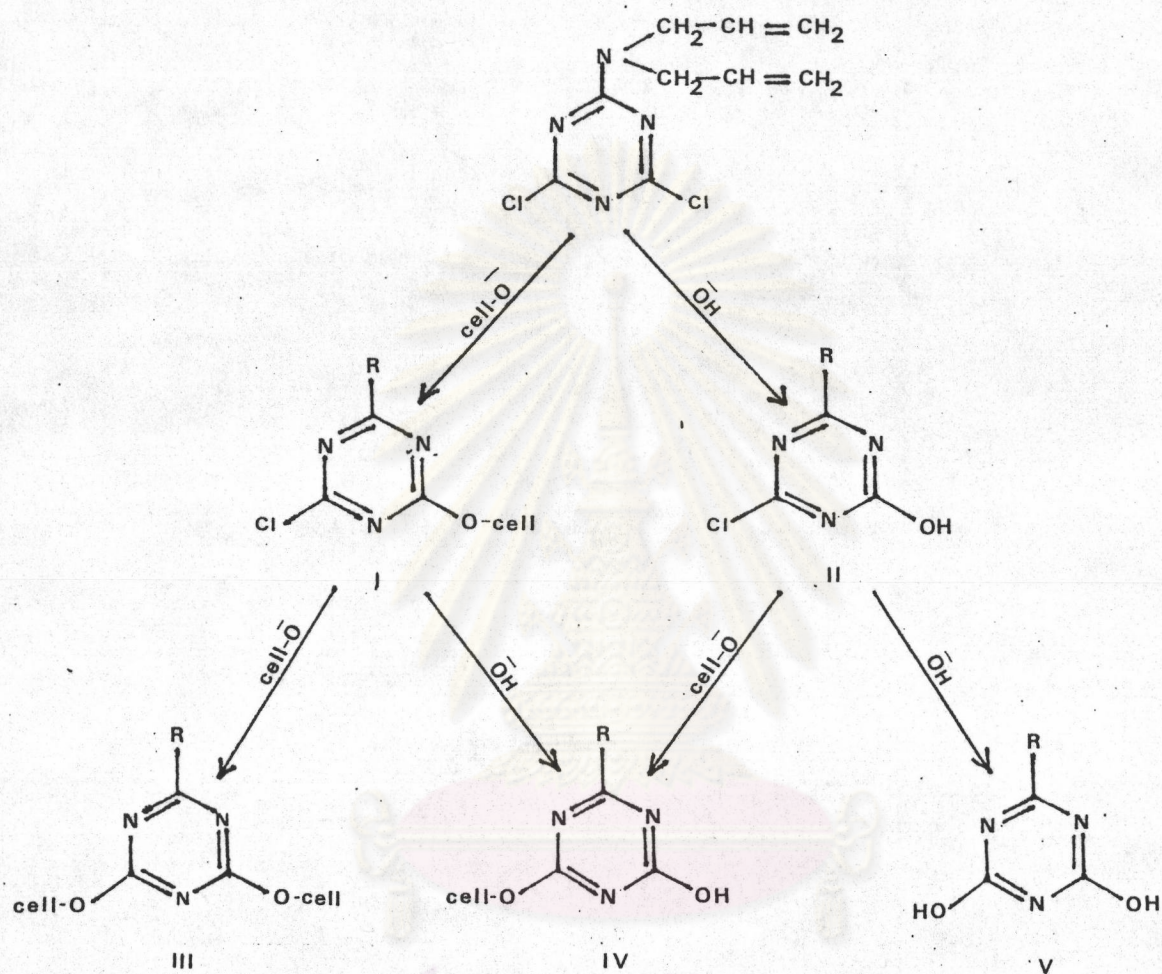


Figure XII Chemical reaction between cellulose and 2-diallylamino-4,6-dichloro-1,3,5-triazine.



### 3.4 Measurement of mechanical properties

The experimental results in Table V showed that the strength and the stiffness of the unsaturated polyester were considerably increased by reinforcement of either glass fiber or coir fiber. However, there was a difference in mechanical properties between the composite obtained from untreated coir fibers and from the coir fibers treated with the coupling agent (2-diallylamino-4,6-dichloro-1,3,5-triazine). The incorporation of the coupling agent in the coir fibers resulted in an increased in the flexural strength and impact strength by about 14% and 32% respectively compared to those of the composite from untreated coir fibers. Similarly the compressive strength and tensile strength of the treated fiber composite were comparable to that of the untreated coir fiber composite.

Consequently, the mechanical properties of the treated coir fiber composite were higher than those of the untreated coir fiber composite as shown in Table V. It would be due to the interfacial adhesion of the treated coir fiber composite.

The impact strength or toughness of the treated coir fiber reinforced composite was shown to be comparable to the glass-fiber reinforced composite. In addition, the impact strength of fiber-reinforced materials is a property that can arise from the ductility of the matrix in its ability to blunt cracks or notches by flow, or from delamination in which the fiber-matrix interface fails. It should be mentioned that the interfacial bonding which maintains the shear stress of the interface and consequently results in the ductility of coir fibers with providing the remarkable impact strength to the composite.

The effect of the coupling agent on changes of the mechanical properties of the composite was attributable to the chemical reaction



between the diallylamine group of the coupling agent and the unsaturated moieties of the unsaturated polyester which would modified the adhesion strength of the fibers in addition to the crosslinking of the coupling agents to the cellulosic hydroxyl group of the fibers. In addition, the mechanical properties of treated coir fiber with 5 % coupling agent composites are higher than the treated coir fiber with 2 % coupling agent composites and comparable to the treated coir fiber with 8 % coupling agent composites. It is indicated that 5 % coupling agent treatment is the optimum.

Table V Effect of the Fiber Treatment on the Mechanical Properties of the composites.

Materials	Coupling agent	Impact strength Ft.lb/in.	Compressive strength psi'	Tensile strength psi	Flexural strength psi
Unsaturated polyester	-	0.47	9797.16	3815.32	6055.69
30 % Unsaturated coir fiber polyester	-	5.39	10879.96	5838.04	8060.32
30 % Treated coir fiber polyester	2 %	6.03	10942.89	5927.69	8419.22
30 % Treated coir fiber polyester	5 %	7.93	12260.44	6433.21	9327.89
30 % Treated coir fiber polyester	8 %	7.86	12232.74	6374.90	9375.50
30 % Glass fiber polyester	-	7.77	16072.72	13233.99	26818.19