CHAPTER V

PREPARATION OF *N*-(2-HYDROXY-3-METHOXY-5-ALLYLBENZYL)-*N*-(2'-HYDROXY-3',5'-DIMETHYLBENZYL)CYCLOHEXYLAMINE WITH ALLYL MONOMER FOR POLYMERIZAION OF MEMBRANE ELECTRODE

5.1 Abstract

A well-defined allyl-containing benzoxazine dimer, *N*-(2-hydroxy-3-methoxy-5-allylbenzyl)-*N*-(2'-hydroxy-3',5'-dimethylbenzyl)cyclohexylamine is successfully developed. Based on the allyl group for further polymerization, this molecule is a good model compound to study a novel approach of Pt catalyst layer on membrane electrode. A model host compound containing benzoxazine dimer which consists of aza methylene group for metal ion complexation and allyl group for further polymerization is proposed. The self termination of benzoxazine in dimerization step enables us to accomplish a well defined *N*-(2-hydroxy-3-methoxy-5-allylbenzyl)-*N*-(2'-hydroxy-3',5'-dimethylbenzyl)cyclohexylamine. The structural characterization by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) confirms the successful preparation. Single crystal analysis shows a unique packing structure which chloroform exists as a guest molecule. A trial on radical polymerization is also carried out to clarify the optimum condition.

Keyword: Benzoxazine dimer, Allyl, Radical polymerization

5.2 Introduction

Benzoxazine monomer is a heterocyclic compound obtained from the cyclization between formaldehyde, phenol and primary amine derivatives via Mannich reaction.[1] The ring opening reaction of benzoxazine monomer with phenol derivatives can provide a linear aza-methylene-linked phenol-based polymer.[2] However, Laobuthee *et al.*, found that the reaction tends to terminate at dimerization step. This might be due to the inter- and intramolecular hydrogen bonding between reactive hydroxyl groups of the dimer.[3] There are several advantages of benzoxazine dimer including simple preparation, high yield of the products, ability to form complex with transition metals and molecular design flexibility. Numerous functional groups can be introduced into the phenol and primary amine derivatives to provide the desired properties.

The original idea intends to develop the embedding catalyst layer aligned at the interface via supramolecular structure. We expect that this approach may improve Pt aggromeration and detachment from carbon support. In order to achieve the idea case, we need the host molecules that have a site for accept guests which are Pt ions and other reactive site for further polymerization. Based on the model compound of *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine with $PtCl_4$ ions, a host compound containing benzoxazine dimer which consists of aza methylene group for Pt ion complexation and allyl group for further polymerization is proposed. The work shows not only the synthesis and structural characterization of the host compound but also a trial on radical polymerization.

5.3 Experimental

5.3.1 Materials

All chemicals were reagent grade and used without further purification. 2,4-Dimethylphenol and paraformaldehyde were purchased from Merck, Germany. Chloroform-*d* was purchased from Aldrich, Germany. Eugenol, maleimide, α,α-azobisisobutyronitrile (AIBN), petroleum ether and chloroform were from Wako, Japan. Methanol and 1,4-dioxane were purchased from Labscan, Ireland.

5.3.2 Instruments and Equipment

5.3.2.1 Fourier Transform Infrared (FTIR) Spectrophotometer

Fourier transform infrared (FTIR) spectra were recorded by using a Nicolet Spectrophotometer with 32 scans at a resolution of 2 cm^{-1}. A frequency range of 4000-400 cm^{-1} was observed by using deuterated triglycerinesulfate detector (DTGS) with specific detectivity of 1 x 10^9 $cm \cdot Hz^{1/2} \cdot w^{-1}$.

5.3.2.2 Nuclear Magnetic Resonance (NMR)

NMR spectra were obtained from a Varian Mercury 400 MHz spectrometer (USA). The deuterated solvent used was $CDCl_3$. The internal reference for ^1H NMR was tetramethylsilane.

5.3.2.3 X-ray Diffractometer

Single crystal analysis was collected by a Rigaku RAXIS RAPID diffractometer with a graphite monochromated Mo-K_α radiation at 296 K. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares on F^2 with RAPID AUTO program. All non-hydrogen atoms were refined with anisotropic displacement parameters.

5.3.3 Methodology

Synthesis of 3,4-dihydro-6-allyl-3-cyclohexyl-2*H*-1,3-benzoxazine, **3**

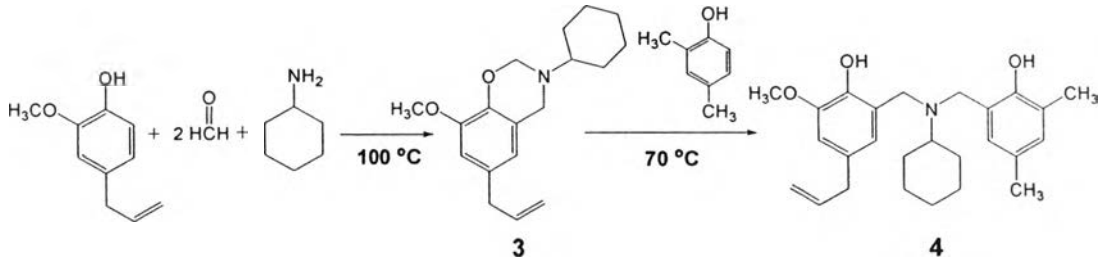
Allyl-containing benzoxazine monomer, **3** was prepared by mixing eugenol (12.28 ml, 0.080 mole), paraformaldehyde (4.80 g, 0.160 mole) and cyclohexylamine (9.12 ml, 0.080 mole) heated at 100 °C overnight (Scheme 5.1). Cooled methanol is added into the mixture. Then, methanol solution of the mixture was left at 0 °C for precipitation. The precipitates were collected and washed with cooled methanol before drying to obtain **3**.

Synthesis of *N*-(2-hydroxy-3-methoxy-5-allylbenzyl)-*N*-(2'-hydroxy-3',5'-dimethyl-benzyl)cyclohexylamine, **4**

Allyl-containing benzoxazine dimer, **4** was prepared by mixing **3** (7.46 g, 0.027 mole) and 2,4-dimethylphenol (3.23 ml, 0.027 mole) and heating at 70 °C overnight (Scheme 5.1). The obtained orange viscous was added with petroleum

ether and it was left for precipitation. The precipitates were collected and recrystallized in chloroform to obtain **4**.

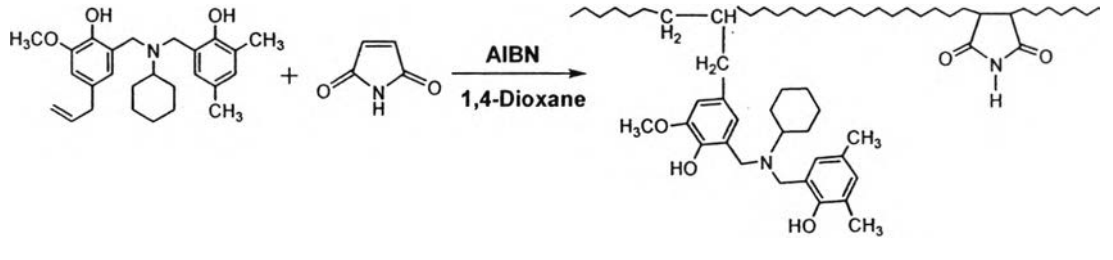
Scheme 5.1



Polymerization of **4**

Copolymer **4**-maleimide was prepared by mixing equimolar ratio of **4** (404.46 mg, 0.988 mmol) and maleimide (95.887 mg, 0.988 mmol) in 1,4-dioxane and using AIBN (16.221 mg, 10 mol%) as an initiator (Scheme 5.2). The polymerization mixture was degassed and heated under nitrogen atmosphere at 55 °C for 2 days. The solvent was removed under reduced pressure. The reaction mixture was precipitated by adding excess amount of diethyl ether. Both precipitate and solution parts were determined the structure by using FTIR.

Scheme 5.2



5.4 Results and Discussion

Figure 5.1 confirms the success of the reaction of **3** to obtain **4**. The characteristic absorption band due to the oxazine ring at 917 cm^{-1} disappeared after the reaction at 70 °C overnight indicates the ring-opening at this stage. A new broad peak at 3345 cm^{-1} corresponds to hydrogen bond is clearly observed in allyl containing benzoxazine dimer. The characteristic peaks belonging to allyl group are at 1639-1640 and 993-994 cm^{-1}.

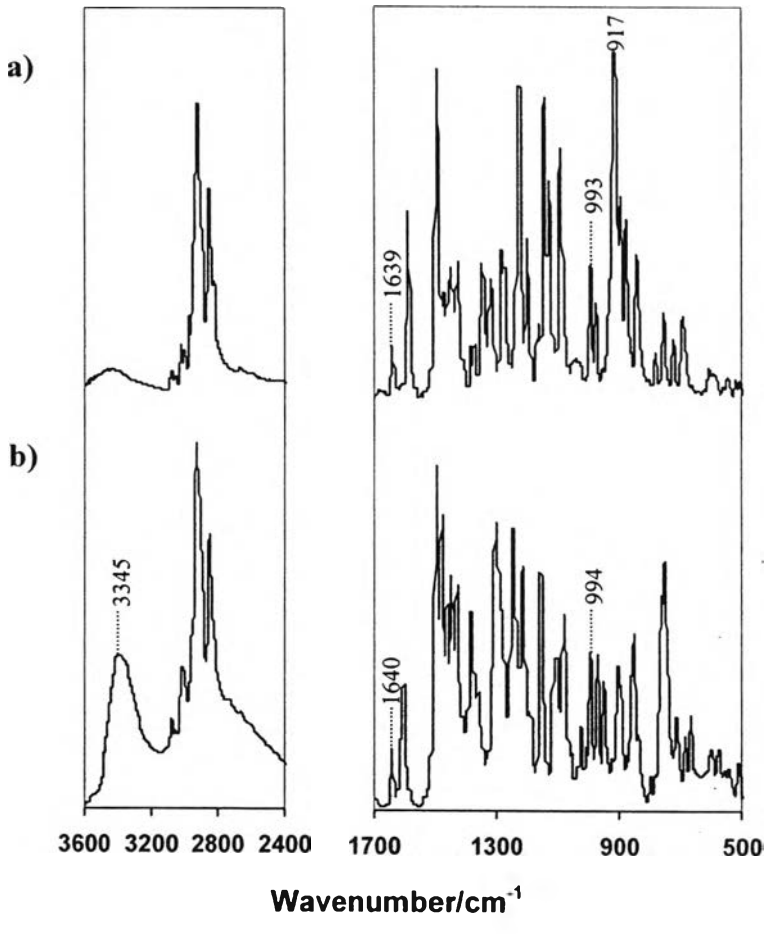


Figure 5.1 FTIR spectra of a) **3** and b) **4**.

^{1}H NMR spectrum of **4** indicates the Mannich bridge (-CH_2-N-CH_2-) at 3.67 and 3.78 ppm (Figure 5.2). The new peaks at 2.16 and 2.20 ppm corresponding to methyl groups confirm dimethylphenol functional group. The disappearances of the peaks at 4.05 and 5.03 ppm as compared to ^{1}H-NMR spectrum of **4** further confirm the oxazine ring opening structure.

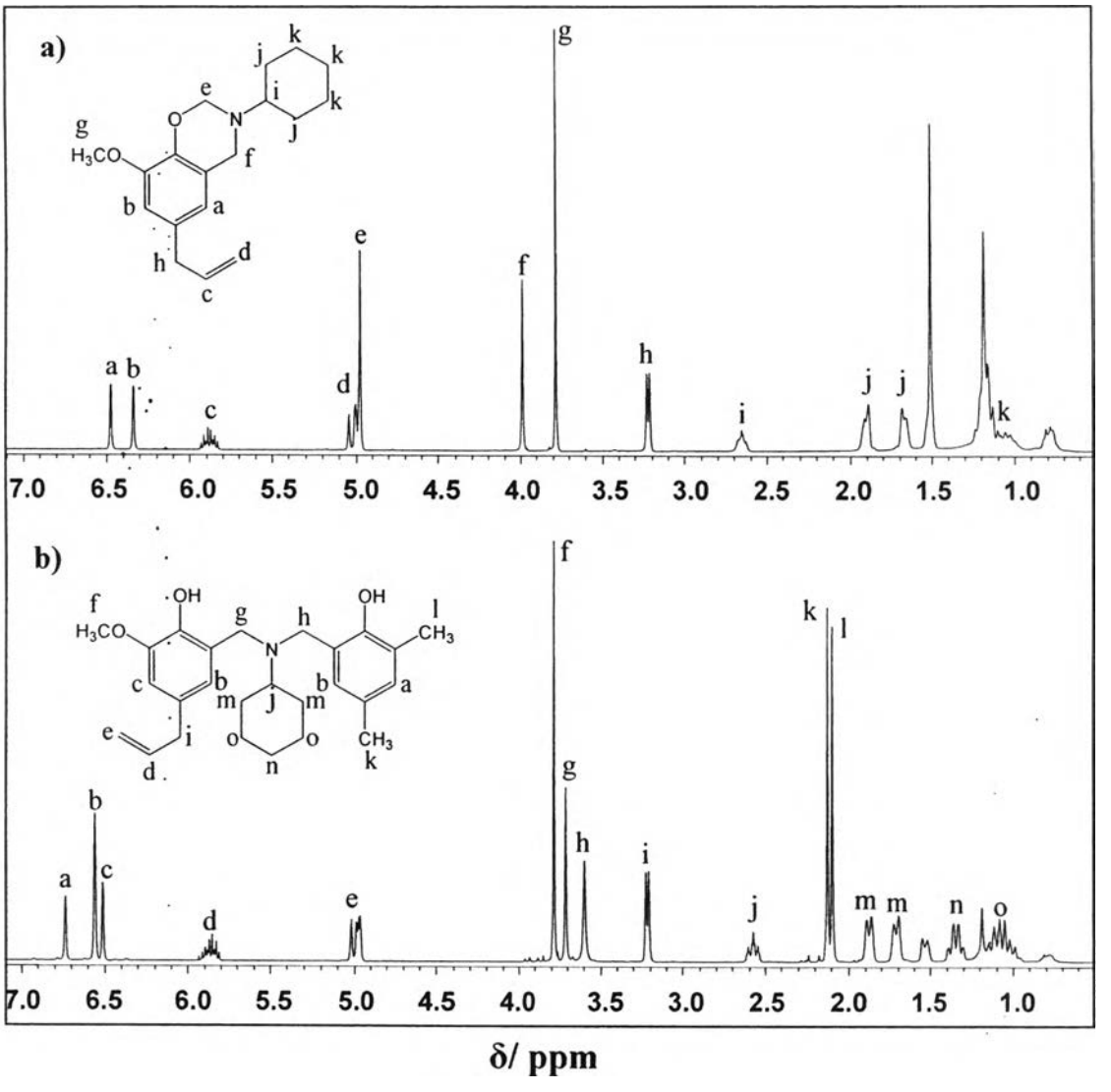


Figure 5.2 ^{1}H-NMR spectra of a) **3** and b) **4**.

Compound **4** was recrystallized in chloroform at room temperature and the single crystal analysis was further carried out as shown the results in Table 5.1 and Figure 5.3. Table 5.1 shows the X-ray data of **4** which is monoclinic crystal system and $P2_1/c$ space group.

Table 5.1 Crystallographic data of **4**

Empirical formula	$C_{27}H_{36}Cl_3NO_3$
Formula weight	528.95
Temperature (K)	296(1)
Wavelength (Å)	0.71075
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.531(2)
b (Å)	14.953(4)
c (Å)	19.400(5)
β (°)	96.084(10)
Volume ($Å^3$)	2749.3(11)
Z	4
ρ_{calc} (g/cm^3)	1.278
μ (mm^{-1})	3.609
Max. and min. transmission	0.860 and 0.881
Crystal size (mm^3)	0.10 x 0.35 x 0.35
Reflections collected	3862
Independent reflections	848 [$R_{(int)}$ = 0.027]
Observed reflections [$I > 2\sigma(I)$]	3506
Goodness-of-fit on F^2	0.933
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0642
	$\omega R2$ = 0.2023
Largest diff. peak and hole ($eÅ^{-3}$)	0.69 and -0.79

Two molecules of **4** are stabilized to each other by intermolecular hydrogen bonding between O(1)-H···O(2)-H with a distance 2.995 Å and intramolecular hydrogen bonding between O(1)-H···N(1) with a distance 2.835 Å. The crystallographic structure of **4** shows that there is a chloroform molecule maintained in the structure but it is not located in the framework of **4** (Figure 5.3).

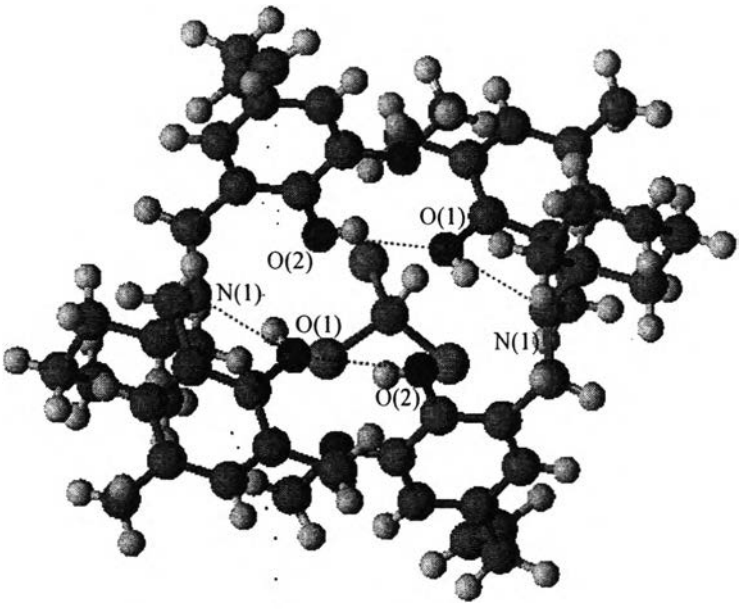


Figure 5.3 Crystal structure of **4**.

The successful copolymerization of maleimide derivatives with various monomers containing unsaturated (vinyl, allyl, propenyl, alkynyl, etc.) bonds have been reported in many papers.[4-8] As a result, this work extended to radical polymerization reaction of **4** with maleimide. After the reaction was finished, the mixture was precipitated into diethyl ether. Both precipitates and solution parts were collected and determined the structure by using FTIR.

The remaining of bands at 994 cm^{-1} and 1641 cm^{-1} (allyl group) in solution part (Figure 5.4b) and characteristic bands of maleimide at 1713 cm^{-1}(–C=O) and 856 cm^{-1}(=C-N) in precipitate part (Figure 5.4a) implied the more polymerization conditions are needed.

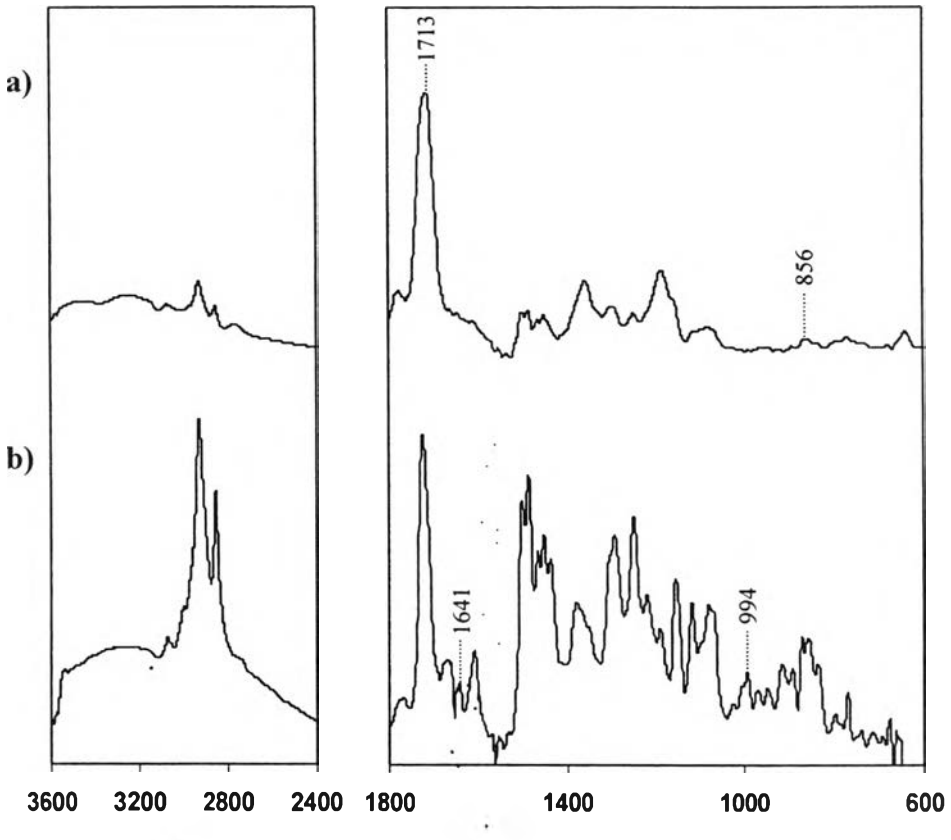


Figure 5.4 FTIR spectra of a) precipitate part, and b) solution part obtained from polymerization reaction between **4** and maleimide.

5.5 Conclusions

The work succeeded in preparation of *N*-(2-hydroxy-3-methoxy-5-allyl-benzyl)-*N*-(2'-hydroxy-3',5'-dimethylbenxyl)cyclohexylamine with allyl group for further polymerization. The trial on radical polymerization was carried out but the results from FTIR spectra showed the unsuccessful polymerization reaction of the allyl groups in the presence of maleimide monomers. The future work should extend to find the optimum condition for allyl-containing benzoxazine dimer polymerization. In addition, the study on Pt inclusion in to the host molecules should also be carried out.

5.6 Acknowledgements

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5.7 References

(1) Holly, F. W.; Cope, A. C. *J. Am. Chem. Soc.* **1994,** *66,* 1875.

(2) Phongtamrug, S.; Tashiro, K.; Miyata, M.; Chirachanchai, S. *J. Phys. Chem.* **2006**, *110*, 21365.

(3) Laobuthee, A.; Chirachanchai, S.; Ishida, H.; Tashiro, K. *J. Am. Chem. Soc.* **2001,** *123,* 9947.

(4) Francis, R.; Jijil, C. P.; Prabhu, C. A.; Suresh, C. H. *Polymer* **2007**, *48*, 6707.

(5) Guzman, S. S.; Lara, L.; Camacho, O. P.; Fernandez, O. R.; Olivas, A.; Escudero, R. *Polymer* **2007**, *48*, 720.

(6) Yilmaz, F.; Cianga, L.; Guner, Y.; Topppare, L.; Yagci, Y. *Polymer* **2004**, *45*, 5765.

(7) Rozenberg, B. A.; Dzhavadyan, E. A.; Morgan, R.; Shin, E. *Polym. Adv. Technol.* **2002**, *13*, 837.

(8) Yoo, J. H.; Kim, S. Y.; Cho, I.; Kim, J. M.; Anh, K. D.; Lee, J. H. *Polymer* **2004**, *45*, 5391.