CHAPTER IV

RESULTS AND DISCUSSION

## 4.1 Chemical Modification of Poly(vinyl alcohol)

Pinnau (Pinnau *et al.*, 1996) reported the gas separation membrane of poly(1-trimethylsilyl-1-propyne)(PTMSP) as a solubility selectivity system by showing methylsilyl groups as an effective VOCs sensing group for a glassy polymer of poly(1-trimethylsilyl-1-propyne)(PTMSP). In the present work, PVA can be considered as a glassy polymer matrix with $T_g = 80^{\circ}C$ while the hydroxyl group can be modified with methylsilyl compounds to achieve the VOCs sensing group in the main chain. Thus, the molecular design is concerned on the addition of trimethylsilyl group onto the hydroxyl group of PVA.

4.1.1 Coupling with Trimethylsilylchlorosulfonate(TMSCS)

In order to synthesize the modified poly(vinyl alcohol) with trimethylsilyl group(-Si(CH$_3$)$_3$) or (PVA-TMSCS) as a VOCs sensing group, trimethylsilylchlorosulfonate was applied. The reaction between poly(vinyl alcohol) and acid chloride was previously reported by Henglein (Henglein *et al.*, 1956) for the reaction between acid chloride and alcohol in the presence of pyridine as a catalyst.

Because of silane coupling agent is very sensitive to water, the reaction has to be performed in non-aqueous solution to avoid the degradation of the silane. Thus, *N,N'*-dimethylacetamide(DMAc), *N,N'*-dimethylformamide(DMF) and dimethylsulfoxide(DMSO) are considered to be suitable solvents for the reaction. In addition, to avoid the formation of

amine salt, DMSO was chosen as the solvent in the reaction with a catalytic amount of pyridine.
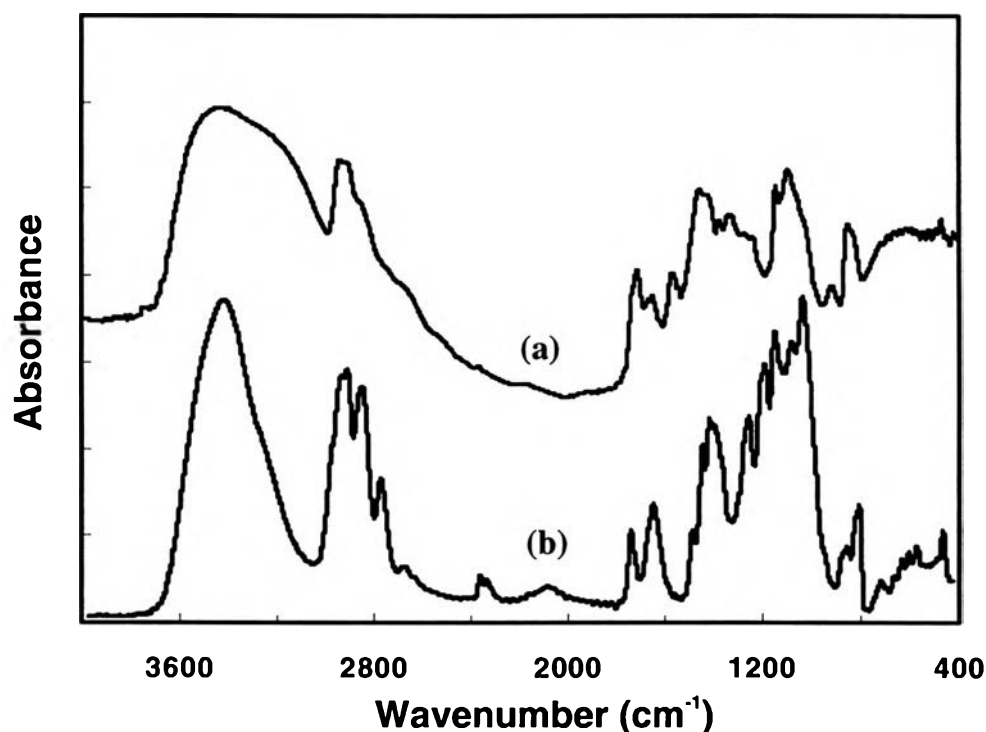

Figure 4.1 FTIR spectra of, (a) poly(vinyl alcohol), (b) poly(viny alcohol) after coupling with trimethylsilylchlorosulfonate(PVA-TMSCS).

As shown in Figure 4.1, the poly(vinyl alcohol) after coupling with trimethylsilylchlorosulfonate (PVA-TMSCS) shows characteristic peaks of trimethylsilyl group (-Si(CH$_3$)$_3$) at 1253 cm^{-1} and Si-O-S at 1020 cm^{-1} while sulfonyl peak appears at 1176 cm^{-1}. The intensity of the peaks around 2800-2950 cm^{-1} of C-H stretching is increased significantly. The result suggests that the trimethylsilylchlorosulfonate is coupled on the poly(vinyl alcohol) successfully.

It should be noted that the trimethylsilylchlorosulfonate is reactive but has low stability, thus pyridine was used as a catalyst to generate

an intermediate with high reactivity and stability. This intermediate can react with poly(vinyl alcohol) by nucleophilic substitution following the mechanism shown in Figure 4.2.
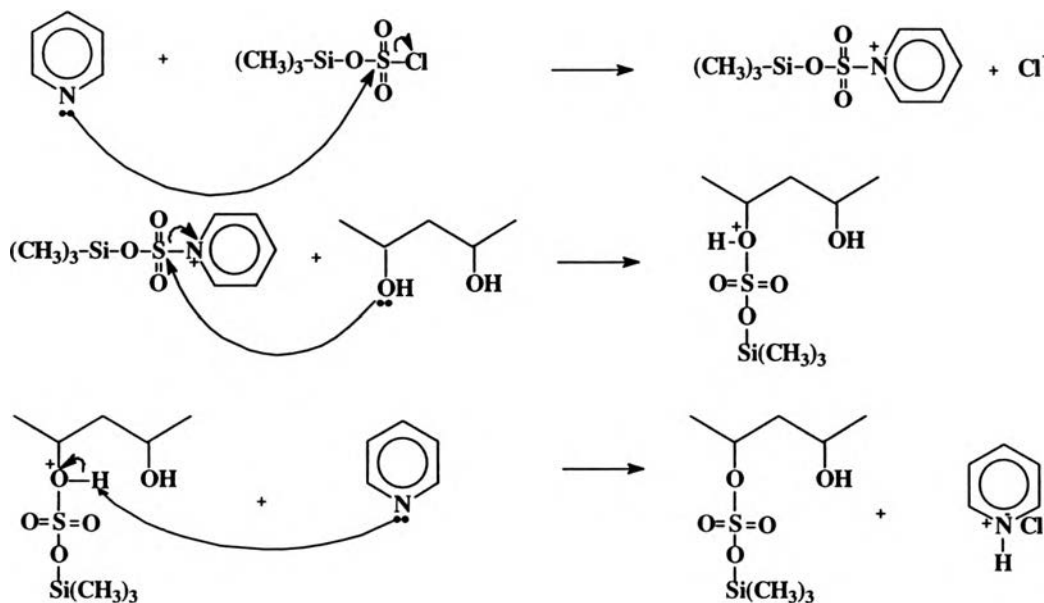
Figure 4.2 Mechanism of poly(vinyl alcohol) and trimethysilylchloro sulfonate with pyridine as a catalyst.

In this reaction, the by–product is obtained as a pyridine salt. The purification process is necessary by dissolving the crude product in 1,4-dioxane followed by reprecipitation in water.

4.1.2 Coupling with 3-Aminopropyltriethoxysilane via PVA-CDI Precursor

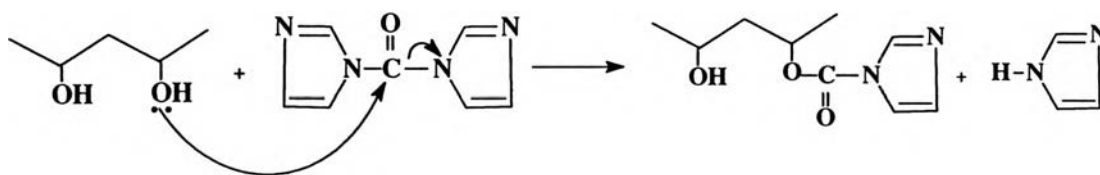*4.1.2.1 Reaction of Poly(vinyl alcohol) and N,N'-Carbonyldi imidazole (CDI)*

Since the direct reaction between the hydroxyl group and amino group of 3-aminopropyltriethoxysilane is difficult to occur, in the present work, N,N'-carbonyldiimidazole(CDI), which has high reactivity with alcohols, carboxylic acids, amine, etc., was chosen as a coupling agent to form an active ester. The active ester is expected to react with 3-aminopropyltriethoxysilane quantitatively.

However, according to the decomposition of CDI by water, the reaction has to be carried out in non-aqueous system, thus N,N'-dimethylacetamide(DMAc) and N,N'-dimethylformamide(DMF) are considered to be the solvents. The reaction with CDI was done under severe conditions, i.e., at 80°C in vacuum for 24 hours by using DMF as the solvent. In this case, degradation of DMF can occurr easily at high temperature. As a result, the crude product is difficult to purify after the reaction. Hence, DMAc is considered to be an better alternative solvent because of its thermal stability. The FTIR spectrum of the obtained product is shown in Figure 4.3.
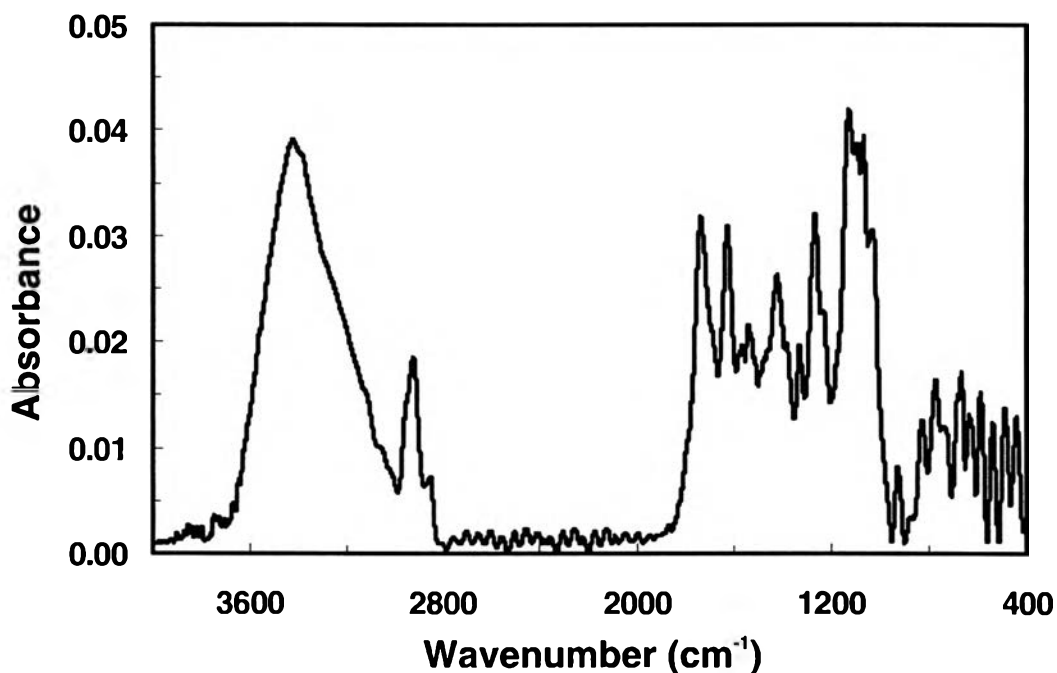
Figure 4.3 FTIR spectrum of poly(vinyl alcohol) after coupling with CDI.

The obtained product shows the peak at 1730 cm^{-1} which is the active ester of carbonylimidazolide. The reaction succeeded in the severe conditions, i.e., 80°C in vacuum for 3 hours without a catalyst. The reaction mechanism is proposed to be the nucleophilic substitution as shown in Figure 4.4.


Figure 4.4 Reaction mechanism of poly(vinyl alcohol) and CDI.

The amount of CDI used was 0.25 mole equivalent of PVA in order to control the degree of substitution to be the same as PVA-TMSCS. In the reaction, by-product was obtained as an imidazolide. The purification process used was reprecipitation of the crude product in acetone to eliminate imidazolide and to remove the unreacted CDI.
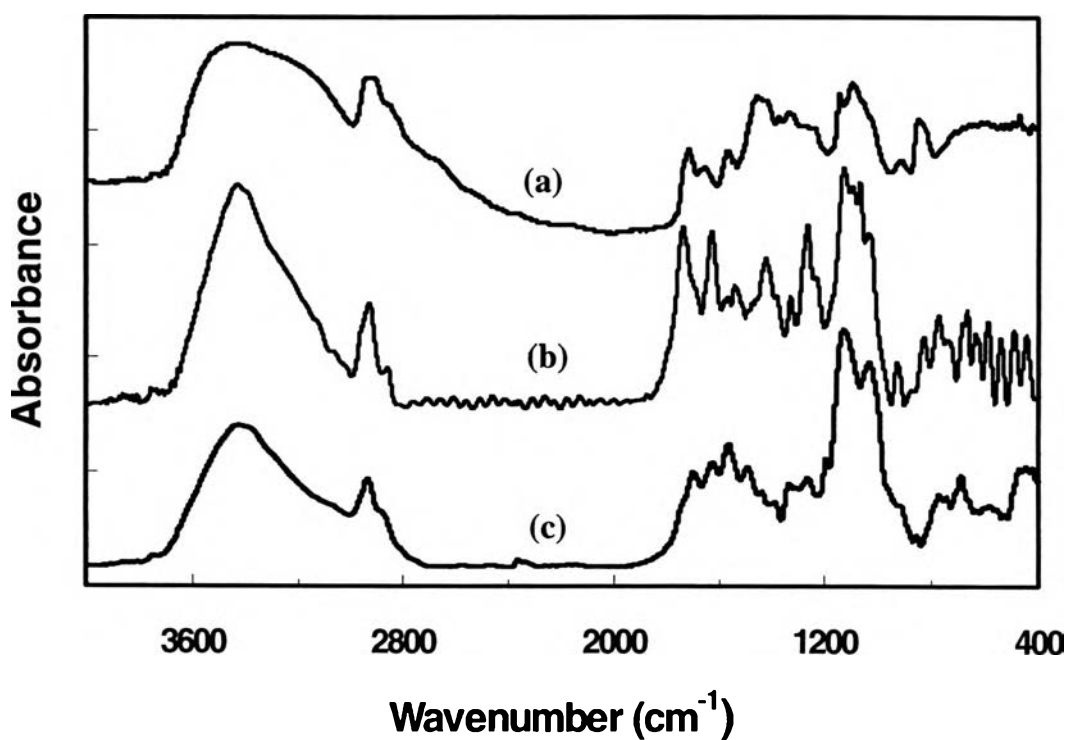
4.1.2.2 Reaction of PVA-CDI and 3- Aminopropyltriethoxysilane (3ATS)

3-Aminopropyltriethoxysilane was chosen for its amino group which can react further with PVA-CDI precursor. The coupling reaction between 3-aminopropyltriethoxysilane and PVA-CDI precursor can be done under the same conditions as the PVA-CDI precursor preparation. Hence, the amount of 3-aminopripyltriethoxysilane was 0.25 mole equivalent of PVA. The FTIR spectrum of the 3-aminopropyltriethoxysilane coupling on to PVA (PVA-3ATS) is shown in Figure 4.5.
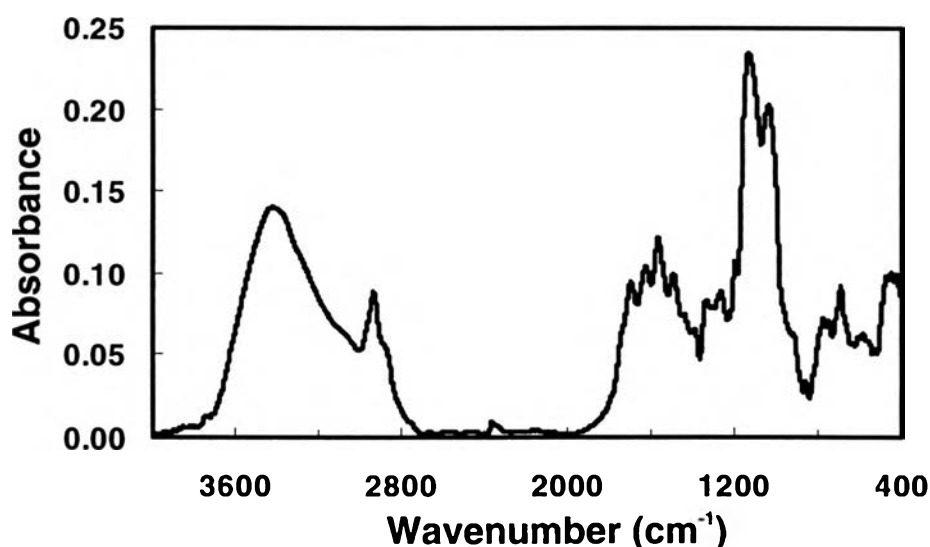

Figure 4.5 FTIR spectrum of PVA-CDI precursor after coupling with 3-aminopropyltriethoxysilane(PVA-3ATS).

The obtained product PVA-3ATS shows the characteristic peaks of 3-aminopropyltriethoxysilane at 1104 cm^{-1} and 1080 cm^{-1}. Moreover, the peak at 1730 cm^{-1}, which is the absorption of carbonylimidazolide, is reduced significantly (Figure 4.6). This can be concluded that 3-aminopropyl triethoxysilane is chemically bound to the PVA via PVA-CDI precursor. However, PVA-3ATS can not be dissolved in any solvents, this may be due to the crosslinking between chains as shown in Figure 4.7.

Figure 4.6 FTIR spectra of, (a) PVA, (b) PVA-CDI precursor, and (c) PVA after coupling with 3-aminopropyltriethoxysilane(PVA-3ATS).
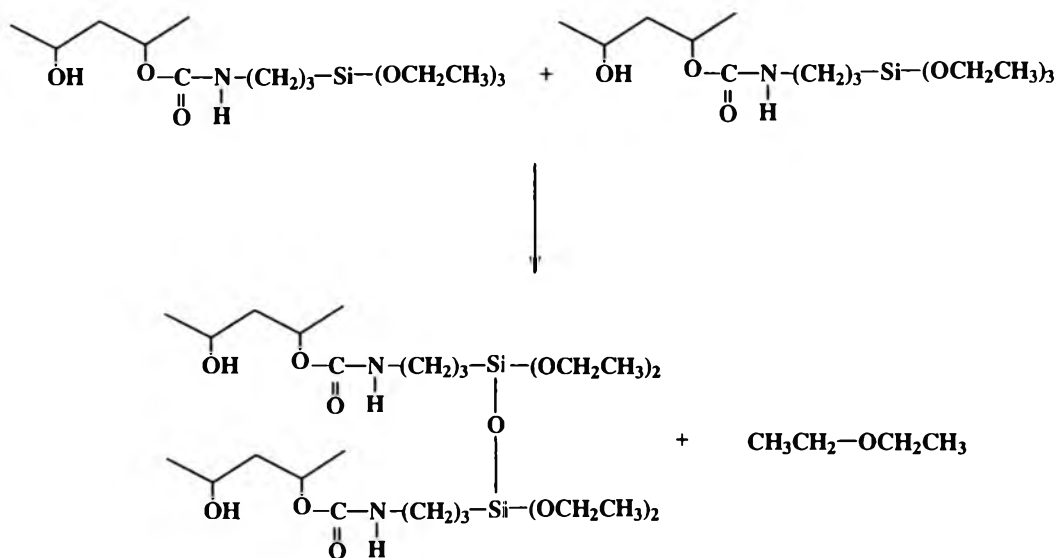
Figure 4.7 Crosslink reaction of PVA-3ATS.

4.2 Membrane Preparation

4.2.1 Membrane Preparation Condition

4.2.1.1 PVA Membrane

Generally, poly(vinyl alcohol) membrane is prepared by the crosslinking of dialdehyde with an acid catalyst. In this work, poly(vinyl alcohol) was reacted with glutaraldehyde in the presence of hydrochloric acid catalyst.

PVA membrane preparation conditions were studied in order to determine the best conditions to obtain a good membrane. In this work, the concentration of PVA solution, the concentration of hydrochloric acid and glutaraldehyde were varied and the appearance of the obtained membrane was observed. The results are shown in Table 4.1.

Table 4.1 Condition for PVA membrane preparation.

Concentration of PVA solution (%w/v)	Concentration of Hydrochloric acid (N)	Concentration of Glutaraldehyde(GA) (M)	Appearance
20	1.50	5.60	Brittle
10	3.00	2.80	Brittle
10	1.50	1.40	Brittle
5	0.75	1.40	Shrunken
10	1.50	1.70	Shrunken
10	1.50	0.35	Transparent
10	1.50	0.17	Dissolving

* For all membranes, PVA solution = 2.0 ml, GA = 0.2 ml and a catalytic amount of HCl.

From Table 4.1, at high concentrations of PVA solution and high concentration of crosslinker, i.e., 20% PVA solution and 5.60 M glutaraldehyde, the obtained membrane is brittle. This may be due to the high amount of crosslinking in the matrix. If the concentration of PVA solution and concentration of crosslinker are low (5-10 % W/V and 1.40-2.80 M, respectively), the obtained membrane shrinks because the crosslinking reaction occurrs very fast due to the excess amount of crosslinker. In the case of the low concentrations of crosslinker (0.17-0.35 M), the obtained membrane dissolves in the treatment by water before use. This may be due to the unsatisfactory amount of crosslinking in membrane matrix. The best condition for PVA membrane preparation was found to be at 10% PVA solution with 1.50 N HCl and 0.35 M glutaraldehyde at room temperature for overnight reaction.

4.2.1.2 Modified PVA Membrane

In order to use the modified PVA membrane in gas permeation and comparing it to PVA membrane, the modified membrane was prepared under identical conditions as the PVA membrane. The PVA-TMSCS membrane was obtained by using 1,4-dioxane as a solvent. In the case of PVA-3ATS, membrane preparation was not successful. This may be due to the crosslinked structure of PVA-3ATS as discussed in 4.1.2.2.

4.2.2 Membrane Characterization

The obtained membrane was studied by FTIR to understand its structure.

*4.2.2.1 Structurual Analysis of PVA-TMSCS Membrane*
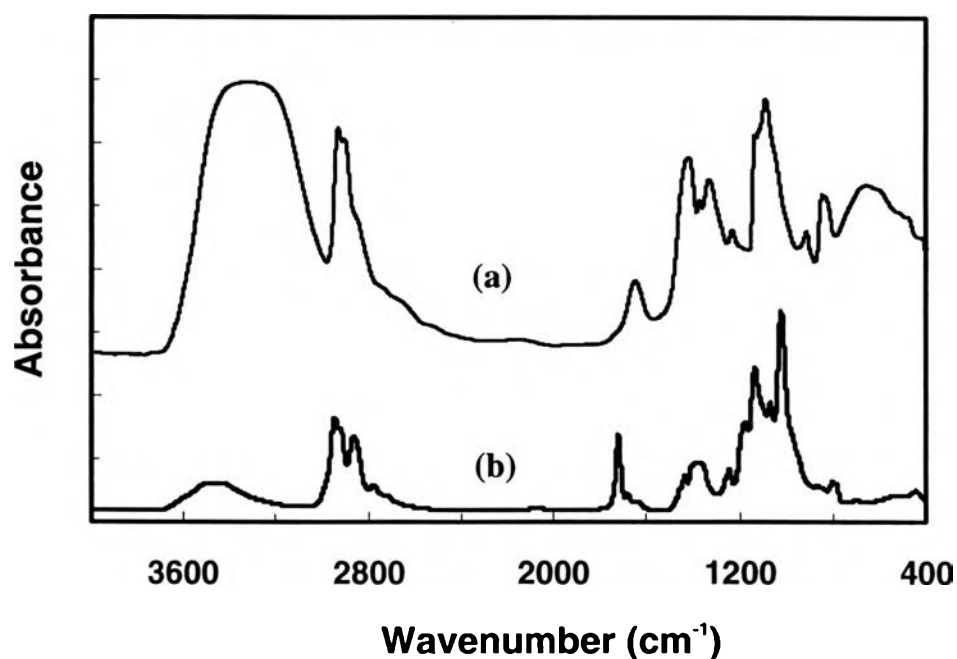
Figure 4.8 FTIR spectra of, (a) PVA membrane, and (b) PVA-TMSCS membrane.

As shown in Figure 4.8, FTIR spectra of PVA-TMSCS membrane shows characteristic peaks of trimethylsilyl group at 1253 cm^{-1} and Si-O-S at 1020 cm^{-1} with sulfonyl group at 1176 cm^{-1}. It is found that PVA-TMSCS membrane shows the decreasing of hydroxyl peak at 3350 cm^{-1} as compared to that of PVA membrane.

4.2.2.2 Thickness Evaluation

For gas permeation study, an important parameter which affects the permeability is the membrane thickness. In this work, the membrane thickness was measured by using interference fringe technique as shown in Figure 4.9. The thickness of PVA membrane is 0.017 mm while PVA-TMSCS membrane is 0.021 mm. The difference between PVA and PVA-TMSCS membrane is about 20 %.
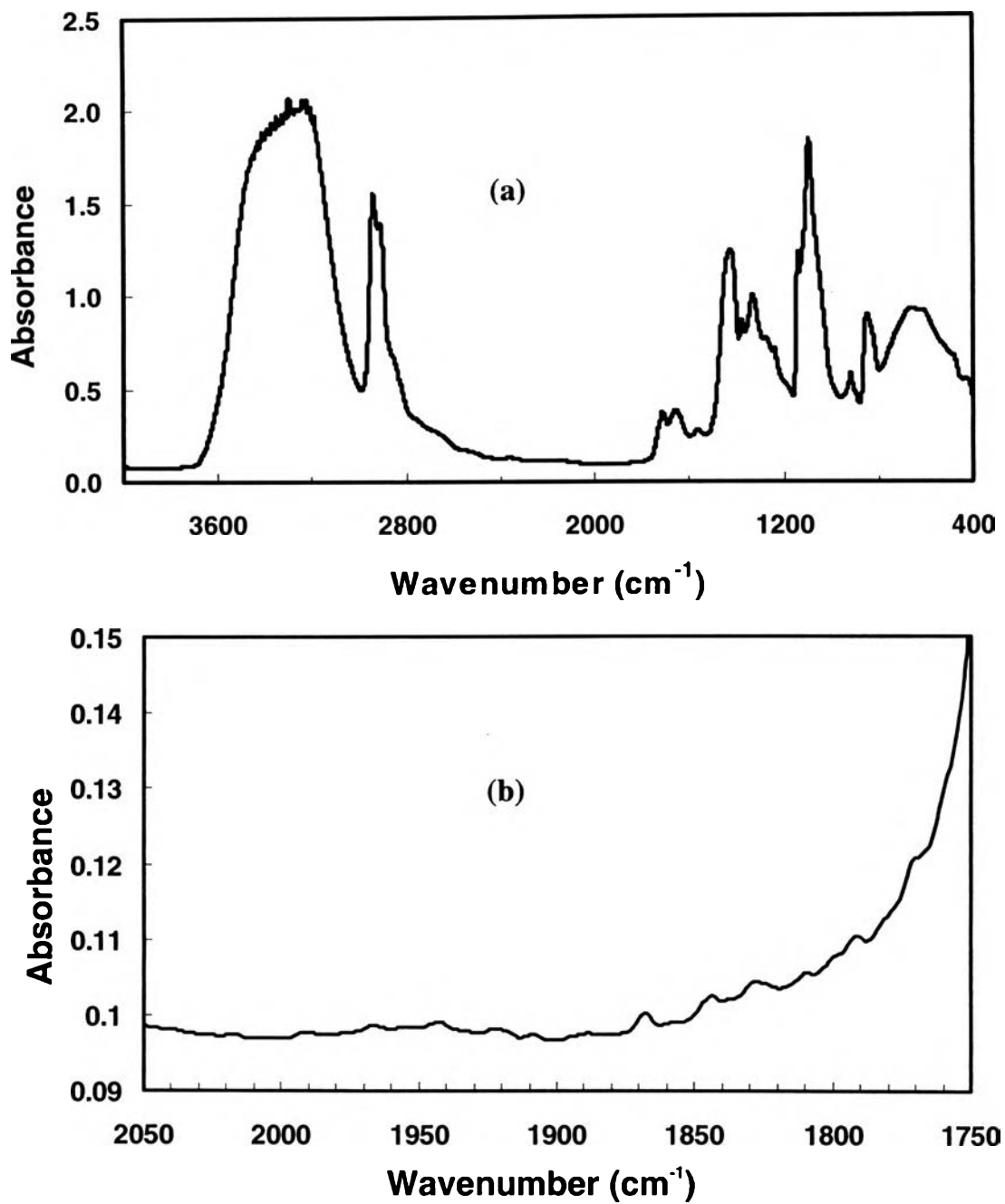
Figure 4.9 FTIR spectra of, (a) PVA membrane, and (b) expand region
for thickness evaluation by fringe pattern.

4.3 Gas Permeation Study

Ideally, gas permeation have to be studied by using a gas cell and gas chromatography(GC) for analysis. The volatile organic compounds such as propane(C_3H_8), butane(C_4H_8) and pentane(C_5H_{10}) are considered to be the substrates for the study. However, owing to the difficulties in handling, the present study investigate gas permeation by using the vapors of particular organic solvents in a liquid cell. The in situ permeability was performed by using liquid cell accessory of FTIR. The 3D-FTIR was used for quantitative analysis.

A representative result by using 3D-FTIR in the system of PVA membrane for chloroform permeability study is shown in Figure 4.10.
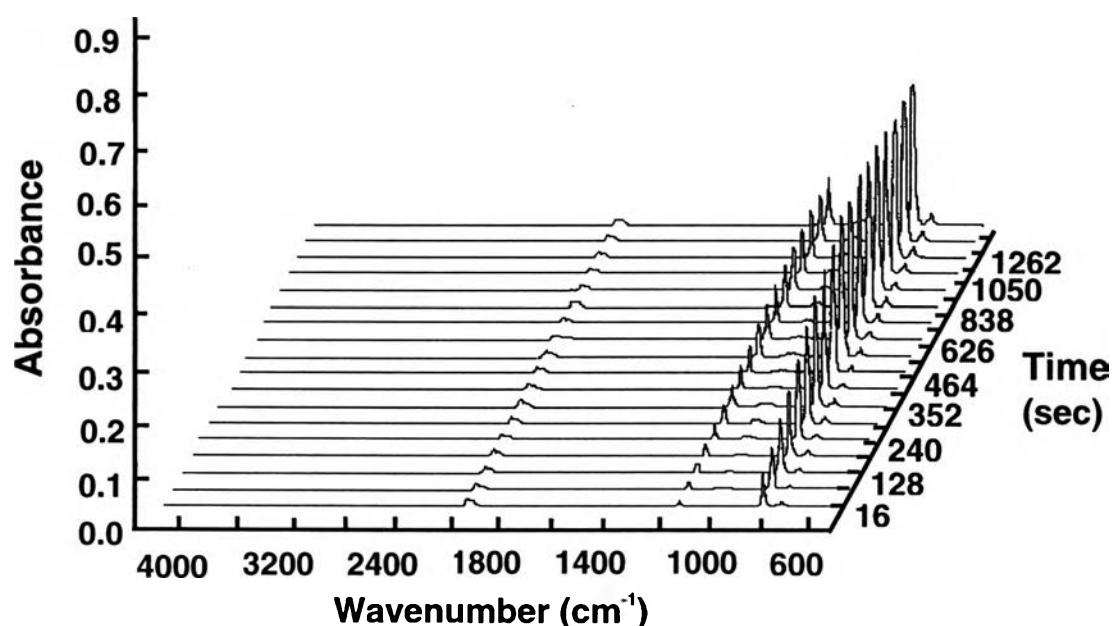
Figure 4.10 3D-FTIR spectra of chloroform permeability in the system of PVA membrane.

Gas permeabilities through PVA and PVA-TMSCS membranes, of various organic solvents are shown in Figures 4.11-4.15. The obtained 3D-FTIR spectra were used for qualitative and quantitative analysis of permeate molecules. As seen in the Figure 4.11(a), the FTIR spectrum of benzene shows peaks of =C-H aromatic bending at 671 cm^{-1} and =C-H aromatic stretching at 3100 cm^{-1}. In the case of cyclohexane (Figure 4.12(a)), the peaks of C-H stretching and C-H bending appears at 2983 cm^{-1} and 1432 cm^{-1}, respectively. For *iso*-propanol, the peaks around 3550 cm^{-1} show the free hydroxyl group, while C-H stretching and C-H bending of isopropyl group appear at 2980 cm^{-1} and 1380 cm^{-1}, respectively, (Figure 4.13(a)). Figure 4.14(a) shows peaks of free hydroxyl group at 3650 cm^{-1} and C-H bending at 1350 cm^{-1} of ethanol. In the case of methanol (Figure 4.15 (a)), the peak of OH stretching and C-H bending appear at 3650 cm^{-1} and 2960 cm^{-1}, respectively. These imply that the permeation of organic vapor through the prepared membranes were successful

Quantitative analysis of the permeation was done by measuring the absorbance change of the specific peaks of each permeant from 3D-FTIR spectra. The results are summarized as a function of time (Figures (b) of 4.11-4.15). It should be noted that the slope of the plot refers to the permeation rate of each substrate, i.e., the higher the slope, the higher the permeation rate. The maximum absorbance exhibits the solubility of the substrate on the membrane at the definite time. In another words, at the maximum point of the permeability, the gas interacts with the membrane at the maximum level.

In the case of low solubility parameter solvents (benzene, δ = 6.2 $(cal/cm^3)^{1/2}$ and cyclohexane, δ = 9.2 $(cal/cm^3)^{1/2}$) as seen in the Figures (b) of 4.11-4.12. The PVA-TMSCS membrane allows the vapor of benzene and cyclohexane permeating higher than that of PVA membrane, as investigated from comparing of the maximum absorbance between both membrane. Moreover, the

amount of the permeant during the permeation through PVA-TMSCS membrane was still higher than PVA membrane. This implies that the PVA-TMSCS membrane has more interaction with benzene and cyclohexane than in the case of PVA membrane. Figure 4.13(b) shows the results of the study by using medium polar substrate (iso-propanol, δ = 11.2 $(cal/cm^3)^{1/2}$). The vapor of these organic substrate still shows high permeation through PVA-TMSCS membrane than that of membrane as observed from the maximum absorbance. In this case the difference of the maximum absorbance of both membrane is less than that of the former case. The amount of permeant after the maximum absorbance of PVA-TMSCS membrane is also lower than that of PVA. The increasing of the polarity of the organic substrate may induce the decreasing of the permeation through PVA-TMSCS membrane owing the nonpolar interaction system. In contrast, for the high solubility parameter solvent (ethanol, δ = 12.7 $(cal/cm^3)^{1/2}$) as seen in Figure 4.14(b). The organic vapor shows the permeation through PVA-TMSCS membrane be lower than that of PVA membrane as investigated from comparing of the maximum absorbance of both membranes. For methanol (δ = 14.5 $(cal/cm^3)^{1/2}$), the result was not clear because the permeation of the substrate through both membrane are the same (Figure 4.15(b)).
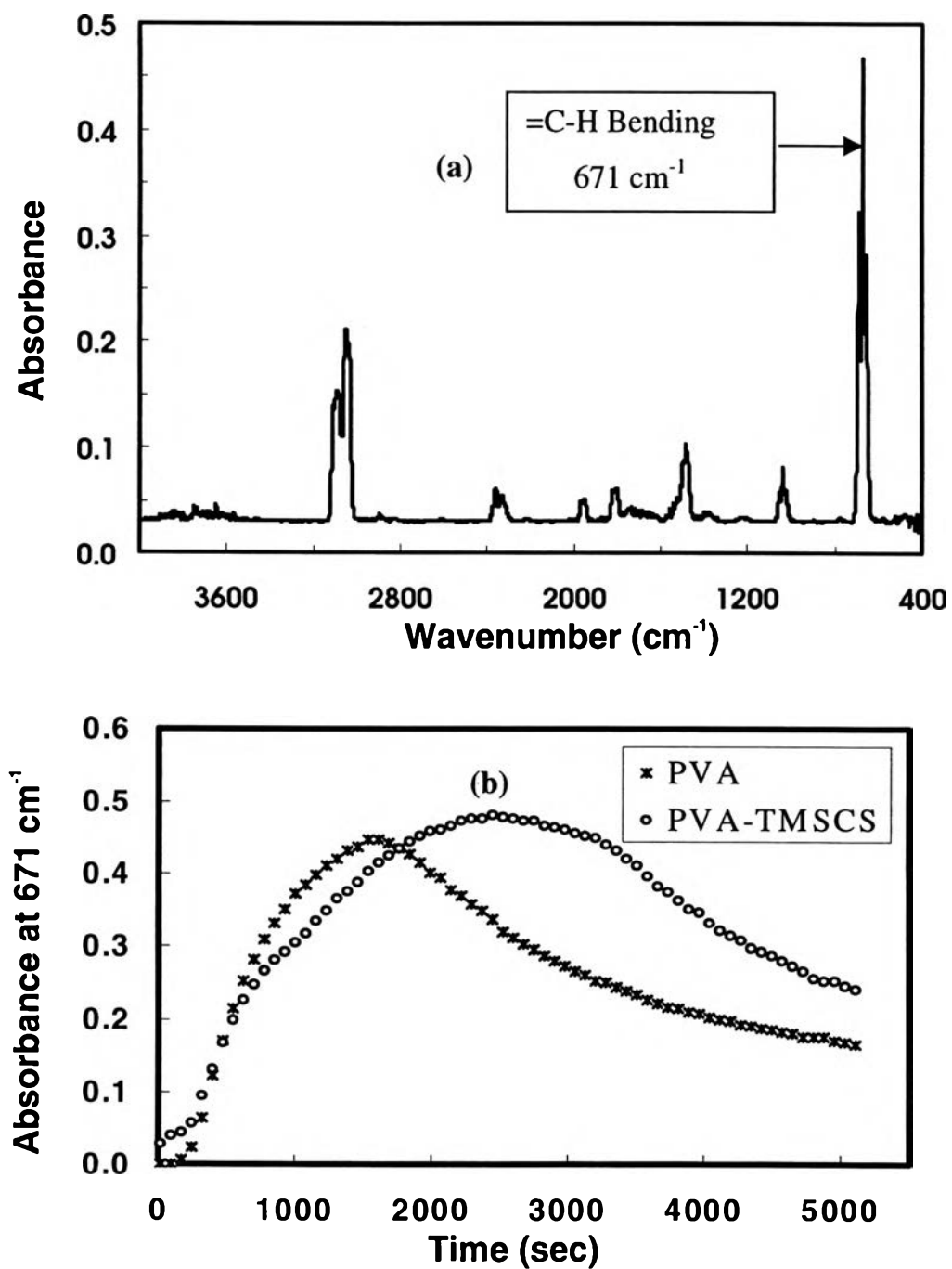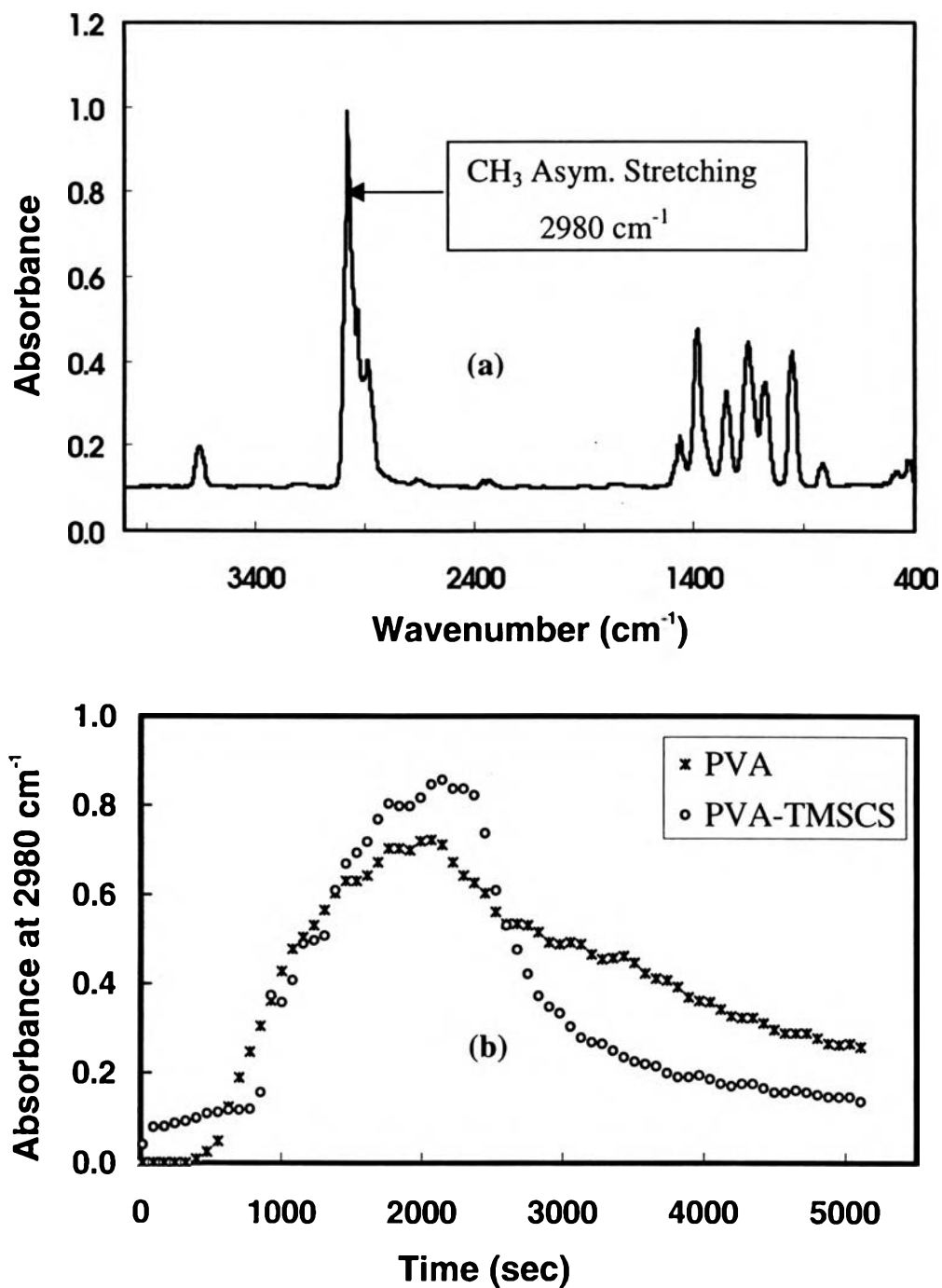
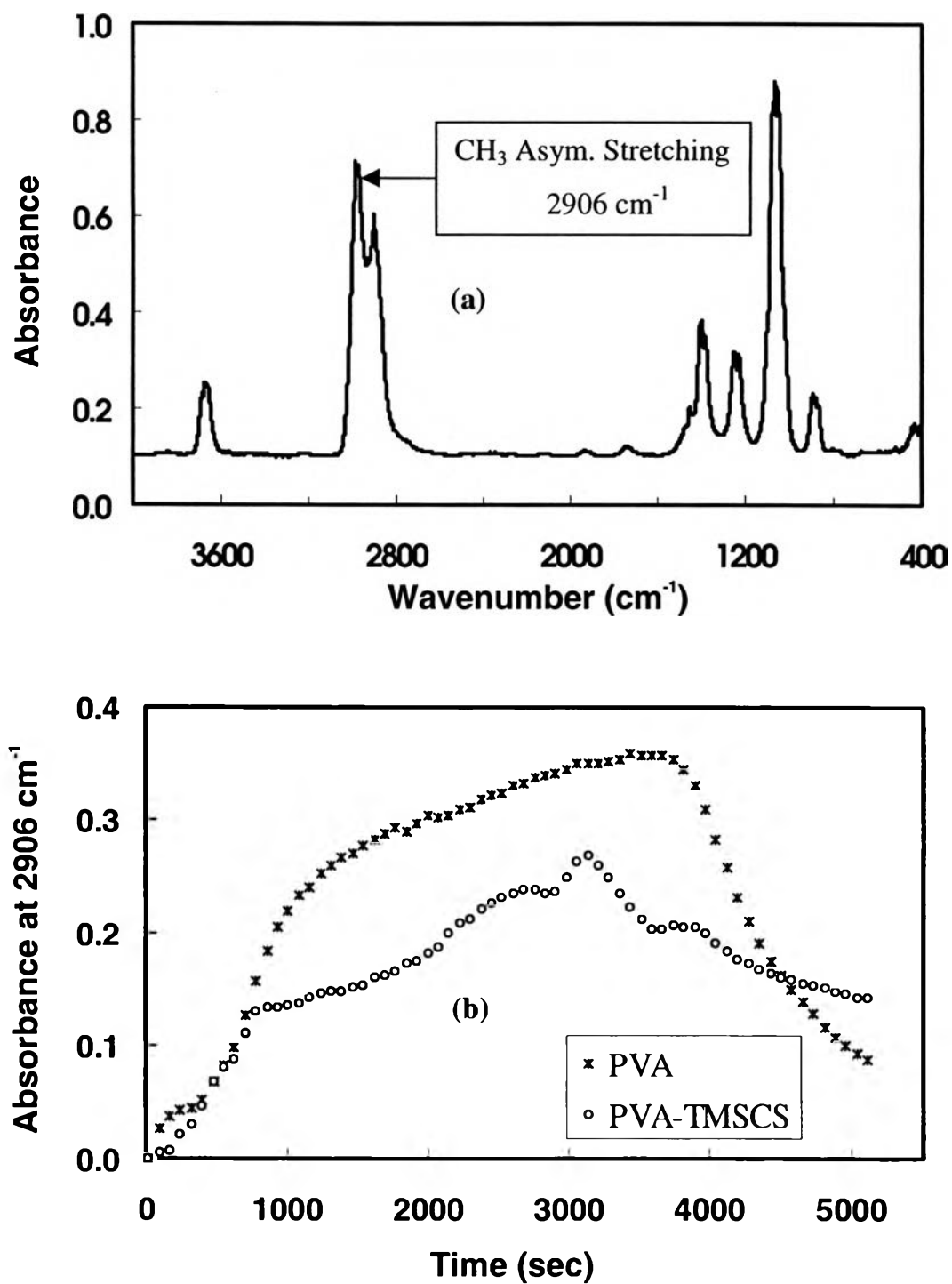**Figure 4.11** (a) FTIR spectra of benzene, and (b) permeability of benzene as a function of time observed by FTIR at 671 cm^{-1}.
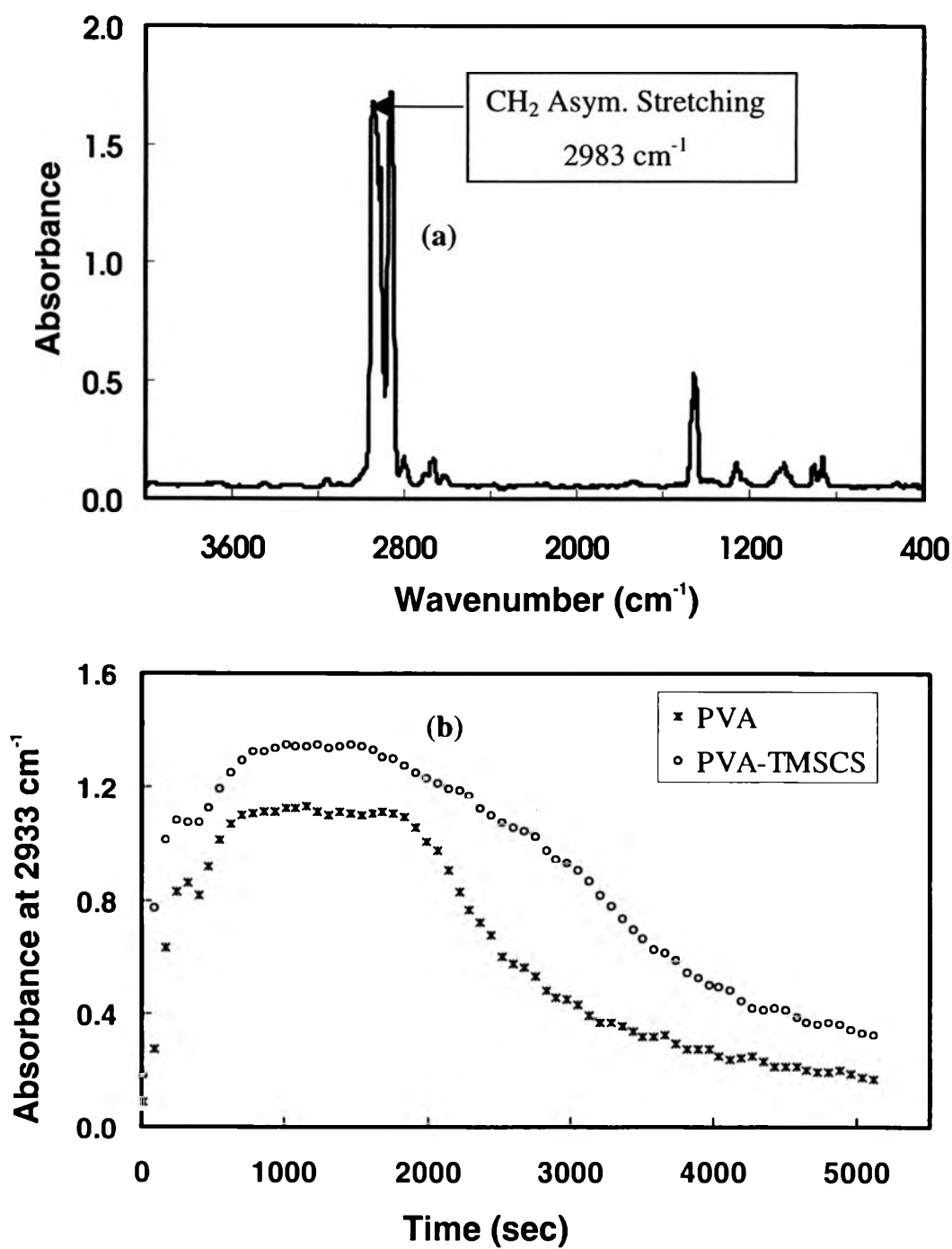
Figure 4.12 (a) FTIR spectra of cyclohexane, and (b) permeability of cyclohexane as a function of time observed by FTIR at 2933 cm^{-1}.
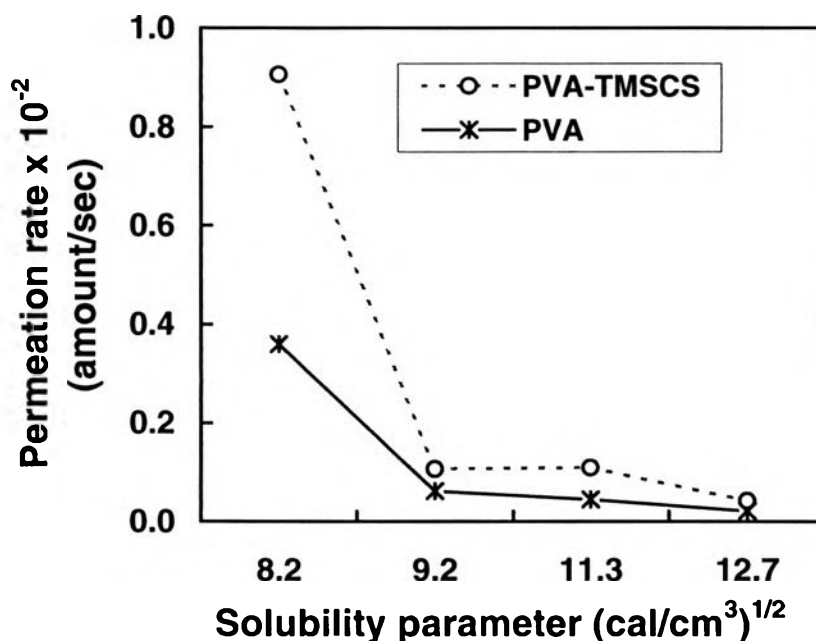
Figure 4.13 (a) FTIR spectrum of *iso*-propanol, and (b) permeability of *iso*-propanol as a function of time observed by FTIR at 2980 cm^{-1}.

Figure 4.14 (a) FTIR spectra of ethanol, and (b) permeability of ethanol as a function of time observed by FTIR at 2906 cm^{-1}.
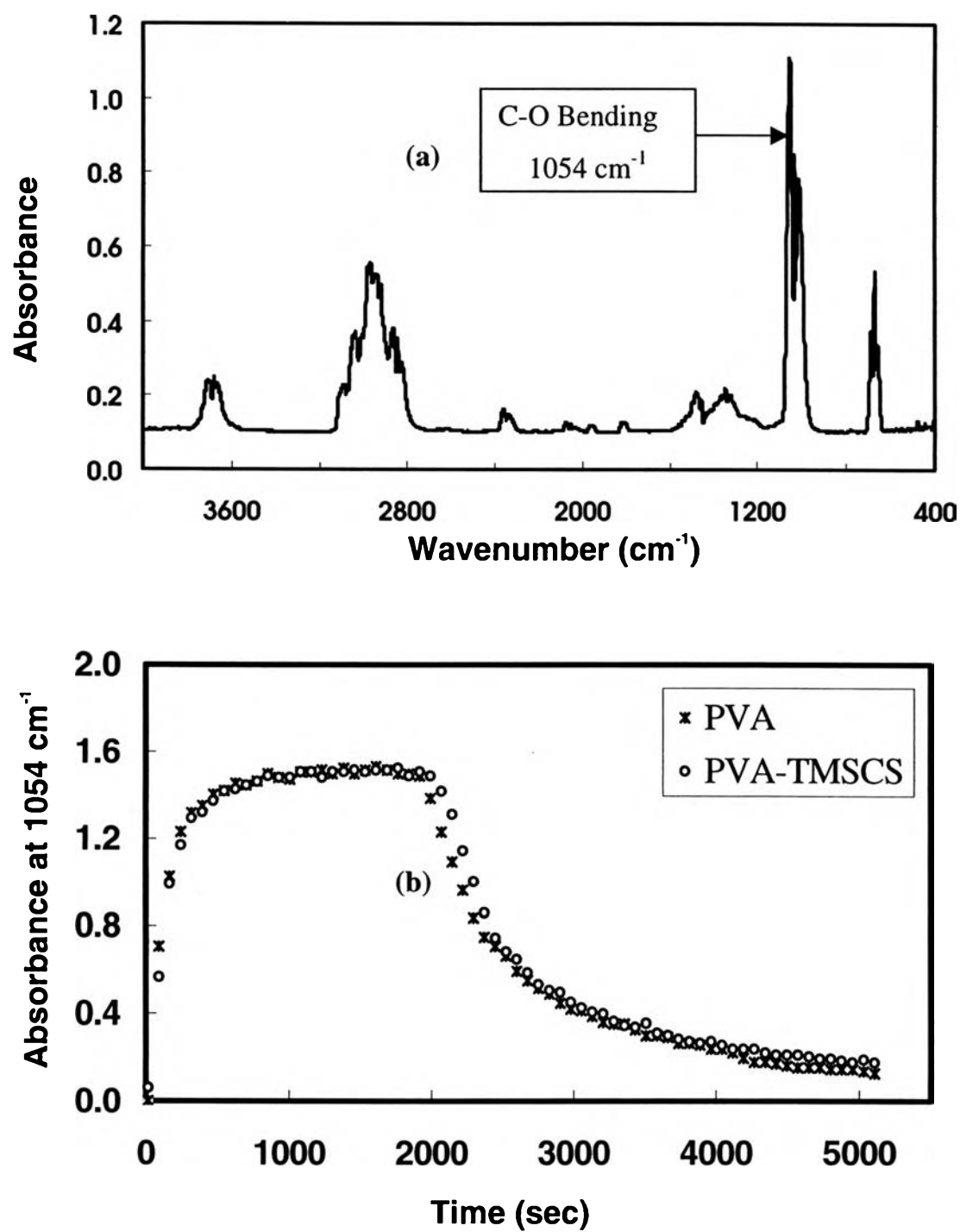
Figure 4.15 (a) FTIR spectrum of methanol, and (b) permeability of methanol as a function of time observed by FTIR at 1054 cm^{-1}.

Figure 4.16 Permeation rates of the organic substrates as varied by solubility parameter for PVA and PVA-TMSCS membranes.

To compare the permeation rate of each organic substrates, the slope are calculated in the range of starting point and maximum absorbance point. As concluded in Figure 4.16, PVA-TMSCS gives the significant permeation rate for the vapor of low solubility parameter solvent (benzene and *iso*-propanol).

To discuss the results, a schematic diagram of interaction between organic substrate and the membrane is presented (Figure 4.17).
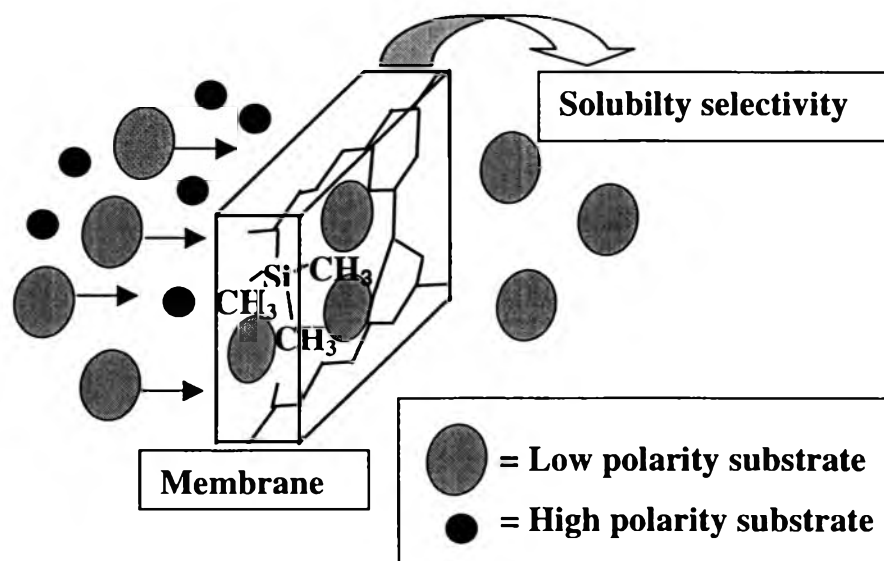
Figure 4.17 Schematic diagram of interaction between trimethylsilyl group and non-polar substrate.

The high permeation rate of the low solubility parameter gas may be due to the appropriate solubility interaction between low polarity substrate and trimethylsilyl group which performs as a non-polar sensing group. In addition, the bulkiness of trimethylsilyl group increases the free volume in the PVA membrane matrix to provide pathway for the large-sized non-polar substrate.