

CHAPTER III

RESULTS AND DISCUSSION

3.1 Antistatic sizing agent

3.1.1 pH of the model treating system

The pH values of the mixture solution between γ -MPS and VTAC at different concentrations is shown in Figure 3.1.

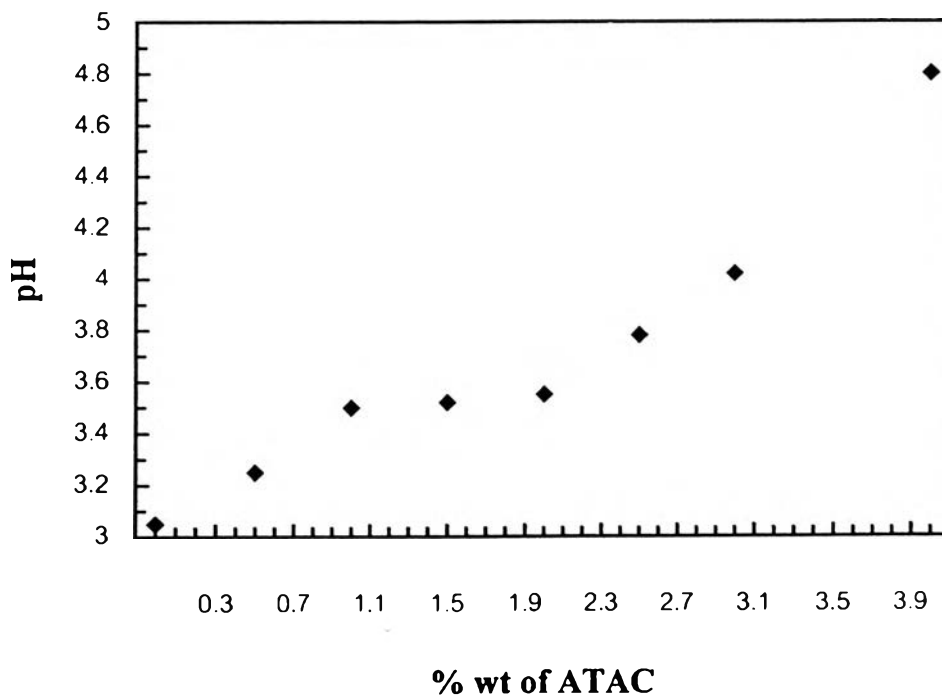


Figure 3.1 pH values of the model sizing system containing VTAC at concentration range of 0-4.0 % by weight.

The solutions of VTAC itself in deionized water and alcoholic solution (92% ethanol) show pH values of 7.01 and 7.03 respectively. From the pH measurements, it can be seen that when the concentration of the VTAC is increased, the basicity of the solution will also increase. pH is known to be an important factor that can influence the silanol condensation[Isida et. al.(1983)]. In actual production of fiber glass, the amount of VTAC used is between 0.1% to 2.0%, which according to Figure 3.1, will change the pH value of the system by about 0.5 unit, and this change in the pH values may have an effect on the silanol condensation.

3.1.2 Characterization of the silanol condensation products by SEC

3.1.2.1 The effect of varying amount of VTAC on silanol condensation

Figure 3.2 shows the chromatograms of γ -MPS at different drying times. It can be seen that the eluting peak becomes broader and shifts to lower time as the drying time increases indicating that the condensation at longer drying time results in larger oligomers with broader molecular weight distribution.

Figures 3.3-3.7 show the chromatograms of γ -MPS in the presence of different concentrations of VTAC. It can be seen that, at higher concentrations of VTAC, the peaks become smaller as compared to the system with γ -MPS alone indicating that the silanol condensation is restricted at high concentrations of VTAC.

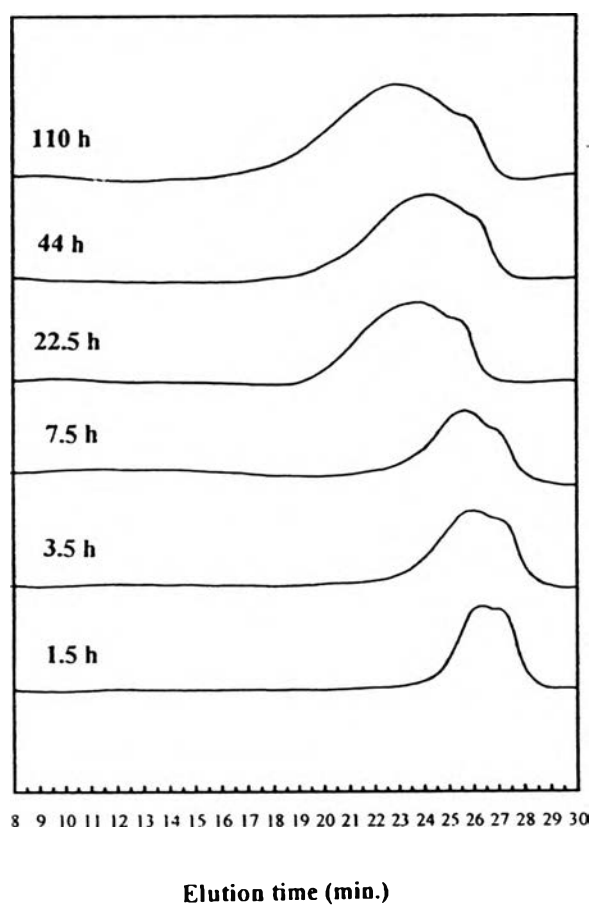


Figure 3.2 SEC chromatograms of γ -MPS hydrolyzate.

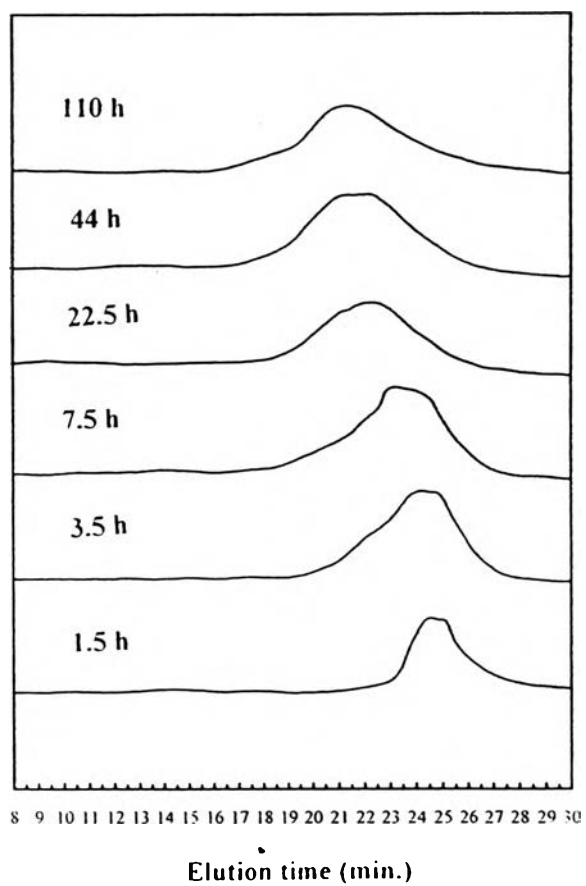


Figure 3.3 SEC chromatograms of the model system consisting of 5% by wt VTAC.

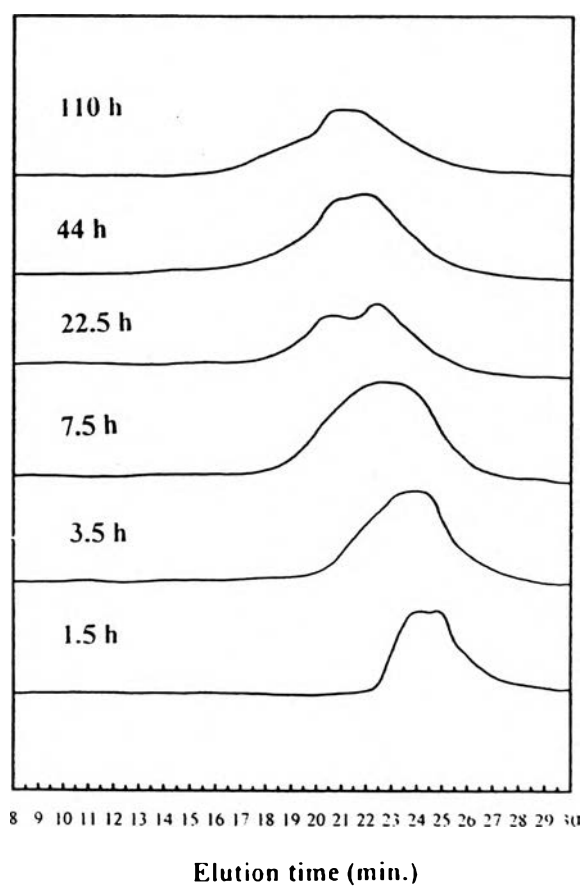


Figure 3.4 SEC chromatograms of the model system consisting of 10% by wt VTAC.

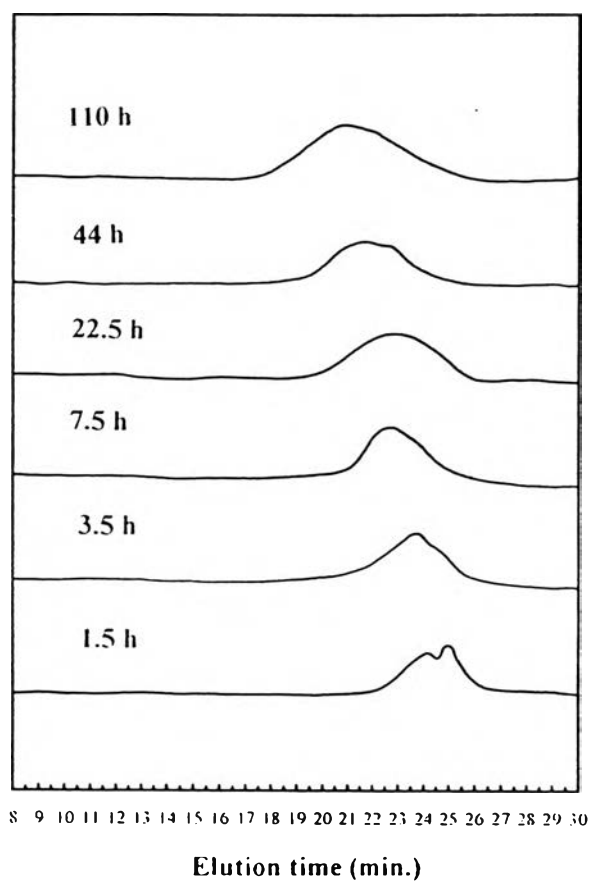


Figure 3.5 SEC chromatograms of the model system consisting of 20% by wt VTAC.

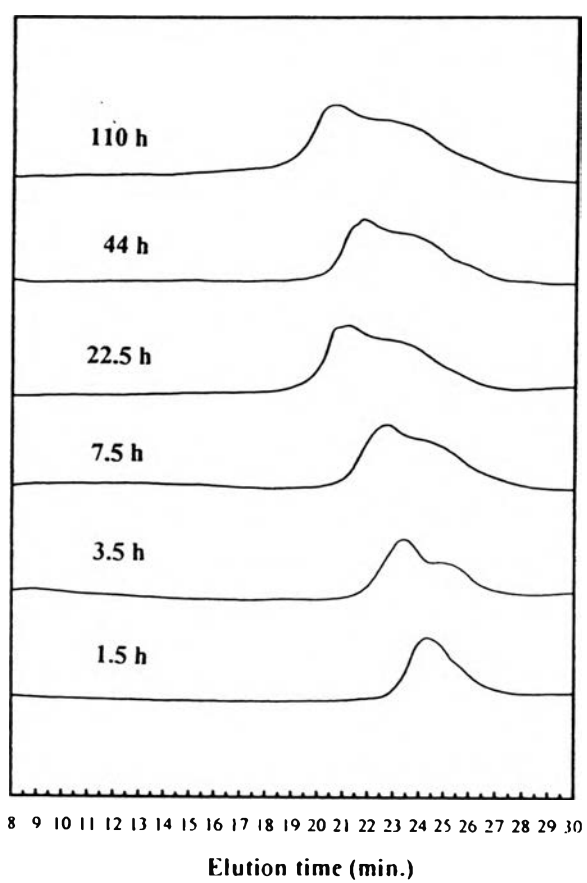


Figure 3.6 SEC chromatograms of the model system consisting of 50% by wt VTAC.

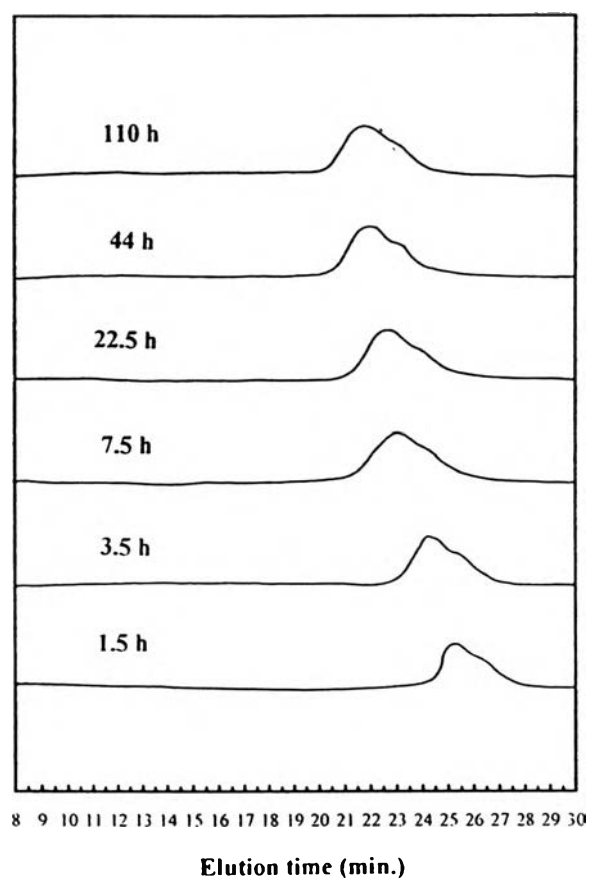


Figure 3.7 SEC chromatograms of the model system consisting of 80% by wt VTAC.

Figure 3.8 shows the plot of the elution time at different concentrations of VTAC. It can be seen that the elution time first decreases sharply with the increase in the concentration of VTAC, it then continues to decrease at a much slower rate up to the concentration of 50%. After this there is a sharp turn and the elution time increases again as the concentration of VTAC is increased to 80%.

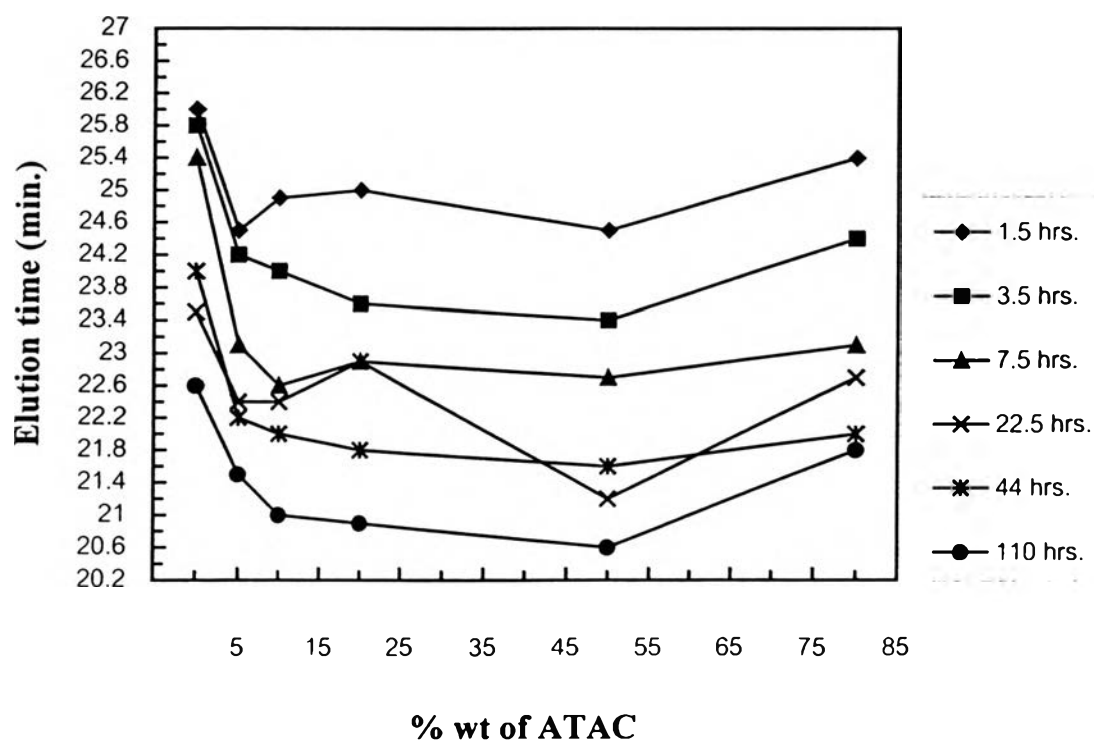


Figure 3.8 Elution time of model sizing system consisting of different concentrations of VTAC.

The results shows that VTAC enhances silanol condensation at low concentrations. It is thought that VTAC may be miscible with the methacryl groups of γ -MPS since they both have a vinyl group in their molecular structures. The interaction between the two groups helps to free

some of the silanol groups that may otherwise form hydrogen bonding with the carbonyl groups of the methacryl groups of other γ -MPS molecules and therefore the silanol condensation is enhanced. However as the concentration of VTAC is increased, the excess VTAC molecules may obstruct the movement of γ -MPS molecules and also as the ratio of the γ -MPS molecules in the mixture system is decreased, the chance of their meeting with each other is also reduced, and these two factors have led to a sharp decrease in the molecular weight of the silanol oligomers at 80% by weight of VTAC.

It is known that the silanol condensation is dependent on pH and as shown earlier (Figure 3.1), the pH of the solution changes with changes in the concentration of VTAC. It is therefore not clear if the above results are due to the change in the pH of the system, or the interfering of the VTAC molecules on the condensation reactions or both. Further experiments have therefore been carried out at fixed pH and the results are discussed in section 3.1.2.3.

3.1.2.2 The effect of drying time on the silanol condensation in the presence of VTAC

Figure 3.9 shows the plot of the elution time with drying time. It can be seen that the elution time decreases as drying time increases at all concentrations of VTAC and the rate of decrease is greatest at the initial stages of drying. The results show that the drying time has a significant effect on the silanol condensation. It is thought that, as the drying time increases, more solvent evaporates, the mixture becomes more concentrated leading to higher molecular weight oligomers. Longer drying time also means longer reaction time and this should also help in the formation of higher molecular weight oligomers. The higher molecular weight poly MPS will enhance its adhesion with the fiber glass surface.

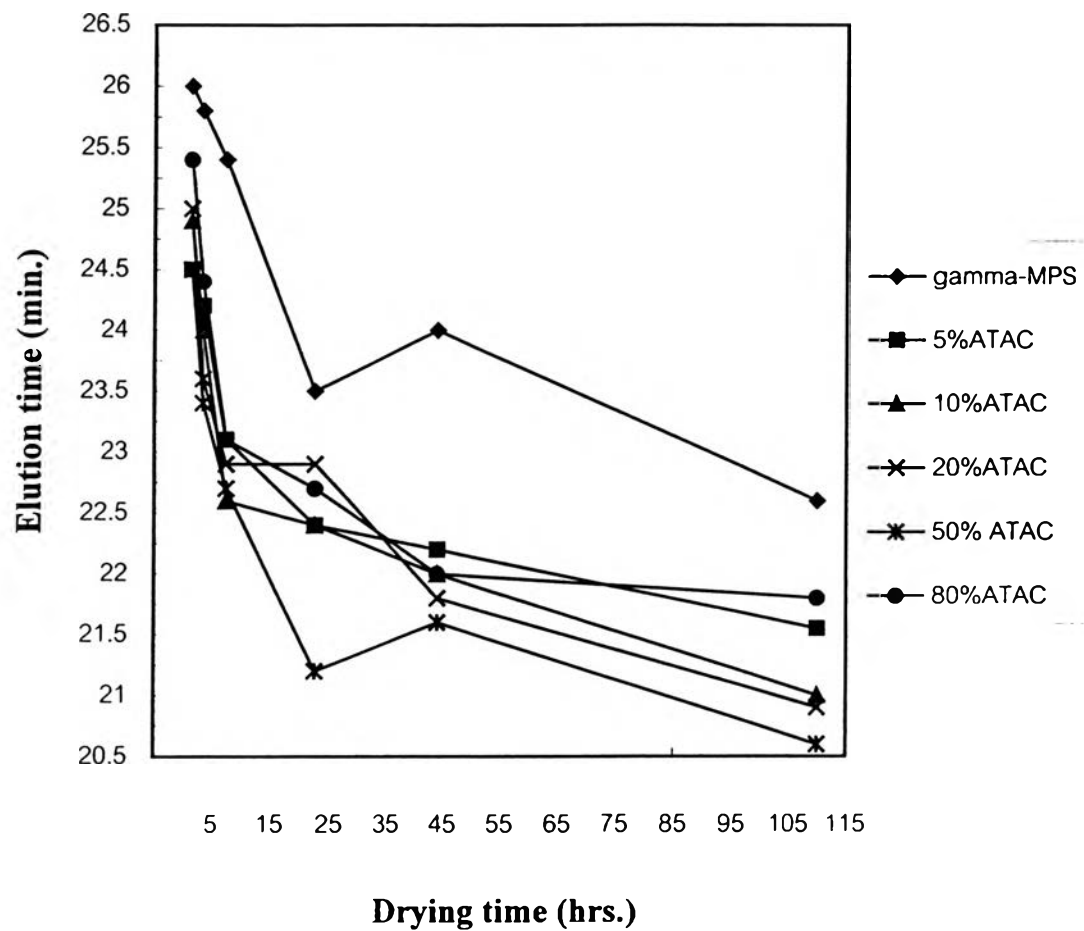


Figure 3.9 Elution time of model sizing system containing VTAC at different drying times.

3.1.2.3 *The effect of VTAC on the silanol condensation at fixed pH*

Figures 3.10-3.14 show the SEC chromatograms of γ -MPS and γ -MPS with different concentrations of VTAC dried at different times at pH 7.0. It can be seen that the peaks in each figure are generally similar in size and shape, except for the few chromatograms at lower drying times where the peaks in the presence of VTAC are found to be narrower than in the system with only γ -MPS.

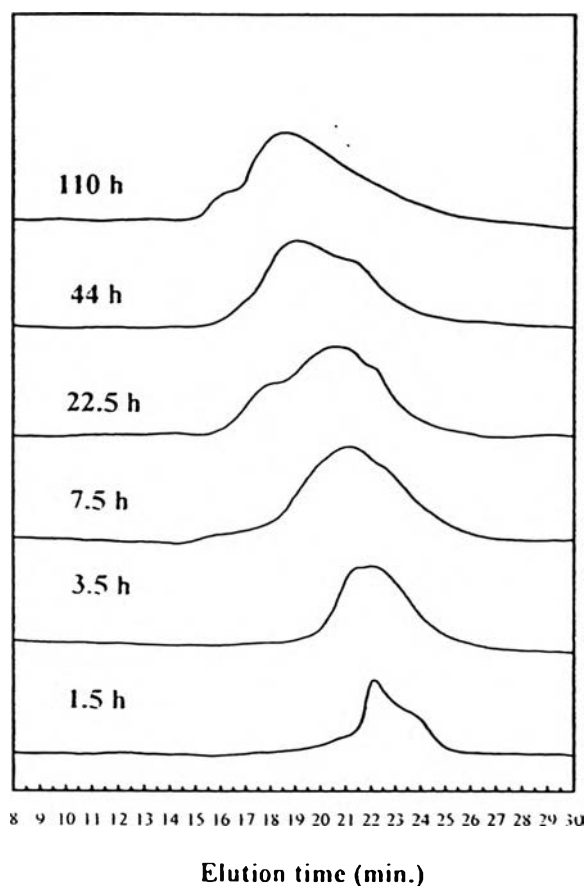


Figure 3.10 SEC chromatograms of γ -MPS hydrolyzate at pH=7.0.

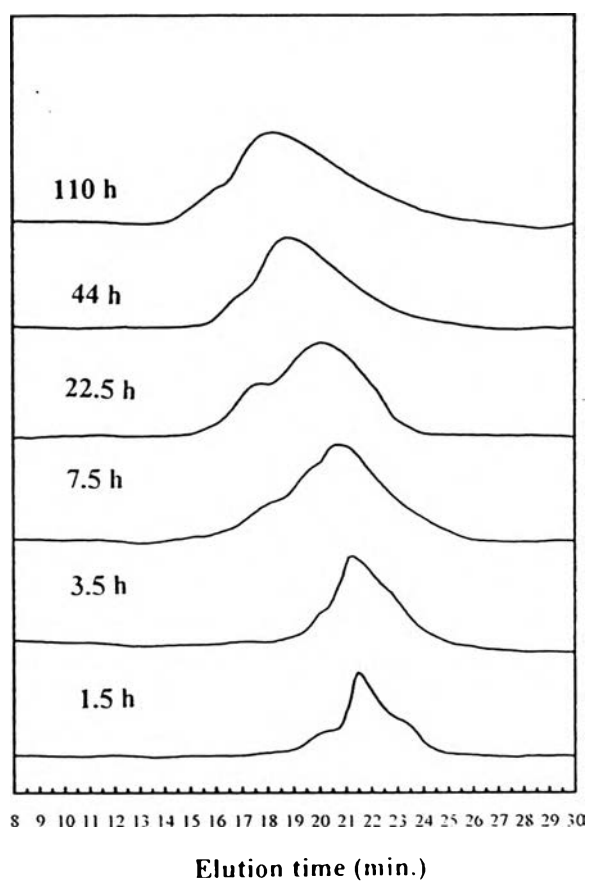


Figure 3.11 SEC chromatograms of the model system consisting of 5% by wt VTAC at pH=7.0.

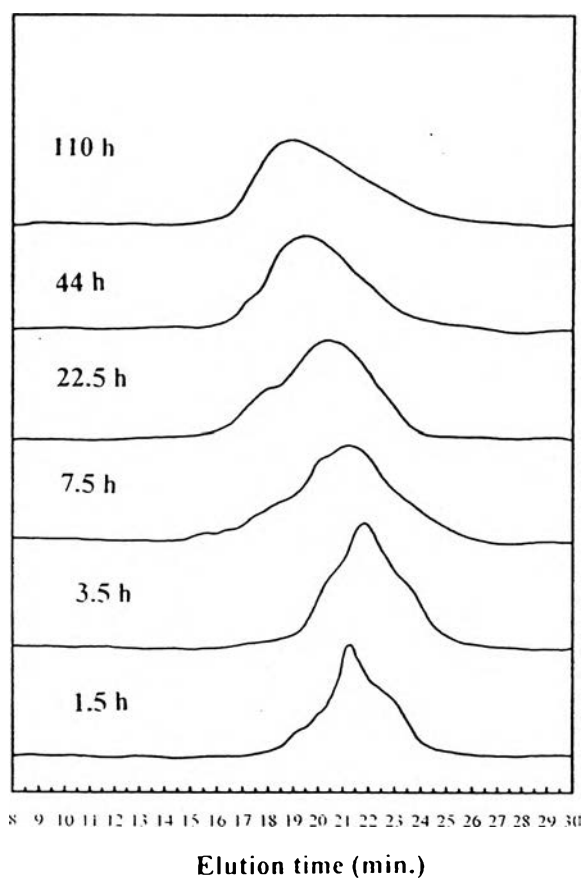


Figure 3.12 SEC chromatograms of the model system consisting of 10% by wt VTAC at pH=7.0.

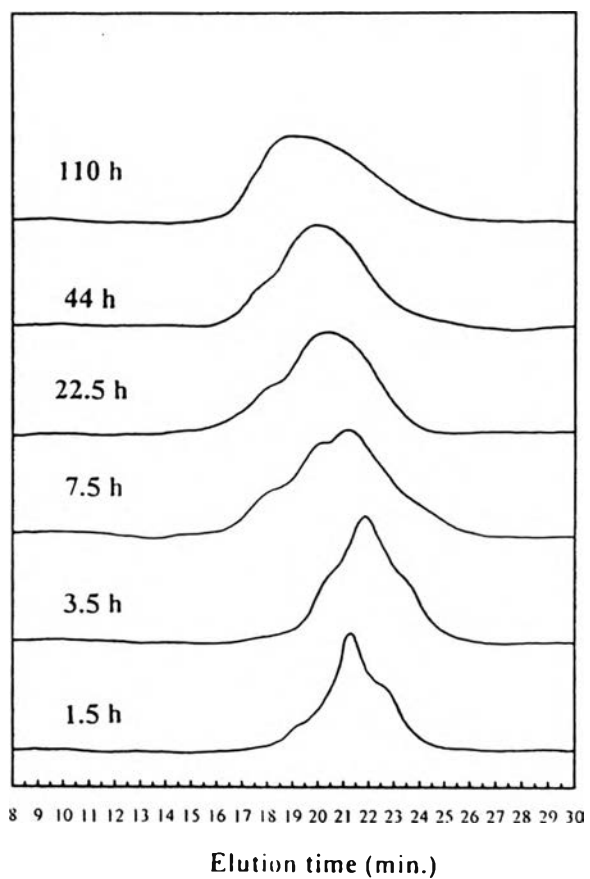


Figure 3.13 SEC chromatograms of the model system consisting of 20% by wt VTAC at pH=7.0.

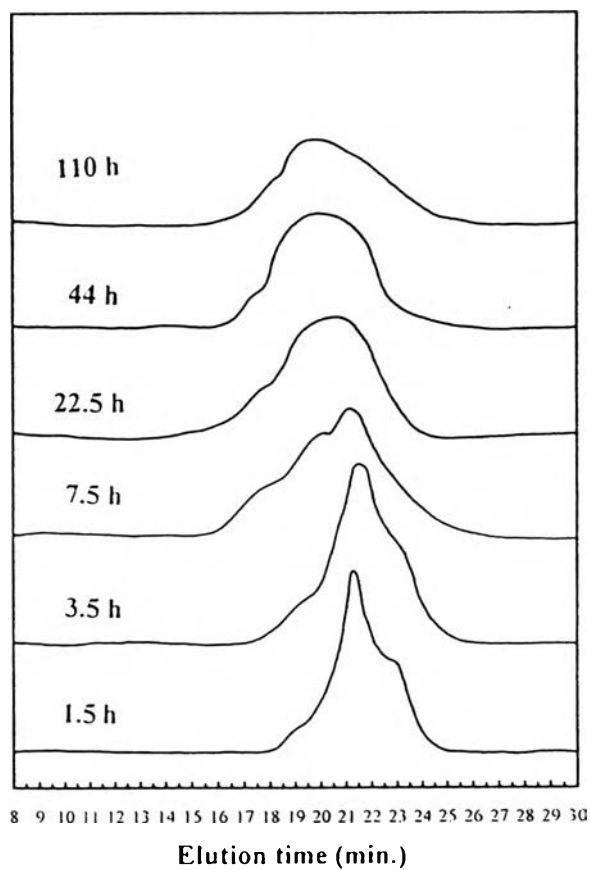


Figure 3.14 SEC chromatograms of the model system consisting of 50% by wt VTAC at pH=7.0.

Figure 3.15 is the plot between the elution time and concentration of VTAC at pH 7.0. It can be seen that the graphs obtained are different from those in Figure 3.14 confirming that pH has an important influence on the silanol condensation.

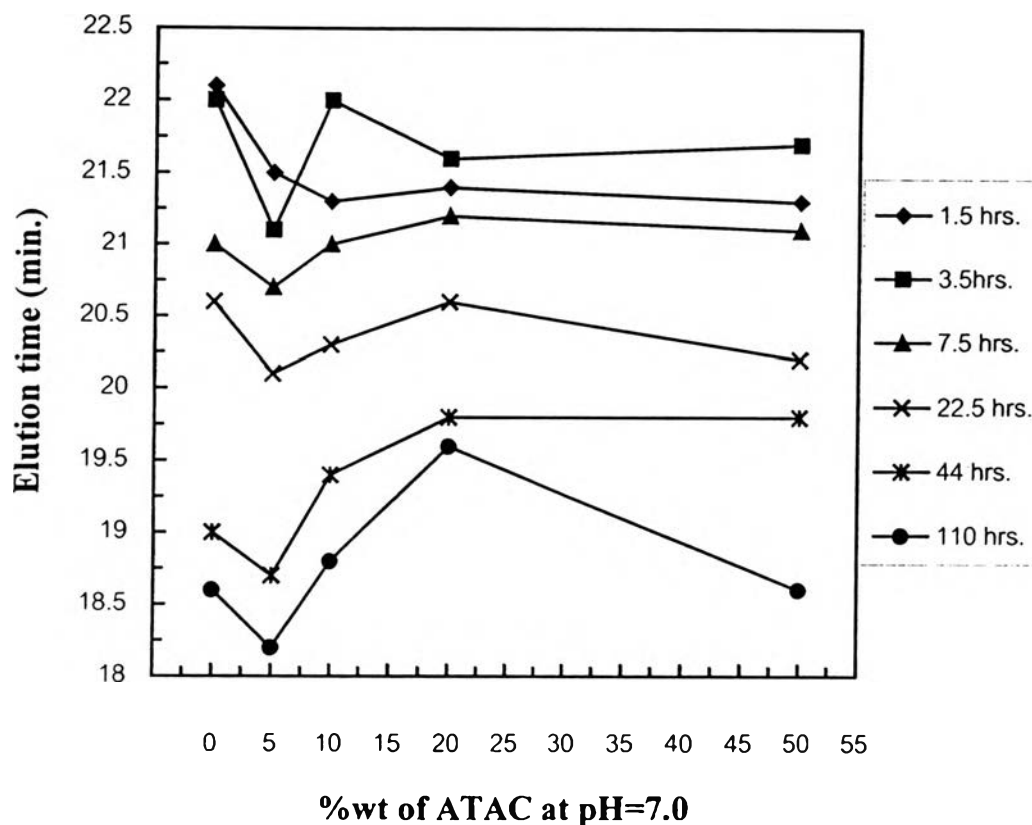


Figure 3.15 Elution time of model sizing system consisting of different concentrations of VTAC at pH=7.0.

In Figure 3.15, the elution time is seen to decrease when 5% by weight of VTAC is present at all drying times. However as the concentration of VTAC is increased further, the elution time increases again

except in the case of 110 hours of drying time where the elution time decreases significantly at 80% by weight of VTAC. The results confirms the enhancement effect of VTAC at the initial concentration of 5%. However. At higher concentrations of VTAC, the hindered effect as described in section 3.1.2.1 becomes predominant and results in a gradual decrease in the molecular weight of the oligomer products.

Figure 3.16 shows the plot between the elution time and the drying time for the systems with different concentrations of VTAC at pH 7.0.

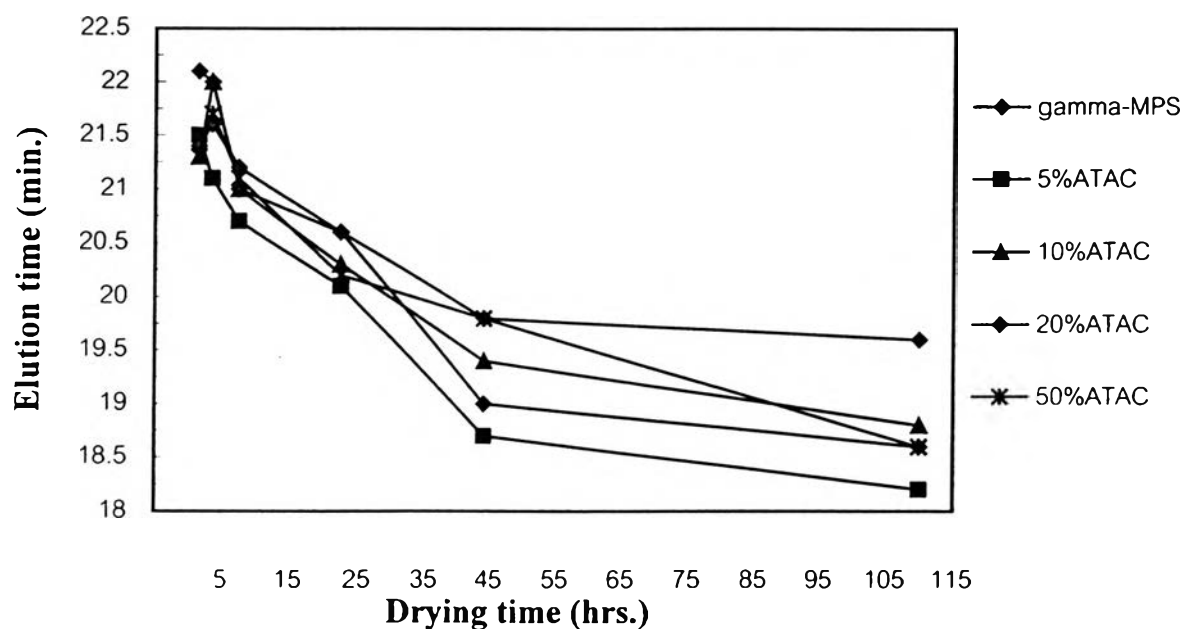


Figure 3.16 The plot of relative elution time of model sizing system containing different concentration of VTAC at pH=7.0 with different times.

It can be seen that, as in the case of Figure 3.9, there is gradual decrease in elution time as the drying time increase in all cases confirming that the silanol condensation is strongly dependent on the drying

time, the longer the drying time the greater the molecular weight of the condensation products.

3.1.3 Characterization of the silanol condensation products by FTIR

Figure 3.17 shows FTIR spectrum of VTAC chains. The bands at 2951 cm^{-1} and 2920 cm^{-1} are assigned to the CH_3 asymmetric stretching and CH_2 asymmetric stretching respectively. The bands at 3017 cm^{-1} and 2849 cm^{-1} are assigned to the CH= stretching and CH_2 symmetric stretching respectively. The bands at 1633 cm^{-1} , 1466 cm^{-1} and 1377 cm^{-1} which are indicative of C=C group, CH_2 symmetric bending and CH_3 symmetric bending of VTAC respectively. The bands in the range $1250\text{-}1020\text{ cm}^{-1}$ are C-N stretching vibration of tertiary aliphatic amines. The band at 722 cm^{-1} is the $\text{CH}_2=\text{CH-}$ rocking vibration mode of alkene [Silverstein and Robert (1991), Fessenden and Ralph (1994)].

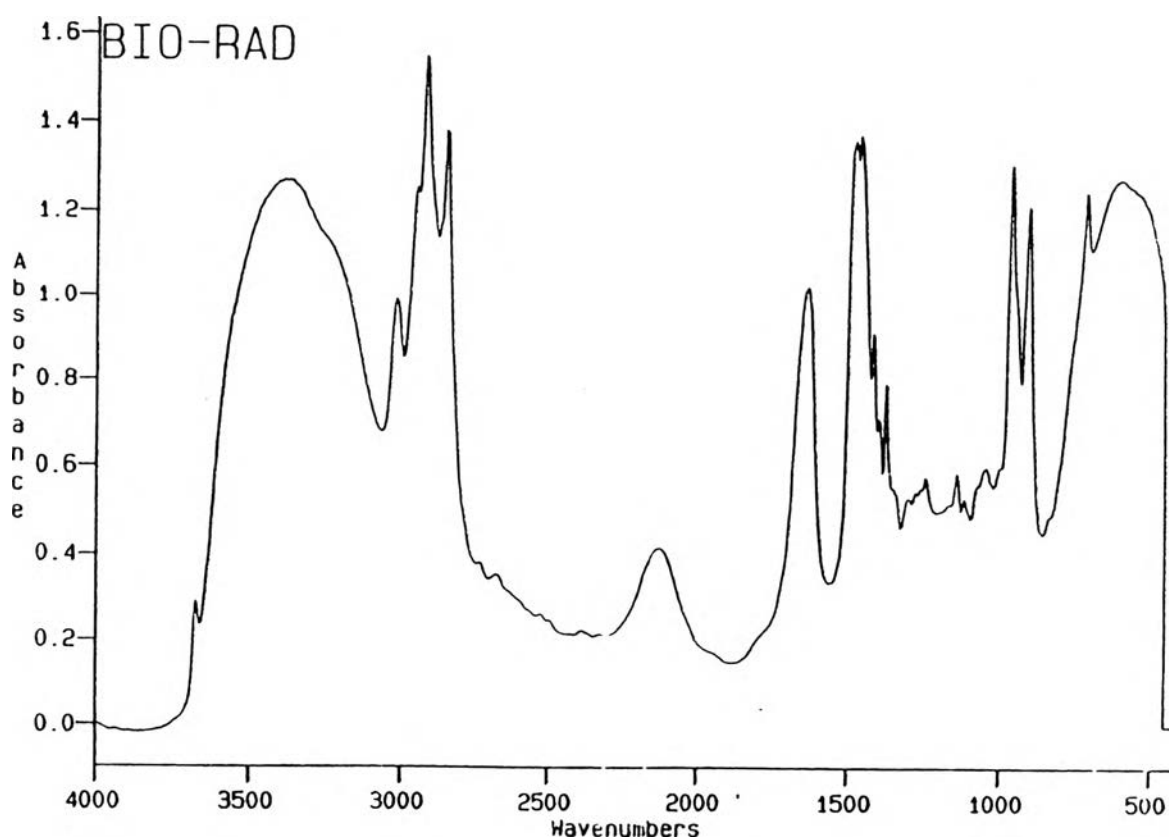


Figure 3.17 FTIR spectra of VTAC.

Figure 3.18 shows the FTIR spectra of the mixture system containing VTAC at the initial stage of drying time 1.5 h. The siloxane bands appear in the region 1200-1000 cm^{-1} . The sharp peak of siloxane bands at 1720 cm^{-1} is non-hydrogen bonded carbonyl group and 1700 cm^{-1} can be allotted to non-hydrogen bonded of carbonyl stretching bands respectively.

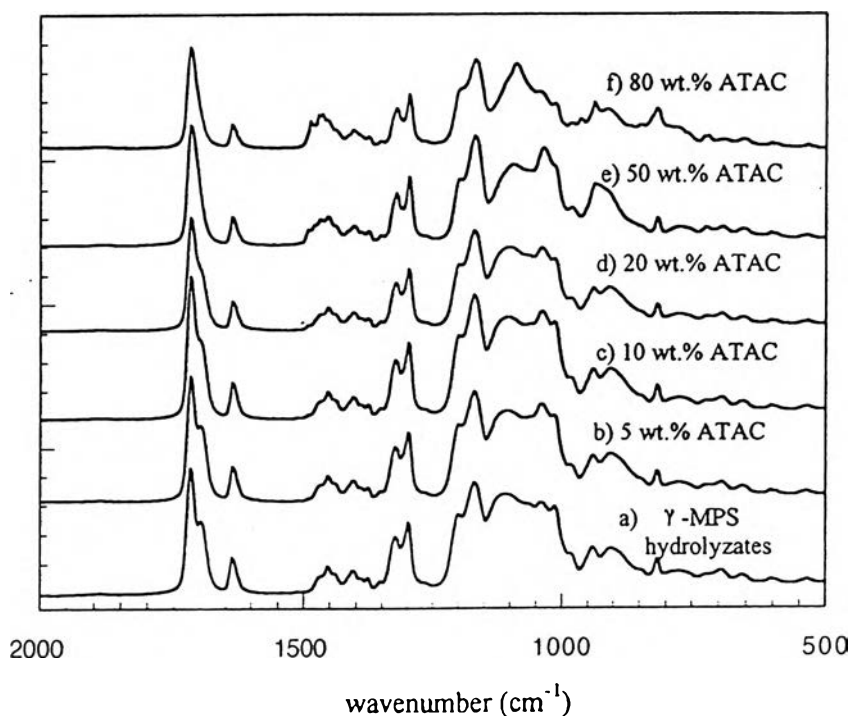


Figure 3.18 FTIR spectra of the model sizing system containing VTAC different % wt at the drying time of 1.5 h.

When the concentration of VTAC is increased up to 80%, significant changes appear in the siloxane bands, showing that VTAC has an effect on silanol condensation. Therefore it is interesting to follow the change of the siloxane bands when VTAC is present in the system.

Figure 3.19(a) shows the siloxane stretching region between 1200-1000 cm^{-1} at the initial stage of drying of 1.5 h. In the γ -MPS hydrolyzate system, the spectrum consists of a strong broad band centered at 1106 cm^{-1} with a weak shoulder around 1065 cm^{-1} and a small band at 1040 cm^{-1} which is the characteristic band Si-O-Si of poly-MPS with double ladder structure[Miller et. al. (1984)].

When the VTAC is present in the system at the concentrations of 5, 10, 20% and 50% by weight, the strong band at 1106 cm^{-1} can still be observed. The weak shoulder at 1065 cm^{-1} becomes weaker but the small band at 1040 cm^{-1} is stronger indicating that the silanol condensation is enhanced in the presence of VTAC in the concentration range of 5-50%. The same trend is found in Figures 3.19(b)-(f) for the drying times of 3.5-110 hrs. respectively. The results confirm the finding from SEC that VTAC enhances the silanol condensation at the concentration below 50%.

As for the sample with 80% by wt of VTAC. At short drying times of 1.5, 3.5, and 7.5 hrs. (Figures 3.19(a)-(c)), the spectra show a distinct peak at 1083 cm^{-1} while the small shoulder at 1040 cm^{-1} which is the Si-O-Si stretching band of the poly-MPS is hardly visible. The results show that, at short drying times, high concentration of VTAC hindered the silanol condensation due to its obstruction of silanol group movement as described in Section 3.1.2.1. However at longer drying times of 22.5, 44, and 110 hrs. respectively, (Figures 3.19(d)-(f)), the spectra of the samples with 80% by wt of VTAC begin to change with the peak at 1040 cm^{-1} appearing with higher intensive at longer drying time. The results show that at longer drying time, the effect of high concentration of VTAC may be reverse. It is postulated that as the drying time increases and more solvent is evaporated, a micelle-like structure as shown in Figure 3.20 may be formed with γ -MPS molecules forming the surrounding phase. The gathering of MPS molecules in the central

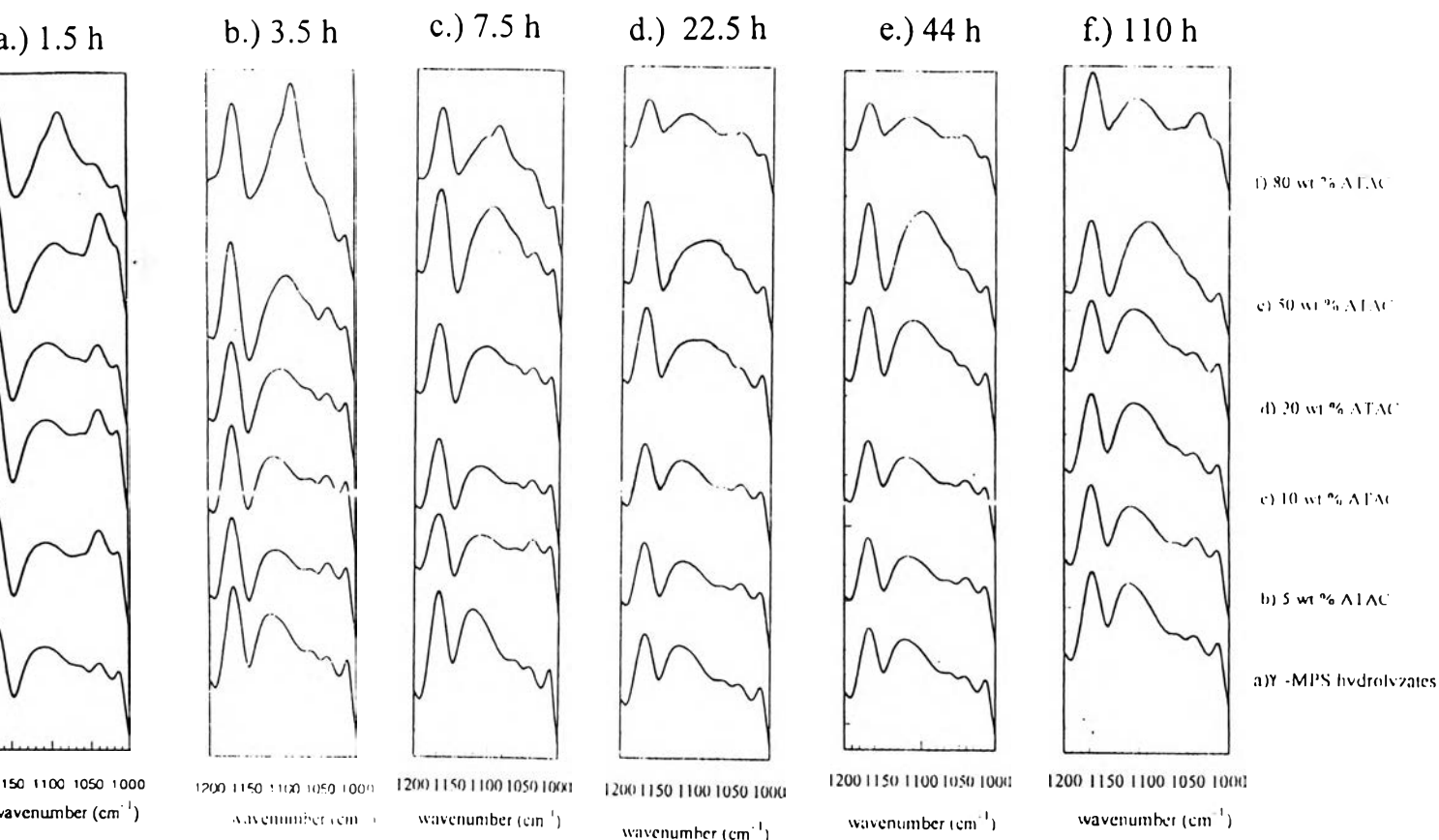


Figure 3.19 FTIR spectra of the siloxane stretching region the model system containing VTAC at drying time 1.5, 3.5, 7.5, 22.5, 44 and 110 h. respectively.

part of the the structure leads to the enhancement of silanol condensation.

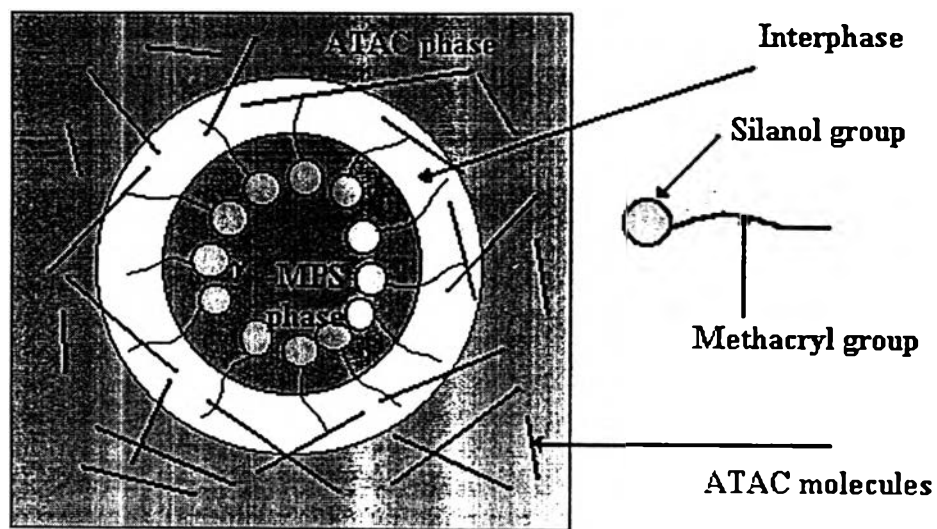


Figure 3.20 Postulated micelle-like structure morphology of the system containing γ -MPS and VTAC.

3.2 Film former and lubricating sizing agent

In the model sizing system consisting of γ -MPS, PEG and PVAc, it is expected that PEG and PVAc would affect silanol condensation of γ -MPS hydrolyzates in several ways, namely: i) the occurrence of H-bonding between silanol groups of γ -MPS with oxygen atoms of PEG; ii) H-bonding between silanol groups of γ -MPS with oxygen atoms of carbonyl groups of other γ -MPS molecules; iii) H-bonding between silanol groups of γ -MPS with oxygen atoms of carbonyl groups of PVAc molecules; and iv) interaction between methacryl groups of γ -MPS and PVAc molecules since they have similar solubility parameter values [Isida et. al.(1983)]. In this work, the effect of PEG and PVAc on the silanol condensation of γ -MPS was studied by using SEC and FTIR.

3.2.1 Characterization of the silanol condensation products by SEC

3.2.1.1 The effect of PEG and PVAc on the silanol condensation of γ -MPS

Figure 3.21 shows the SEC chromatograms of γ -MPS at different drying times. It can be seen that the peak becomes broader and shifts to lower elution time as the drying time increases. The results show that higher molecular weight oligomers with broader molecular weight distribution are formed at longer drying times.

Figure 3.22 shows the SEC chromatograms of γ -MPS in the presence of 40% by weight of PEG at different drying times. It can be observed that, as the drying time is increased, the chromatogram of the system becomes broader and shifts to lower elution time. However, when Figures 3.21 and 3.22 are compared, the peaks in Figure 3.22 are found to be much narrower and located at longer elution times.

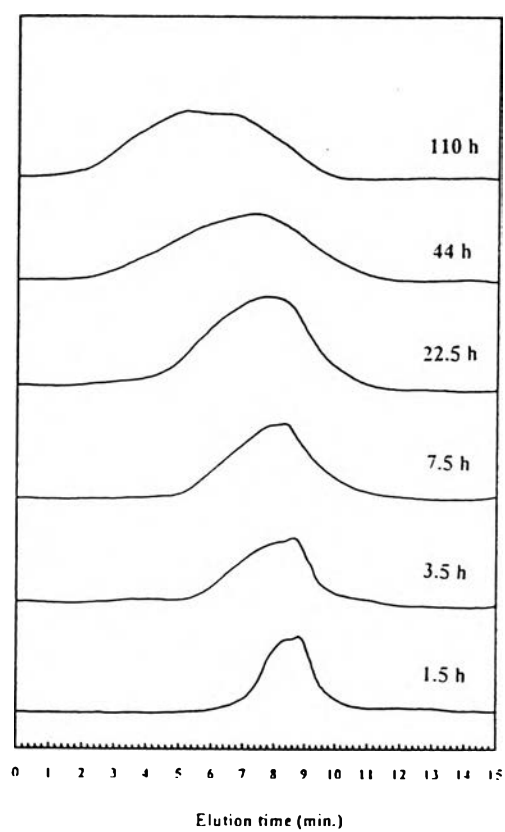


Figure 3.21 SEC chromatograms of γ -MPS oligomers at different drying times.

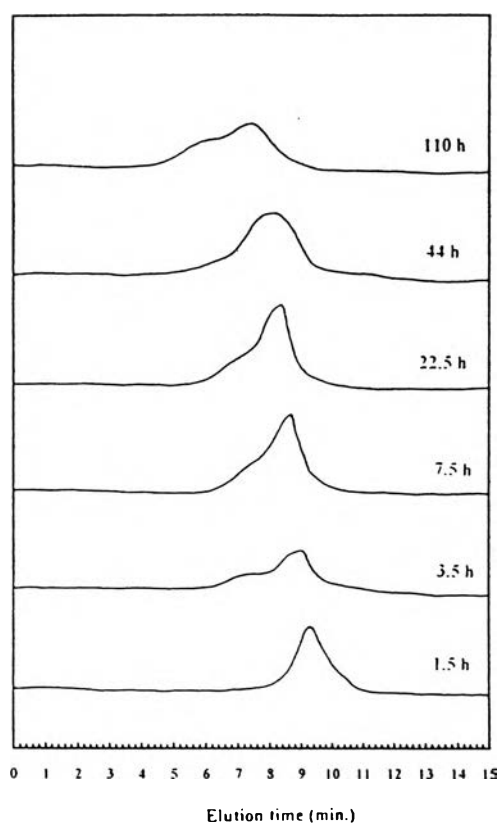


Figure 3.22 SEC chromatograms of γ -MPS oligomers in the presence of 40% by wt of PEG at different drying times.

The results show that the condensation of γ -MPS hydrolyzates in the presence of PEG is slower than in γ -MPS alone.

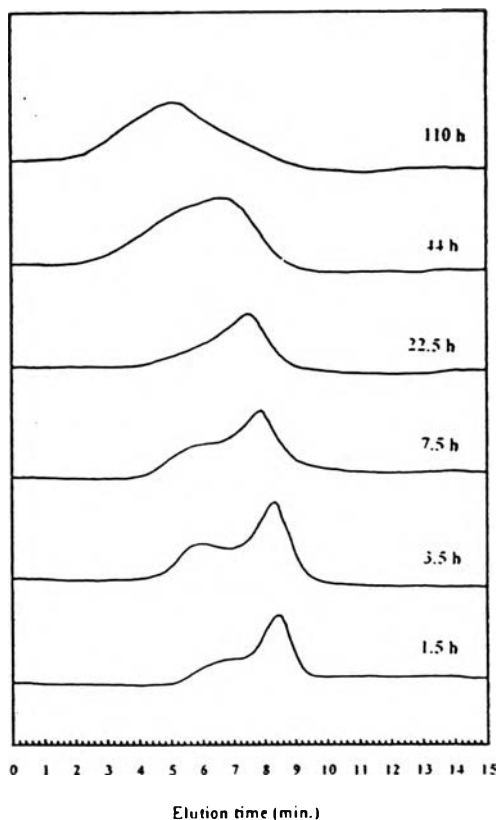


Figure 3.23 SEC chromatograms of γ -MPS oligomers in the presence of 40% by wt of PVAc at different drying times.

Figure 3.23 shows the SEC chromatograms of γ -MPS in the presence of 40% by weight of PVAc at different drying times. It can be seen that the peak becomes broader and shifts to lower elution time as the drying time increases. At the initial stages of drying, a small peak appears next to the main peak at shorter elution time. However, at longer drying time, the small peak merges with the main peak to form one broad peak. When Figures 3.21 and 3.23 are compared, it can be seen that the peaks in Figure 3.23 are generally narrower but with shorter elution times. The results show that silanol

condensation in the presence of PVAc yields higher molecular weight oligomers but with narrower molecular weight distribution.

Figure 3.24 shows the relationship between the main elution time of γ -MPS oligomers and the drying time in γ -MPS alone, and in the presence of PEG and PVAc respectively. It can be seen that the elution time decreases as the drying time increases in all the three cases indicating that higher molecular weight oligomers are formed at longer drying times. However, the elution time in the presence of PEG is much longer than in γ -MPS alone at the same drying time indicating that PEG restricted the silanol condensation resulting in lower molecular weight oligomers. On the contrary, the elution time in the presence of PVAc is found to be slightly shorter than in γ -MPS alone showing that PVAc enhances the silanol condensation.

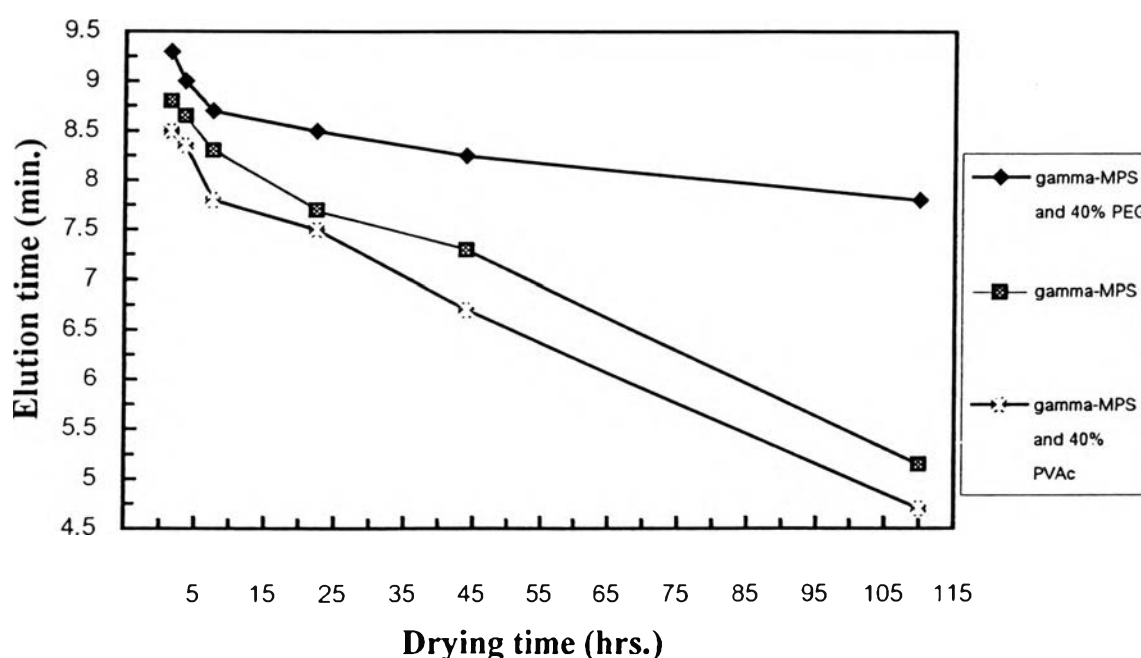


Figure 3.24 Elution time of the model treating systems as a function of the drying time.

The hindrance effect of PEG may be due to the hydrogen bonding between the silanol groups and the oxygen in PEG. The number of silanol groups available for condensation is therefore reduced resulting in lower condensation. In the case of PVAc, since PVAc is miscible with the methacryl group of γ -MPS[Pohl and Osterholtz(1985)], it probably prefers to interact with the methacryl group rather than forming hydrogen bonding with the silanol groups, the silanol groups are therefore free to react with one another. The interaction between PVAc and methacryl groups of γ -MPS may also help to free some of the silanol groups which may otherwise form hydrogen bonding with the carbonyl groups of other γ -MPS molecules thus resulting in greater silanol condensation in the presence of PVAc.

3.2.1.2 The effect of varying amount of PVAc on the silanol condensation with PEG in the mixture system

Figures 3.25-3.29 present the SEC chromatograms of γ -MPS oligomers in varying amount of PVAc with PEG in the mixture system at different drying times. All the chromatograms show the same trend of moving to shorter elution time with broader peaks as the drying time increases. However, they differ in the shape and position of each main peak.

At 5% PVAc (Figure 3.25), the peaks at initial drying times are very narrow indicating a very narrow molecular weight distribution. The same is true for the chromatograms of 10% and 20% PVAc (Figures 3.26 and 3.27). This is thought to be due to the fact that there are more than one component in these systems. Unlike the case when there is only γ -MPS in the system(Figure 3.21), the silanol condensation can take place extensively throughout the whole mass, but in the mixture system, the encountering of the silanol groups is hindered by other components resulting in limited condensation and hence the narrower peaks. However, at longer drying times,

the silanol groups have longer time to find each other leading to more extensive condensation and broader peaks are therefore obtained. In the case of 50% and 80% PVAc (Figures 3.28 and 3.29), a bimodal curve was obtained at the initial drying stages. The results show that two distinctive groups of γ -MPS oligomers with different molecular weights are formed. This may be due to the high concentrations of PVAc in the systems resulting in ununiform condensation in the initial stages. At longer drying times, the condensation reaction becomes more uniform and the two peaks merges into one broad peak.

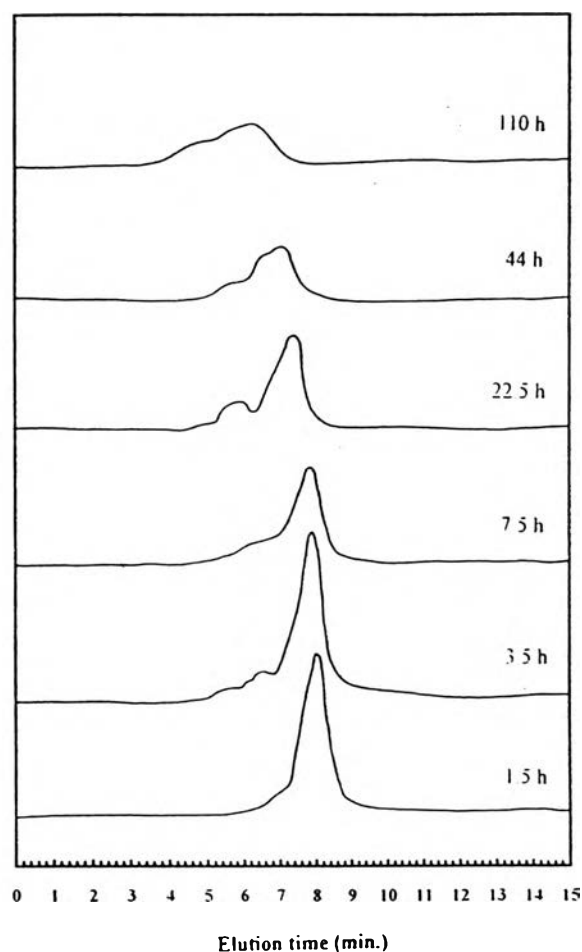


Figure 3.25 SEC chromatograms of γ -MPS oligomers in 5% by wt of PVAc with PEG in the mixture system at different drying times.

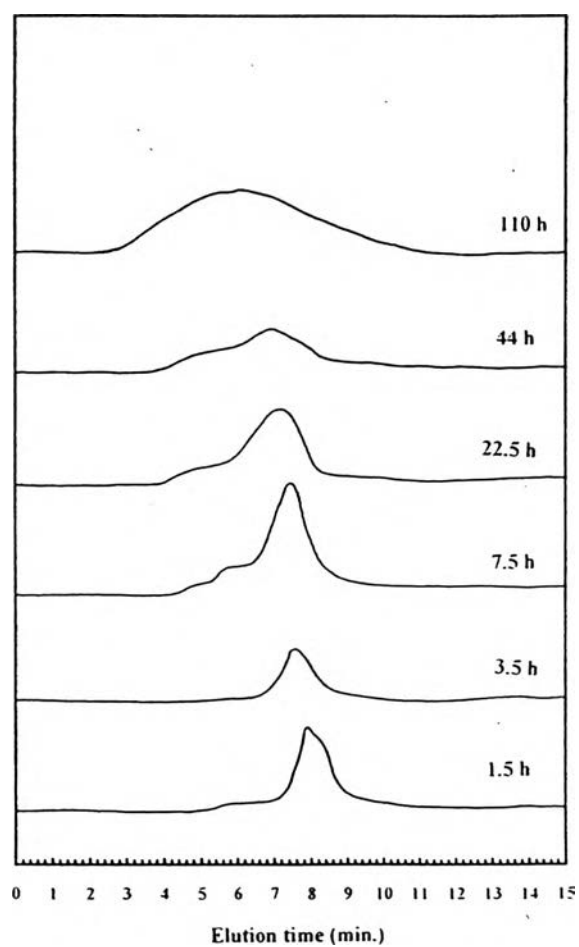


Figure 3.26 SEC chromatograms of γ -MPS oligomers in 10% by wt of PVAc with PEG in the mixture system at different drying times.

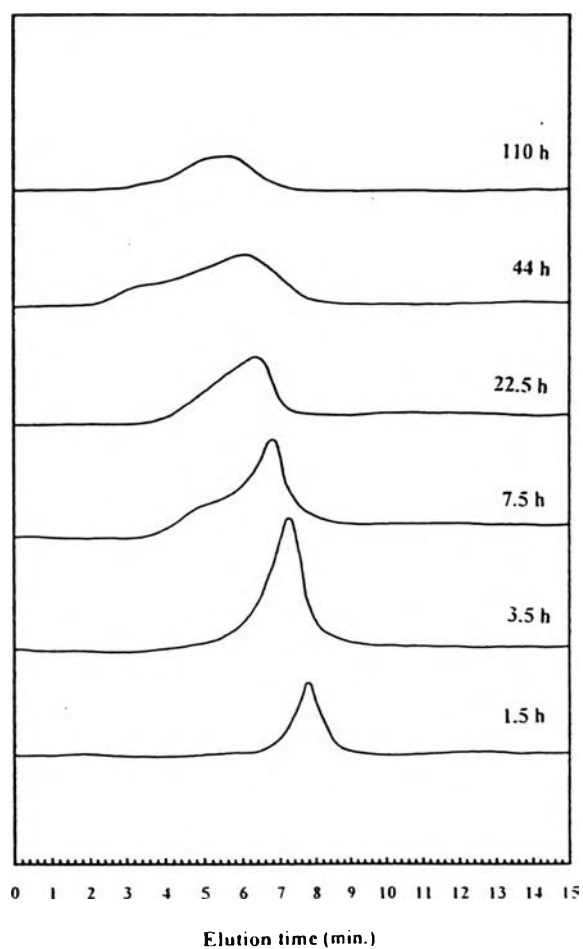


Figure 3.27 SEC chromatograms of γ -MPS oligomers in 20% by wt of PVAc with PEG in the mixture system at different drying times.

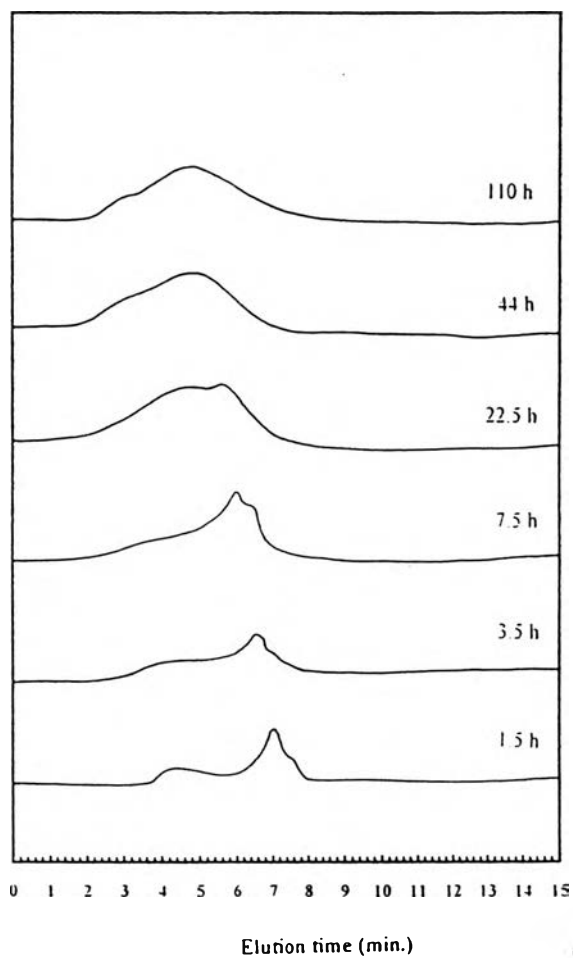


Figure 3.28 SEC chromatograms of γ -MPS oligomers in 50% by wt of PVAc with PEG in the mixture system at different drying times.

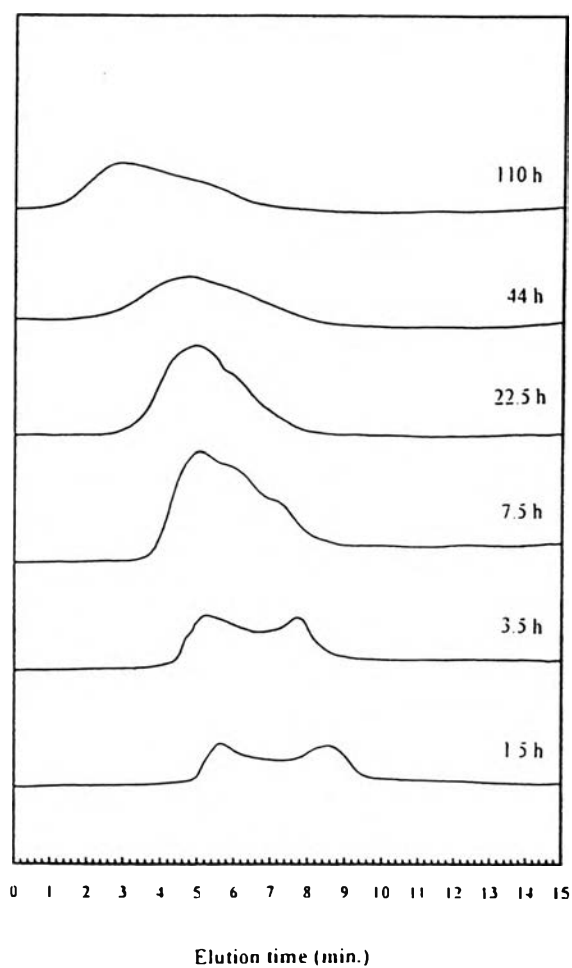


Figure 3.29 SEC chromatograms of γ -MPS oligomers in 80% by wt of PVAc with PEG in the mixture system at different drying times.

Figure 3.30 shows the relationship between the main elution time and the concentration of PVAc at different drying times. It can be seen that, at each drying time, the elution time is found to decrease as the concentration of PVAc increases which confirms that PVAc enhances the silanol condensation resulting in greater molecular weight oligomers and the greater the amount of PVAc in the system, the greater the effect.

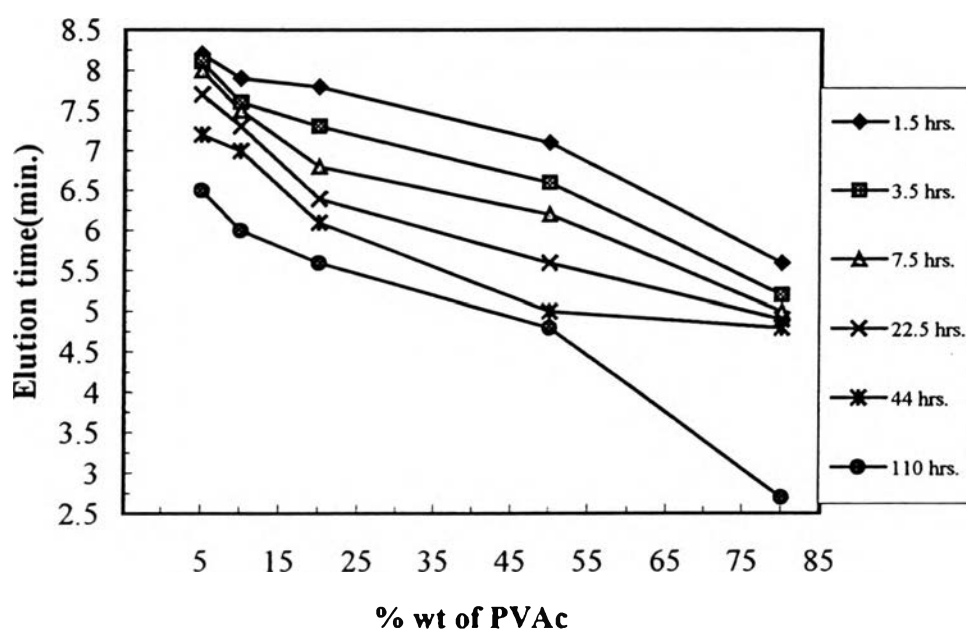


Figure 3.30 Relationship between the elution time of the mixture system containing PEG and different % wt of PVAc at different drying times.

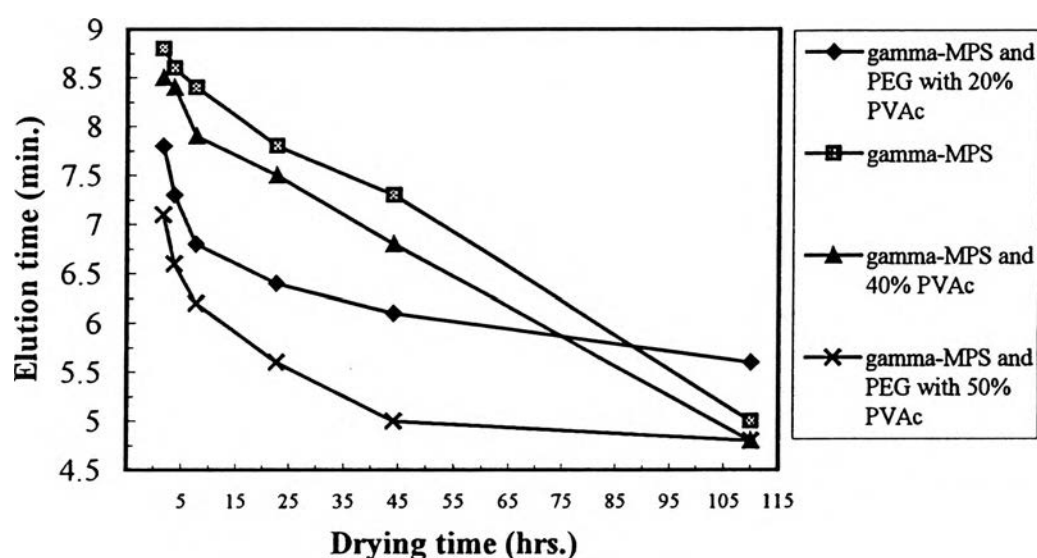


Figure 3.31 Comparison of the elution time of the model systems with and without PEG.

In Figure 3.31, the elution time of the system with γ -MPS and 40% PVAc is compared with the results of the systems with PEG and 20% and 50% of PVAc respectively. The elution time of the system with PEG is found to be shorter than the system without PEG at all drying times except for the last point at 110 hrs. The results show that PEG in the 3-component system has an enhancing effect on silanol condensation leading to higher molecular weight oligomers than in system with only PVAc. The results are rather surprising since it has been shown earlier (Section 3.2.1.1) that PVAc has an enhancing effect on silanol condensation whereas PEG has the opposite hindrance effect. Kulanuch(1996) has suggested that PEG may exert two opposite effects on the

silanol condensation, namely the 'hindrance' effect and the 'neighboring' effect. In the latter effect, a PEG molecule forms hydrogen bonding with two neighboring silanol groups as shown in Figure 3.32 and this helps to facilitate the silanol condensation between the two adjacent silanol groups. In the above 3-component system, it is thought that PEG in the system may exert the 'neighboring' effect on the silanol condensation resulting in greater molecular weight oligomers than in the case of system with only PVAc. This is possible as PEG is immiscible with the methacryl groups of γ -MPS[Suzuki and Ishida (to be submitted)], it is therefore more likely to be found in the neighborhood of the silanol ends of γ -MPS molecules. With PVAc molecules interacting with the methacryl groups of γ -MPS forming a micelle-like structure[Kulanuch (1996)] as shown in Figure 3.33, the PEG is likely to concentrate in the γ -MPS phase and the chance of it forming hydrogen bonding with two neighboring silanol groups is much greater than in system with only PEG, and hence the silanol condensation is enhanced.

From the above results, it can be concluded that both PVAc and PEG have significant effects on silanol condensation. PVAc has an enhancement effect on silanol condensation while PEG has a hindrance effect when each is present in a 2-component system. However, when the two are present in the 3-component mixture, PEG exerts the 'neighboring' effect on the silanol condensation which, when combined with the enhancement effect of the PVAc, leads to condensation products with greater molecular weights than in the case of the 2-component system at the same drying time.

Polyethylene glycol (PEG)

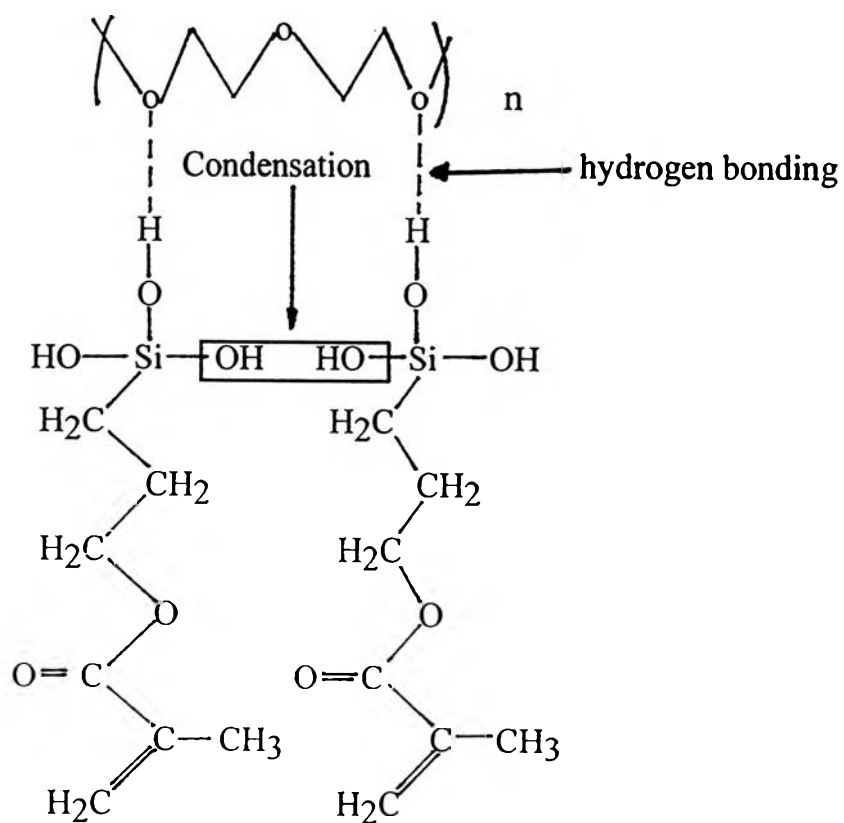


Figure 3.32 Condensation between neighboring silane molecules through the ‘neighboring’ effect of PEG.

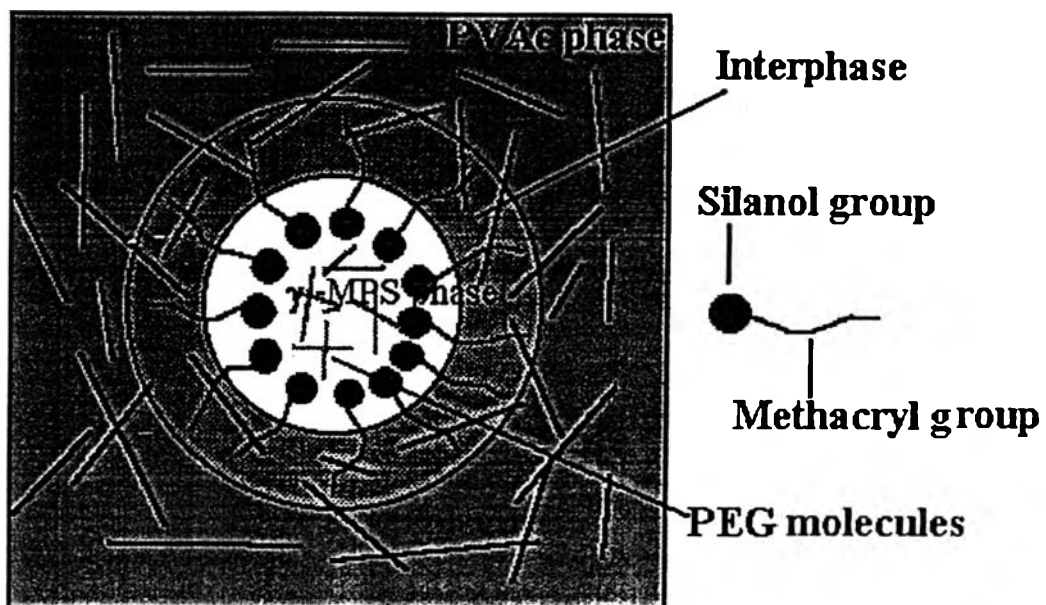


Figure 3.33 Postulated micelle-like structure morphology of the model sizing system containing γ -MPS, PVAc and PEG.

3.2.1.3 The effect of drying time on silanol condensation

Figure 3.34 shows the relationship between the elution time of the main peak and the drying time at different concentrations of PVAc. It can be seen that the elution time decreases as the drying time increases in all cases. The rate of decrease is greatest at the initial stage of drying. The results show that silanol condensation is dependent on the drying time, and the longer the drying time, the higher the molecular weight of the condensation products. There is also a wider molecular weight distribution at longer drying times.

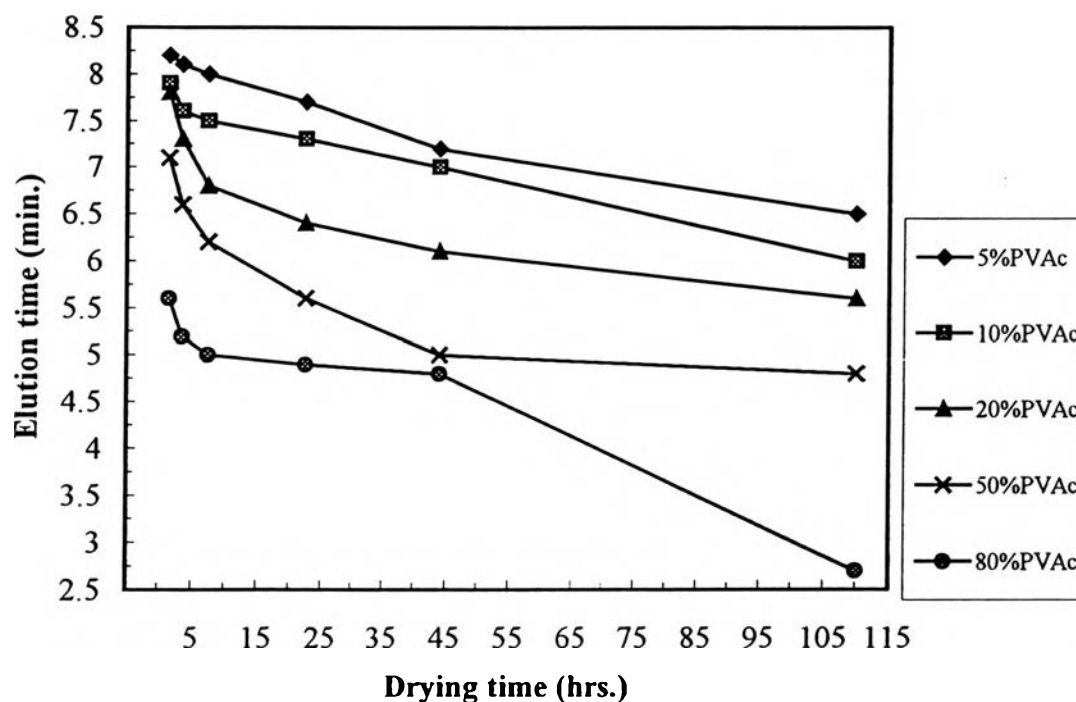


Figure 3.34 Relationship between the elution time of the mixture system and drying time at different % wt of PVAc.

3.2.2 Characterization of the silanol condensation products by FTIR

Figure 3.35 shows FTIR spectra of PEG, PVAc, γ -MPS and the model system containing PVAc at different concentrations with PEG in the mixture system. Figure 3.36 shows FTIR spectra of systems without PEG. In Figure 3.35(a), the bands of PEG at 1467 cm^{-1} and 1358 cm^{-1} are assigned to the CH_2 asymmetric deformation and CH_3 symmetric deformation respectively. The strong bands in the range $1116\text{--}1061\text{ cm}^{-1}$ are the C-O-C asymmetric stretching of PEG chains. Figure 3.35(b) shows the absorption bands of PVAc. The carbonyl stretching band at 1730 cm^{-1} is the carbonyl stretching of PVAc in bulk state. The bands at 1125 , 1044 and 1019 cm^{-1} are due to ester functionality of PVAc. The bands at 2930 cm^{-1} and 2871 cm^{-1} are assigned to the CH_2 asymmetric stretching and CH_3 symmetric stretching respectively. Figure 3.35(c) shows FTIR spectrum of γ -MPS. A broad band of H-bonded silanol group (Si-OH) appears at $3600\text{--}3100\text{ cm}^{-1}$. Carbonyl stretching shows two bands at 1718 cm^{-1} and 1698 cm^{-1} which are indicative of non-H-bonded carbonyl groups (free carbonyl groups) and H-bonded carbonyl groups of γ -MPS respectively. The siloxane bands appear in the region $1200\text{--}1000\text{ cm}^{-1}$ and Si-O stretching mode of the silanol group appears at 904 cm^{-1} . The band at 816 cm^{-1} is the Si-O- CH_3 symmetric stretching mode and the vinyl wagging vibration appears at 1635 and 937 cm^{-1} . Figure 3.35(d) shows FTIR spectrum of γ -MPS which is mixed with PEG. The FTIR spectra of mixture systems containing PEG, γ -MPS and PVAc at different concentrations are shown in Figures 3.35(E-I).

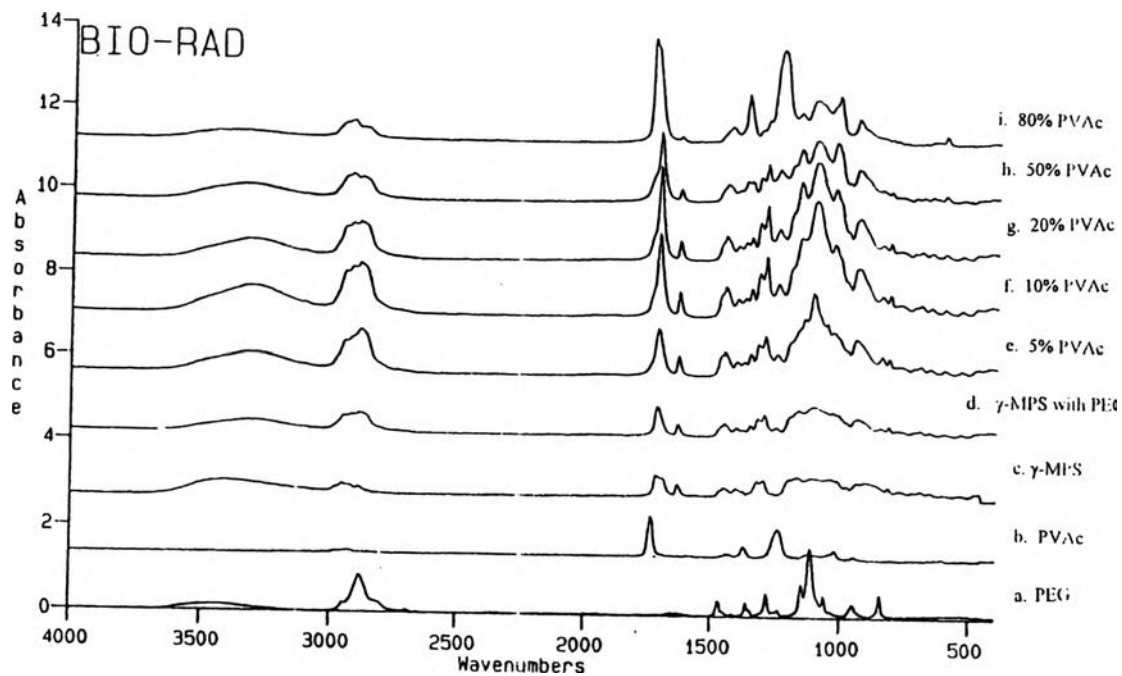


Figure 3.35 FTIR spectra of the model system containing PVAc at different % wt with PEG in the mixture system.

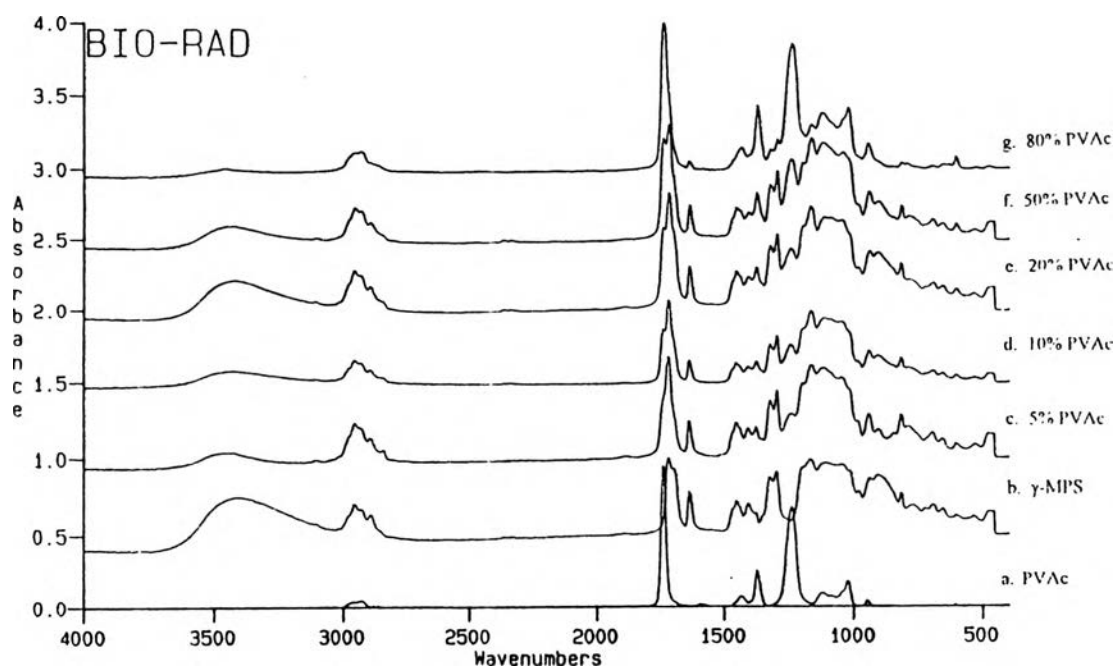
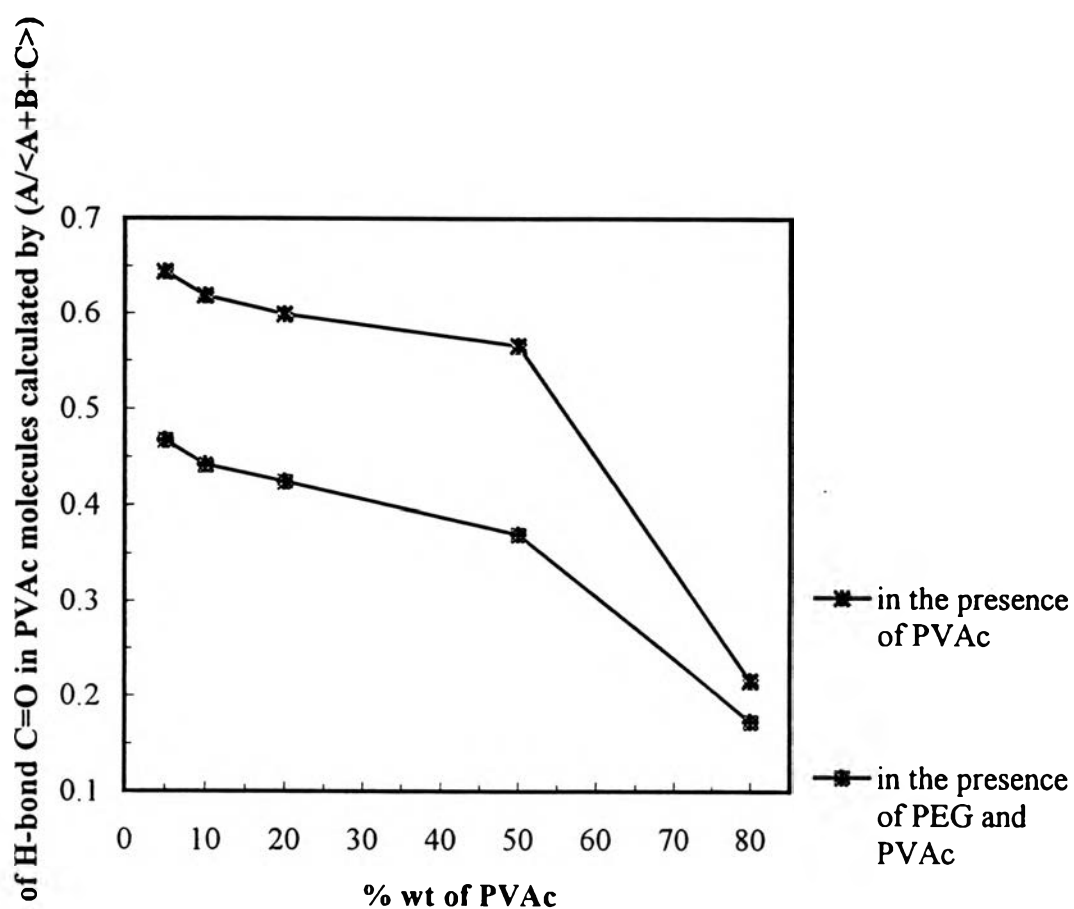


Figure 3.36 FTIR spectra of the model system containing PVAc at different % wt without PEG in the mixture system.

In FTIR, carbonyl groups in different environments have different absorption bands. Thus, by following the changes in the absorption of the different carbonyl groups, useful information can be obtained. In PVAc, three bands have been assigned to its carbonyl groups in different environments[Kulanuch(1996)]. The bands at 1745 cm^{-1} is assigned to the stretching mode of carbonyl groups which form hydrogen bonding with silanol groups of γ -MPS. The band at 1735 cm^{-1} is assigned to the carbonyl groups of PVAc in bulk state, and the band at 1715 cm^{-1} is assigned to the carbonyl groups of PVAc molecules which are miscible with the methacryl groups of γ -MPS. Figure 3.37 shows the relationship between the ratio of H-bonded carbonyl group in PVAc and the concentration of PVAc. The ratio is found to decrease with increase in PVAc concentration in both the systems with and without PEG. The results show that in the mixture system, PVAc prefers to exist in bulk state and in interaction with the methacryl groups than to form hydrogen bonding with the silanol groups. In the system with PEG, since PEG can compete with PVAc in forming hydrogen bonding with silanol groups, therefore the number of H-bonded carbonyl groups in PVAc that may form hydrogen bonding with the silanol groups is further reduced.

Figure 3.38 shows the plot of H-bonded C=O groups of γ -MPS ratio as a function of the concentration of PVAc with and without PEG in the system. The ratio is found to decrease with increase in PVAc concentration in both systems. The results may be explained as follow: in the system with only γ -MPS, some of the carbonyl groups may form hydrogen bonding with silanol groups of other γ -MPS molecules, however, when PVAc is added to the system, there is an interaction between PVAc and the methacryl groups, since the two groups are miscible, leading to the reduction of H-bonded carbonyl groups in γ -MPS. The reduction is greater as the concentration of PVAc in the

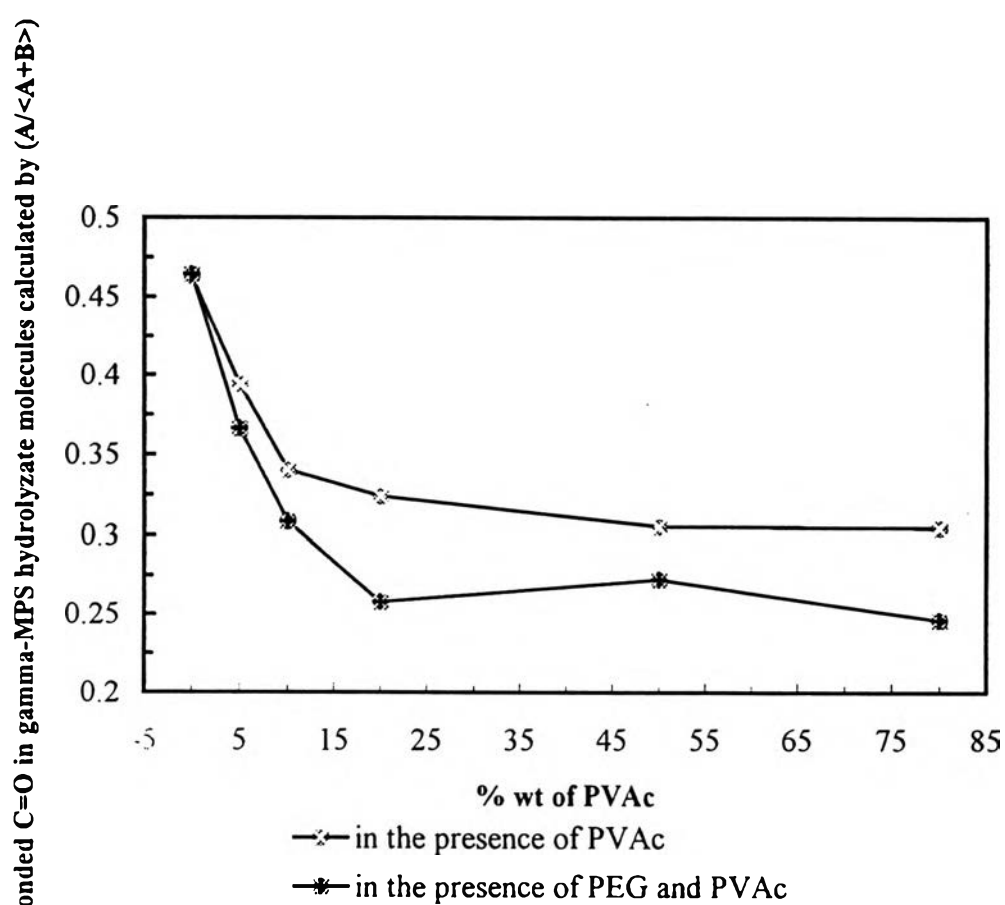
system is increased. In the case of system with PEG, the oxygen groups of PEG may form



A = Absorbance of H-bonded C=O stretching at 1715 cm⁻¹
 B = Absorbance of non-H-bonded C=O stretching at 1737 cm⁻¹
 C = Absorbance of C=O stretching which is miscible with methacryl group of γ -MPS at 1745 cm⁻¹

Figure 3.37 Ratio of H-bonded C=O in PVAc as a function of % wt PVAc in the mixture system.

hydrogen bonding with the silanol groups of γ -MPS leading to further reduction of the H-bonded carbonyl groups in γ -MPS.



A = Absorbance of H-bonded C=O stretching at 1698 cm^{-1}

B = Absorbance of non H-bonded C=O stretching at 1718 cm^{-1}

Figure 3.38 Ratio of H-bonded C=O in γ -MPS molecules as a function of % wt PVAc and PEG.

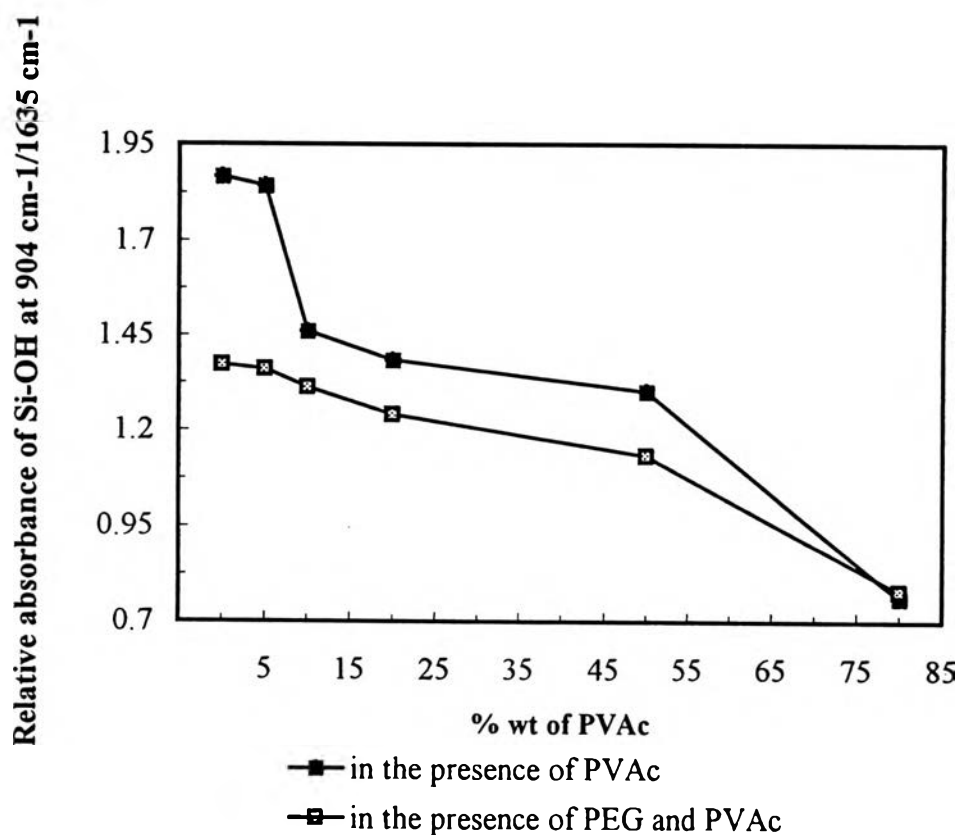


Figure 3.39 Relative absorbance of Si-OH at $904\text{ cm}^{-1}/1635\text{ cm}^{-1}$ as a function of % wt PVAc in the mixture system.

Figure 3.39 shows the plot of the ratio of the absorbance at 904 cm^{-1} and 1635 cm^{-1} of γ -MPS as a function of the concentration of PVAc. The 904 cm^{-1} band is the Si-O stretching mode of the silanol group and the 1635 cm^{-1} band is the vinyl wagging mode. The condensation of the silanol groups is expected to lead to a decrease in the ratio of the silanol groups to the vinyl groups. In Figure 3.39, the ratio of the two groups is found to decrease as

the PVAc concentration increases indicating that PVAc enhances the condensation reaction. In the system with PEG, the decrease in the ratio is greater than in the system without PEG indicating that the condensation reaction is further enhanced by the addition of PEG.

The results from FTIR as described above confirm the results from SEC (Section 3.2.1) that PVAc enhances the silanol condensation of γ -MPS and the condensation is further enhanced by the addition of PEG. It further confirms that PVAc enhances the condensation reaction through its interaction with the methacryl group of γ -MPS whereas PEG exerts the effect through hydrogen bonding with the silanol groups leading to the 'neighboring' effect which accelerates the condensation reaction.