# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Properties of DCA inclusion compound with various solvents

DCA-guests were prepared by recrystallization dioxane and ethyl acetate. The obtained DCA inclusion compounds were studied by FT-IR and TG/DTA.
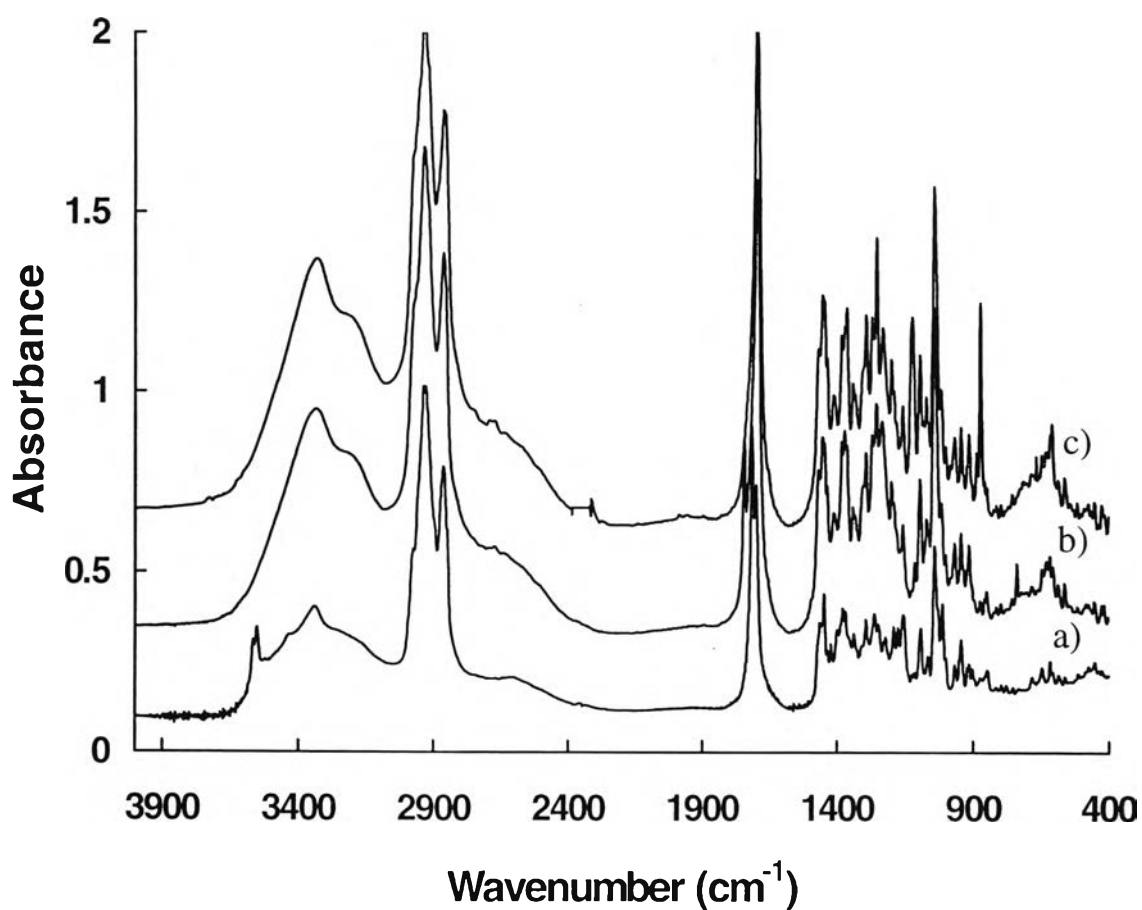


Figure 4.1. FT-IR spectrum of a) deoxycholic acid (DCA), b) DCA-ethyl acetate inclusion compound, and c) DCA-dioxane inclusion compound.

DCA shows a free hydroxyl stretching band at 3552 cm$^{-1}$, hydrogen bonding bands at 3500 cm$^{-1}$ and 3000 cm$^{-1}$, and carbonyl doublet peak at 1714 and 1699 cm$^{-1}$ (Figure 4.1). The splitting is caused by the coexistence of free and hydrogen bonded carbonyl groups. After recrystallization with the solvents, the absorption bands due to O-H and C=O changed from that of pure DCA, indicating that the guest molecules induce different hydrogen-bonding networks in the molecular assembly of DCA. It is found that ethyl acetate can be entrapped in the DCA channel as observed from the carbonyl peak of acetate at 1742 cm$^{-1}$ (Figure 4.1b). DCA-dioxane shows the peak of C-O-C stretching at 1121 and 1196 cm$^{-1}$, respectively (Figure 4.1c). In the case of *o*-xylene aromatic hydrocarbon peak can be observed at 941 cm$^{-1}$.
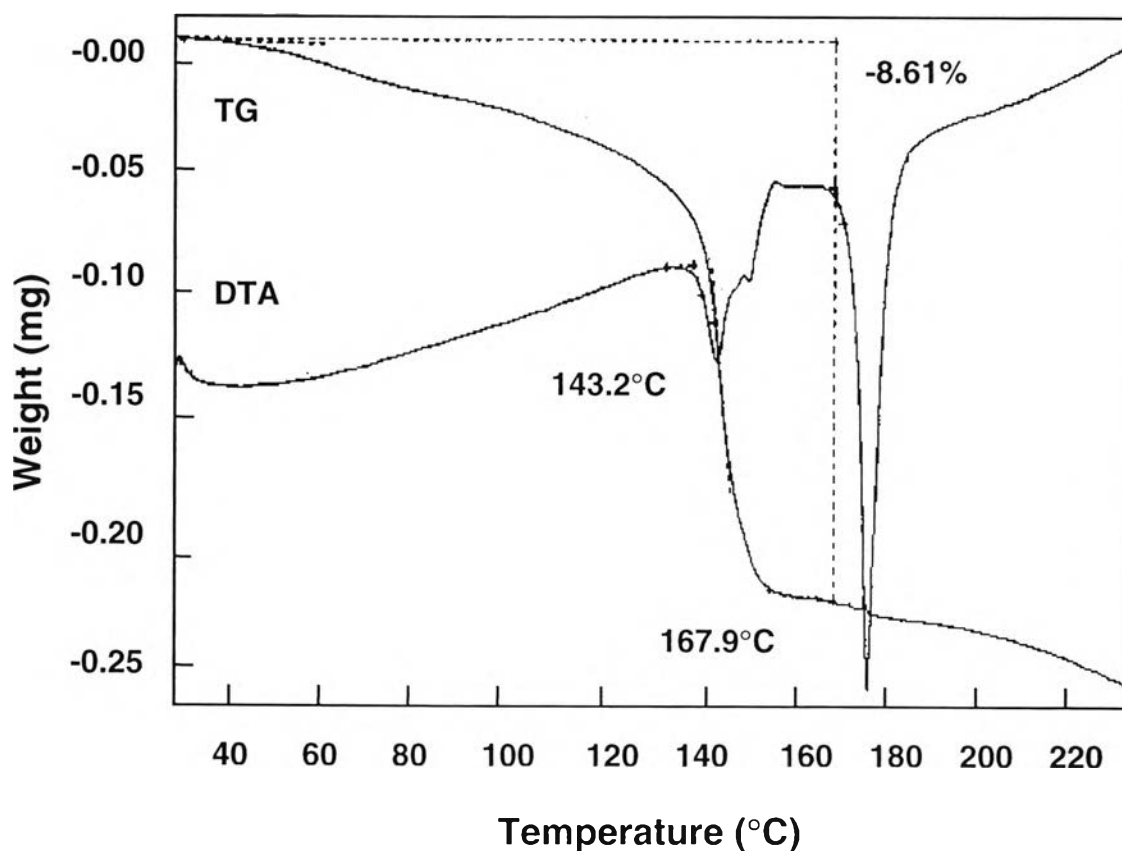


Figure 4.2. TG/DTA thermogram of DCA inclusion compound with dioxane guest.
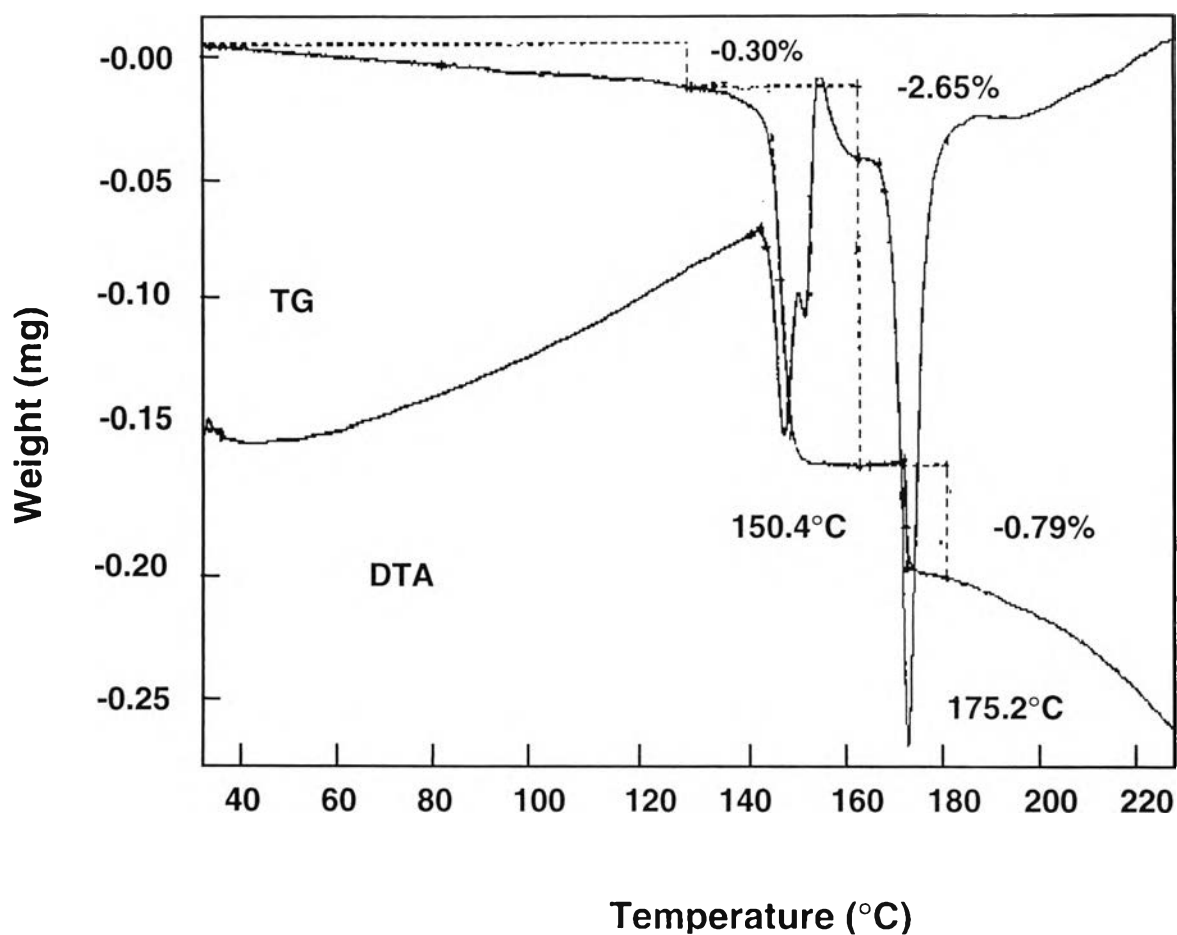
Figure 4.3. TG/DTA thermogram of DCA inclusion compound with ethyl acetate guest.

Thermal stability of guest molecules in DCA channel and molar ratio of compounds are determined by TG/DTA. Figure 4.2 and 4.3 show DTA and TG thermograms of the DCA with dioxane and ethyl acetate guests, respectively. Each DTA diagram has peaks in two separate regions. The peak at 150.4 °C temperature corresponds to the temperature at which the solvent guest is released from DCA crystals and the peak at 170°C is the melting temperature of DCA. Here, it should be noted that two temperatures at 143.2° C and 158.0 °C may be due to the evaporation of the guest molecules from the different stability inside the channel of DCA. The inner region of the DCA channel is expected to stabilize guest molecules much more than the outer

region of the DCA channel, which will be discussed later. The weight loss of the guest molecules is used to calculate the molar ratio of host and guest. The molar ratio between host and guest, and guest releasing temperature are summarized in Table 4.1.

Table 4.1. Thermal stability and molar ratio of DCA inclusion compound in various solvents as guest

| Guest | Guest releasing point (°C) | Percentage of weight loss | Molar ratio of DCA/guest after one week | Molar ratio of DCA/guest after 2 months |
|---|---|---|---|---|
| dioxane | 143.2 | 8.61 | 2.74 | 2.38 |
| ethyl acetate | 150.4 | 3.74 | 2.96 | 5.77 |
| o-xylene | 152.1 | 11.62 | 2.55 | 2.05 |
| p-xylene | 153.9 | 11.64 | 2.16 | 2.05 |

As shown in Table 4.1, it is found that the molar ratios of host-guest for o-xylene are close to two. However, the molar ratio of ethyl acetate is significantly different from other guest solvents. Nassimbeni et al. reported that ethyl acetate guest molecules in DCA channel are disordered both statically and dynamically in nature. Thus, the high molar ratio or non-integral of molar ratio between the host and guest as seen in the case of dioxane and ethyl acetate can be regarded as a result of the guest disorder in the host channel.

## 4.2 Properties of guest free DCA from various DCA- solvent adducts

The unique feature of DCA in the inclusion compound application is the stability of guest free DCA crystal. Hence, a different host-guest compound can be prepared by a guest absorption technique into the guest free DCA crystals, which is very useful for the guest that cannot be directly recrystallized with DCA. As shown in Figure 4.4, *o*-xylene guest can be completely removed from DCA-*o*-xylene to form guest free DCA crystal as confirmed by FT-IR. It is interesting to note that the guest free DCA spectrum is similar to that of the original DCA.
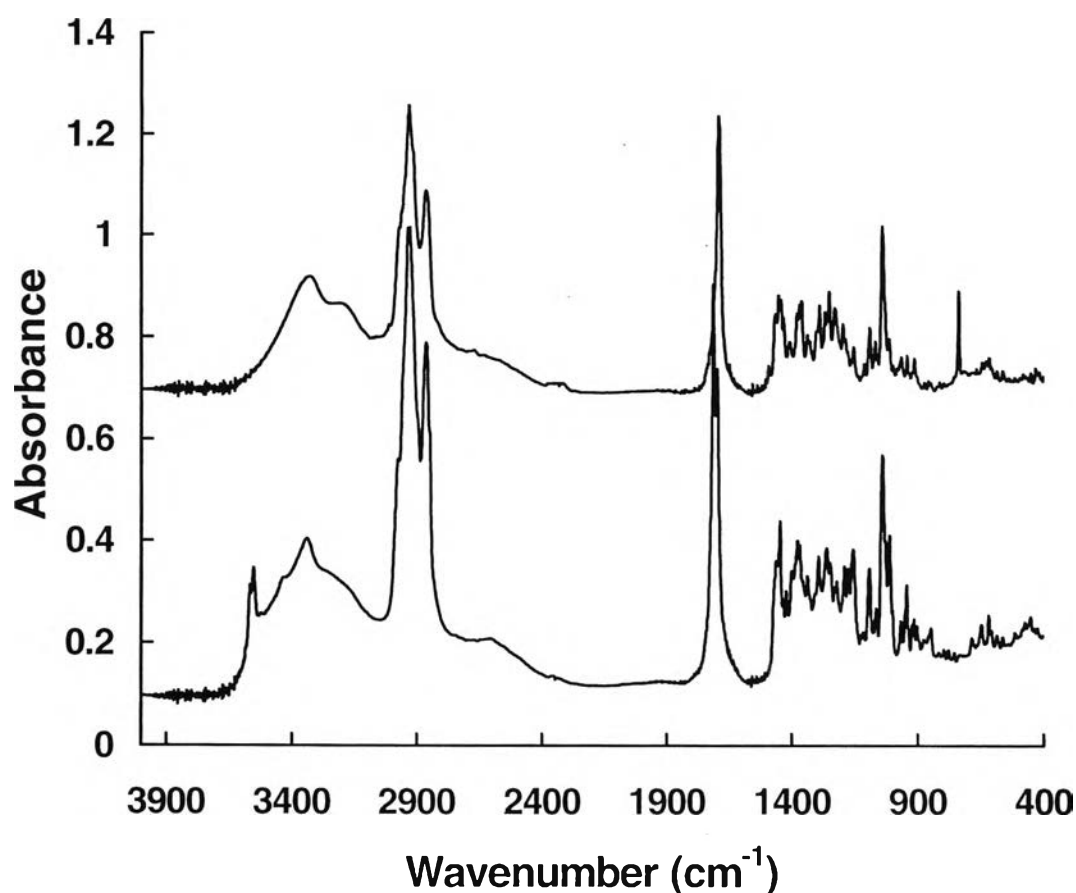


Figure 4.4. FT-IR spectra of DCA-*o*-xylene adduct (top), and the guest free DCA after exclusion from DCA-*o*-xylene (bottom).

XRD was used to study the structure of guest free DCA. As shown in Figure 4.5a, 4.5b, and 4.5c, the DCA-solvent adducts show different XRD patterns. However, after the guest was excluded for either case. The XRD give the same pattern as shown in Figure 5d, which is similar to that of the original DCA (Figure 4.5e). This implies that the guest removal in each case is successful.
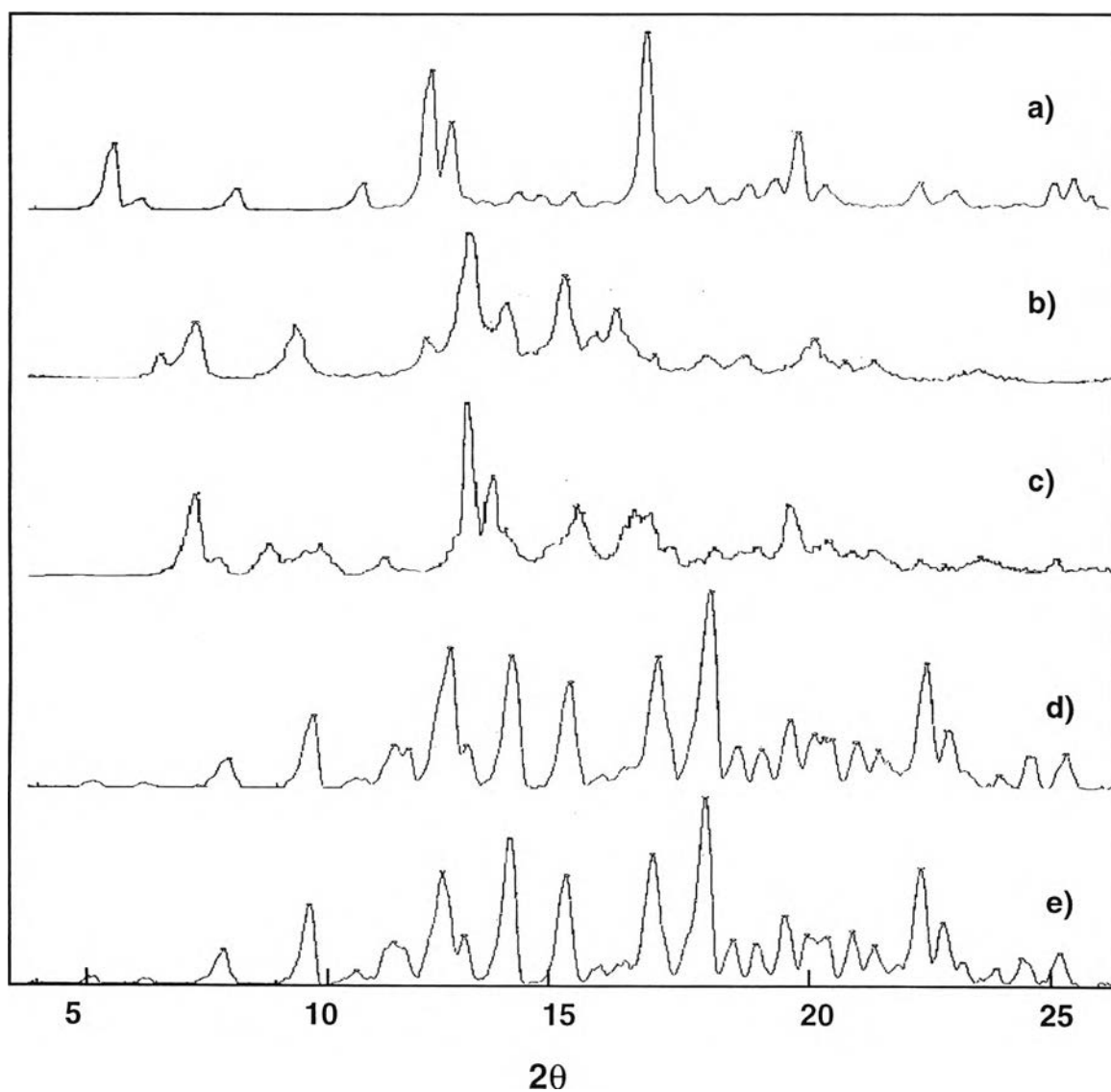


Figure 4.5. XRD patterns of a) DCA-*o*-xylene, b) DCA-dioxane, c) DCA-ethyl acetate, d) guest free (solvent free) DCA and e) DCA starting material.

DCA with guest is found to be a transparent crystal and the crystal structure is maintained even after evacuating the guest to obtain the guest free DCA. However, after guest exclusion, the crystal appears to be a white needle due to sceattering of light. XRD study indicatesthat the white needle crystal shows the same pattern as that of the original DCA (Figure 4.5d). TG/DTA also confirmed the successful of guest removal. As shown in Figure 4.6, when the guest molecules are completely excluded, TG/DTA shows only the melting of DCA.
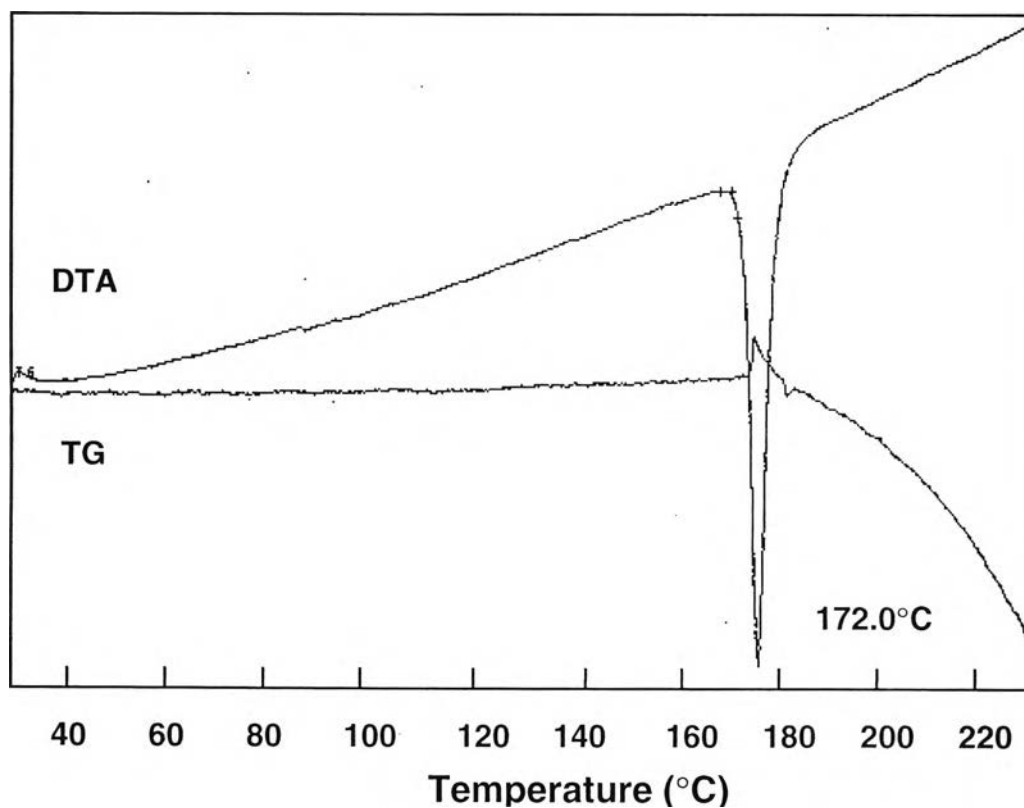


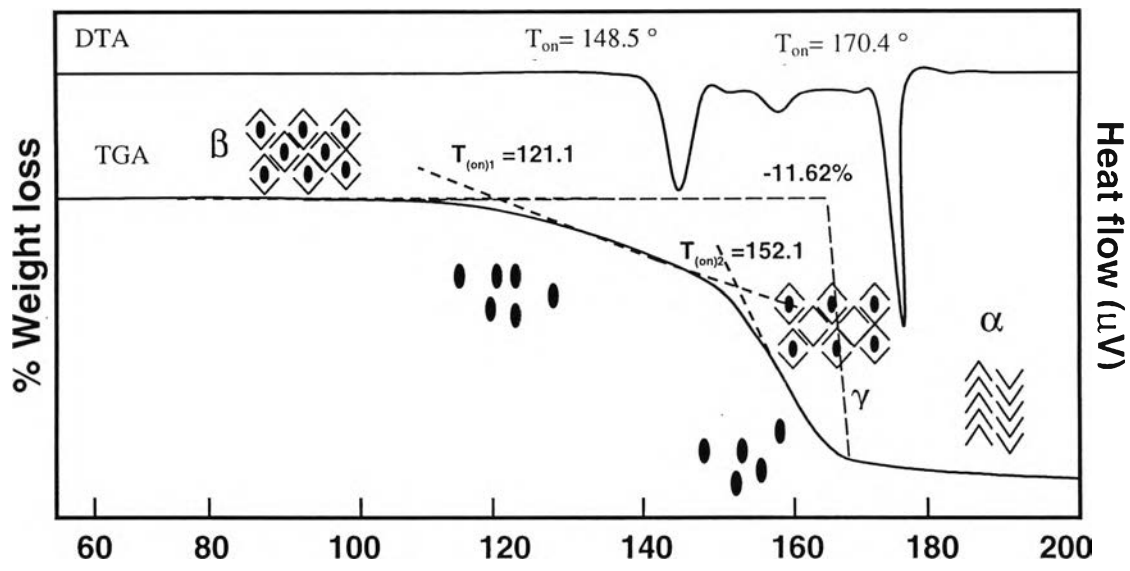Figure 4.6. TG/DTA thermogram of the guest free DCA from DCA-*o*-xylene.

Figure 4.7. Schematic monitoring phase changes in the decomposition of DCA-*o*-xylene adduct.

Caira and Nassimbeni reviewed the phase-transformations in the inclusion compound as a α, β, and γ form. The TG/DTA results of DCA-*o*-xylene adduct can be explained according to phase transformation, as summarized by schematic representation (Figure 4.7). In the early stage, the inclusion compound of DCA-*o*-xylene is in β form, which is the most preferable host guest ratio in the structure. When DCA-*o*-xylene adduct is heated and the guest is allowed to escape, the decomposition of the adduct occurs. Firstly, the adduct may be lost in some part and yield a new γ-phase with a different host-guest ratio. After further heating, the adduct reverts to its original α-phase.

FT-IR and XRD results also support the phase tranformation. Here, the guest free DCA spectrum is similar to that of the original DCA indicating that the conditions for preparing guest free DCA change from the β-phase of DCA-*o*-xylene adduct to α-phase while the γ-phase dose not occur in guest removal step.

## 4.3 Properties of DCA-VCM, and DCA-PVC, and DCA-VCM inclusion polymerization

Tsutsumi *et al.* proposed the preparation of monomer-DCA adduct by the absorption of the monomer into guest free DCA crystals. It was reported that when the monomer of 1-chlorobutadiene was left with DCA at room temperature for a day, the inclusion compound of DCA-1-chlorobutadiene could be achieved. In this case, the ratio of host and monomer can be confirmed by TGA.

In the present work, in order to prepare the vinyl chloride monomer included in the DCA host molecule, the insertion or absorption technique is then applied. However, since the insertion of vinyl chloride to DCA guest free host crystal has to be operated in the liquid state of vinyl chloride monomer under liquid $N_2$, the crystals have to be kept at low temperature. Thus, it is very difficult to study the structure and thermal properties of the DCA-VCM adduct by FT-IR and TGA.

As a preliminary study, trichloroethylene, which has the structure similar to vinyl chloride monomer but can be handled easier at room temperature, is used as the guest molecule. Firstly, DCA guest free crystal was prepared via vacuum drying DCA-ethyl acetate or any solvent crystal. The obtained crystal was then left in trichloroethylene for the insertion process. The guest absorption behavior was observed by FT-IR, TGA and XRD. FT-IR confirms the hydrogen bonding of DCA and guest peaks due to trichloroethylene as shown in Figure 4.8.

Thermal analysis shown in Figure 4.9 indicates that, in either case, 6-8% by weight the trichloroethylene guest is included in the DCA host cavity and is stable untill 170 - 190°C , which is the melting temperature of DCA.
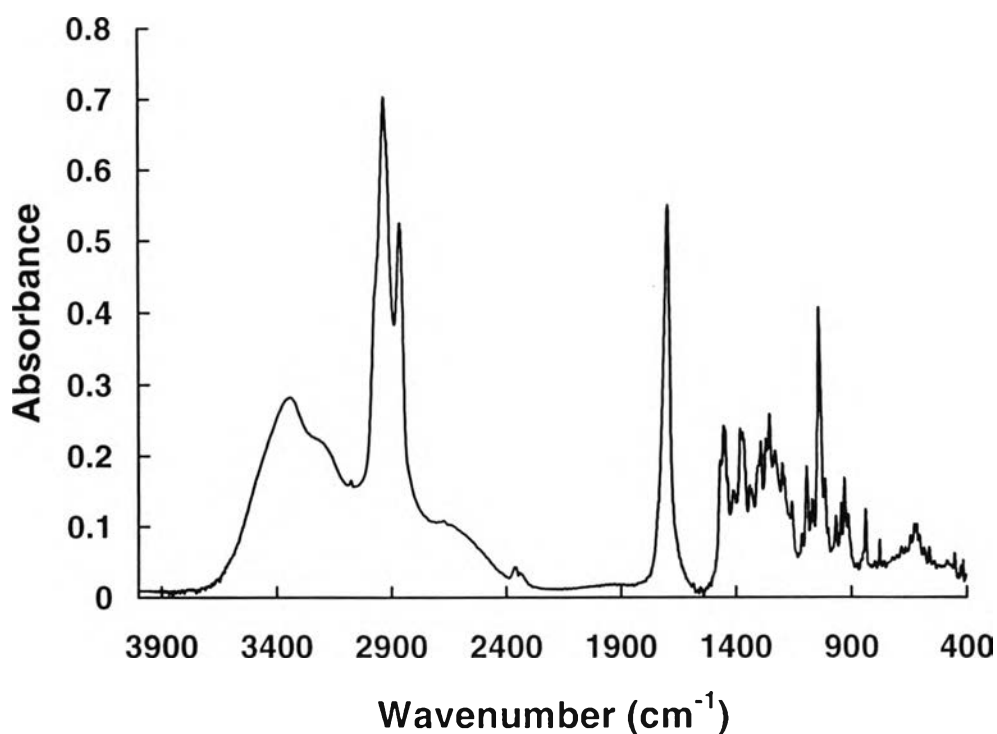
Figure 4.8. FT-IR spectrum of the DCA-trichloroethylene adduct by insertion technique.
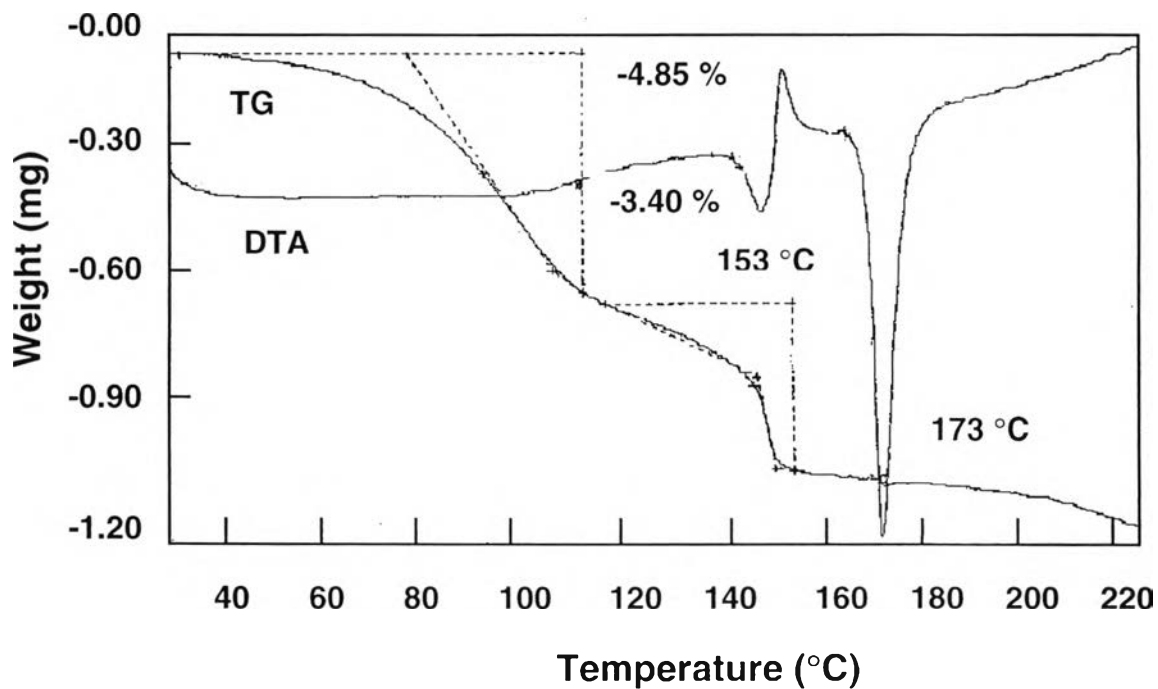


Figure 4.9. TG/DTA thermogram of DCA-trichloroethylene adduct by insertion technique.

As mentioned in the previous section, the guest free DCA should be in the α-phase and the guest free DCA crystal will change to β phase after guest absorption occurred. It is found that the guest adsorption is completed after two days. From the XRD result, DCA-trichloroethylene adduct shows that the diffractogram is nearly recovered to the pattern before the guest removal, indicating that the guest free DCA can be changed to β-phase again (Figure 4.10).

XRD pattern indicates that DCA entraps trichloroethylene with a certain crystal structure (Figure 4.10). It is found that DCA starting material shows the same XRD pattern with guest free DCA. This implies that, though opaque needle crystal is obtained after complete exclusion of the, the microstructure of the solvent free crystal is back to the original unit cell. Immersion with trichloroethylene will allow the trichloroethylene guest molecules penetrating into the layer of DCA which makes XRD pattern of DCA turn out to be a inclusion crystal structure again. From the preliminary study, it can be concluded that trichloroethylene which has the bulky group of chlorine atom can be accepted as a guest in DCA channel. Thus, it is possible to use vinyl chloride monomer as the guest in guest free DCA.
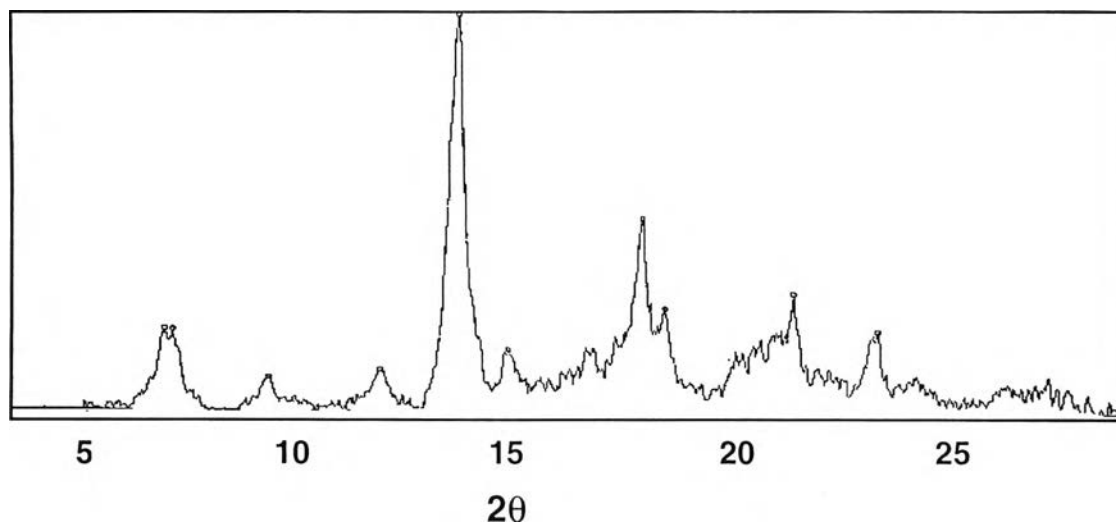
Figure 4.10. XRD of DCA-trichloroethylene adduct by insertion technique.
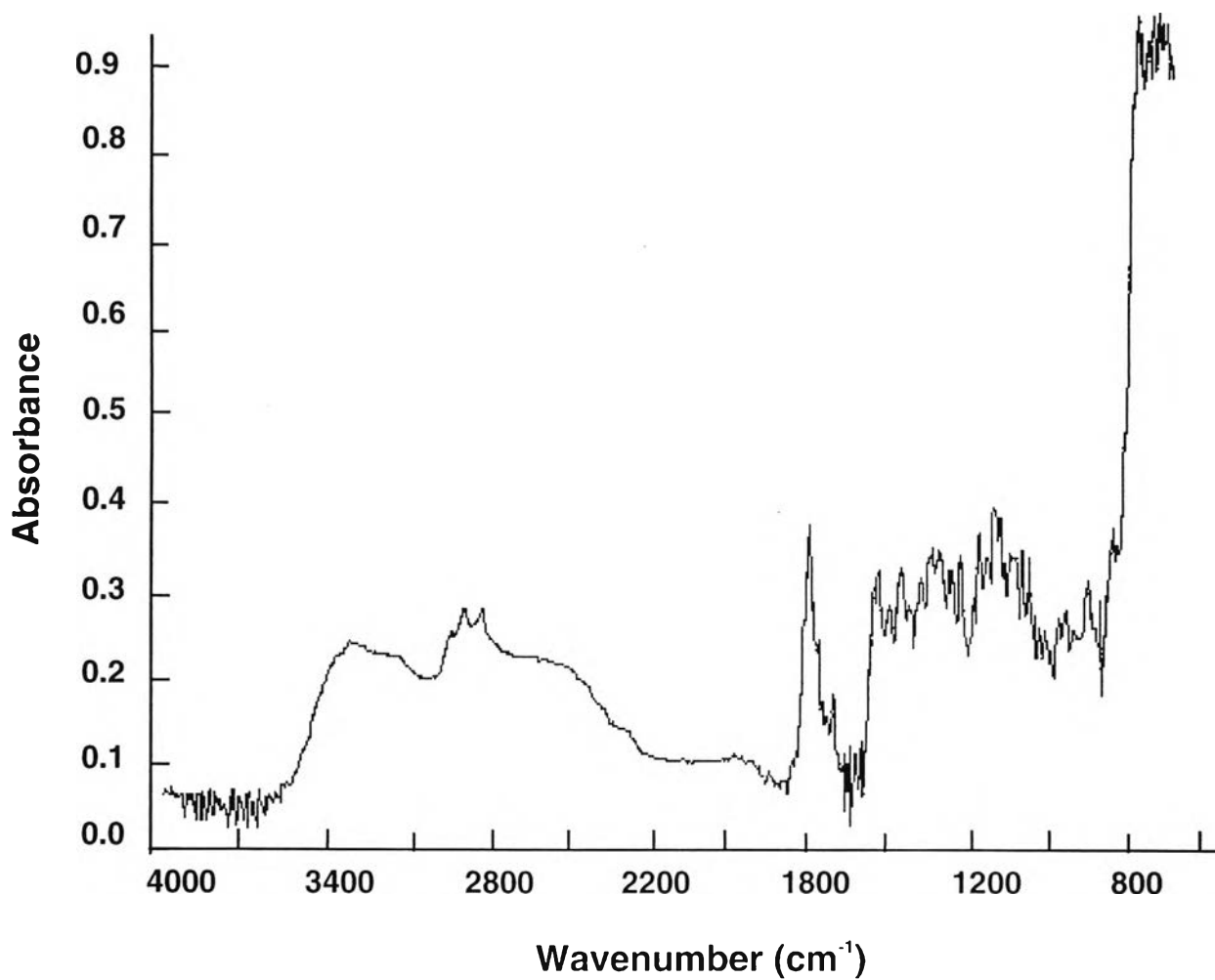


Figure 4.11. FT-IR spectrum of the DCA-VCM crystal using microscope FTIR.

After guest free DCA crystal was immersed in VCM for 2 days, the obtained crystal was analyzed by microscope FT-IR in order to avoid the damage of the crystal and instability of VCM by preparing the sample with KBr technique. As shown in Figure 4.11, the IR spectrum of the DCA-VCM adduct is similar to that of other DCA-solvent adduct which does not show free hydroxyl peak at 3552 cm$^{-1}$ but only a single carbonyl band. This indicates that the VCM intercalation is successful. In order to confirm the stability of the DCA-VCM adduct, DSC study of the DCA-VCM adduct was carried out from 20 to 200 °C to define the VCM releasing temperature of the DCA-VCM adduct (Figure 4.12). DSC thermogram shows the board guest releasing temperature around 40-60°C. The average of guest releasing temperature from eight tests is 51.9 °C.
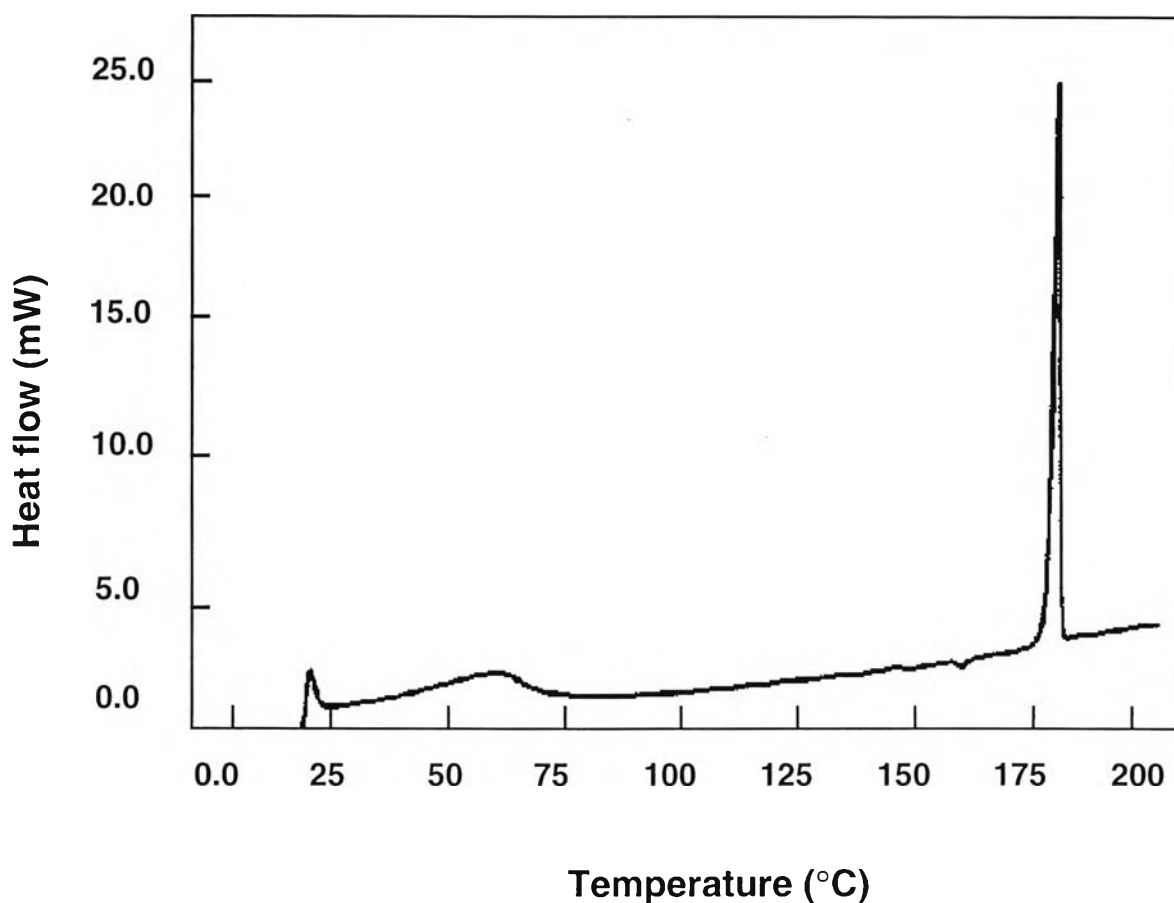


Figure 4.12. DSC of DCA-VCM adduct by insertion technique.

In order to confirm the inclusion polymerization of the DCA-VCM host-guest compound, the DCA-VCM crystals after irradiation by 2 Mrad dose of γ-ray were analyzed. Figure 4.13 shows that the inclusion compound of DCA-VCM is changed to DCA-PVC as can be observed by the C-Cl band of PVC around 700 cm⁻¹. TG/DTA analysis of the DCA-PVC adduct (Figure 4.14) show the endothermic peaks at 130 °C and 145 °C. The small peak 130 °C may be due to the release of the residual monomer. It should be noted that there is a significant peak at 145 °C with a weight loss for 0.6%. This peak reveals the release of guest, i.e., PVC from DCA crystal. The small weight loss supports that PVC is released without degradation. In the other words, DCA-VCM intercalation is successful. The peak near 177 °C is the melting point of the DCA crystals.



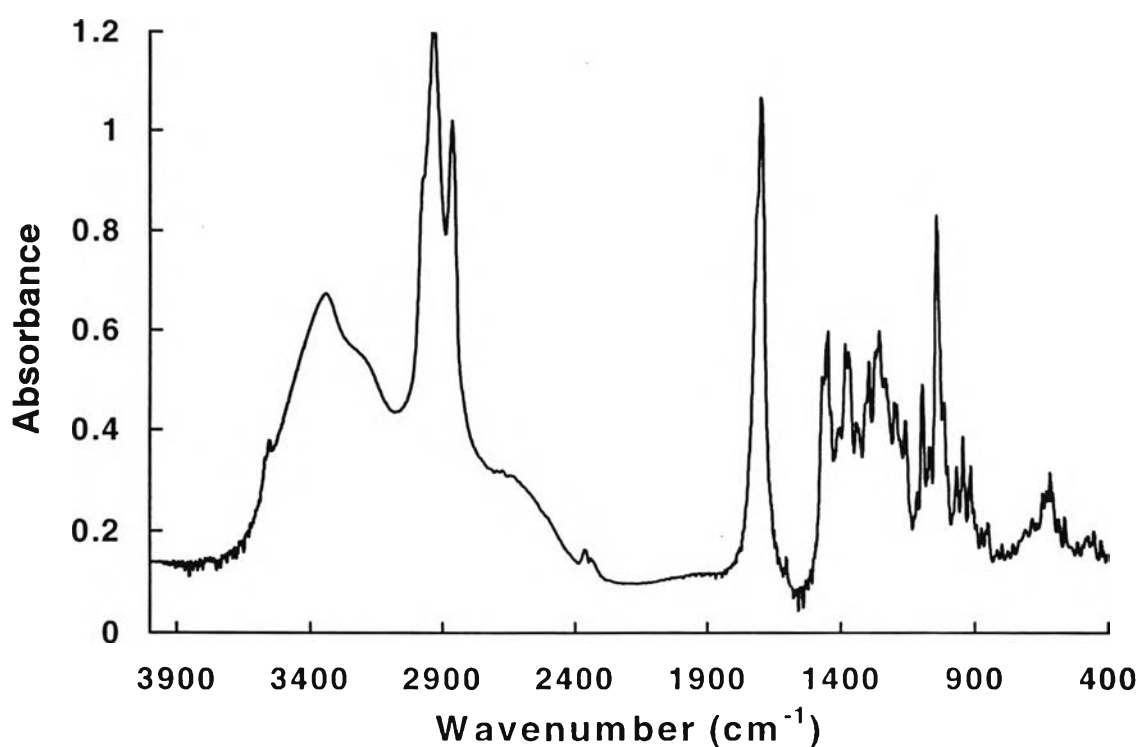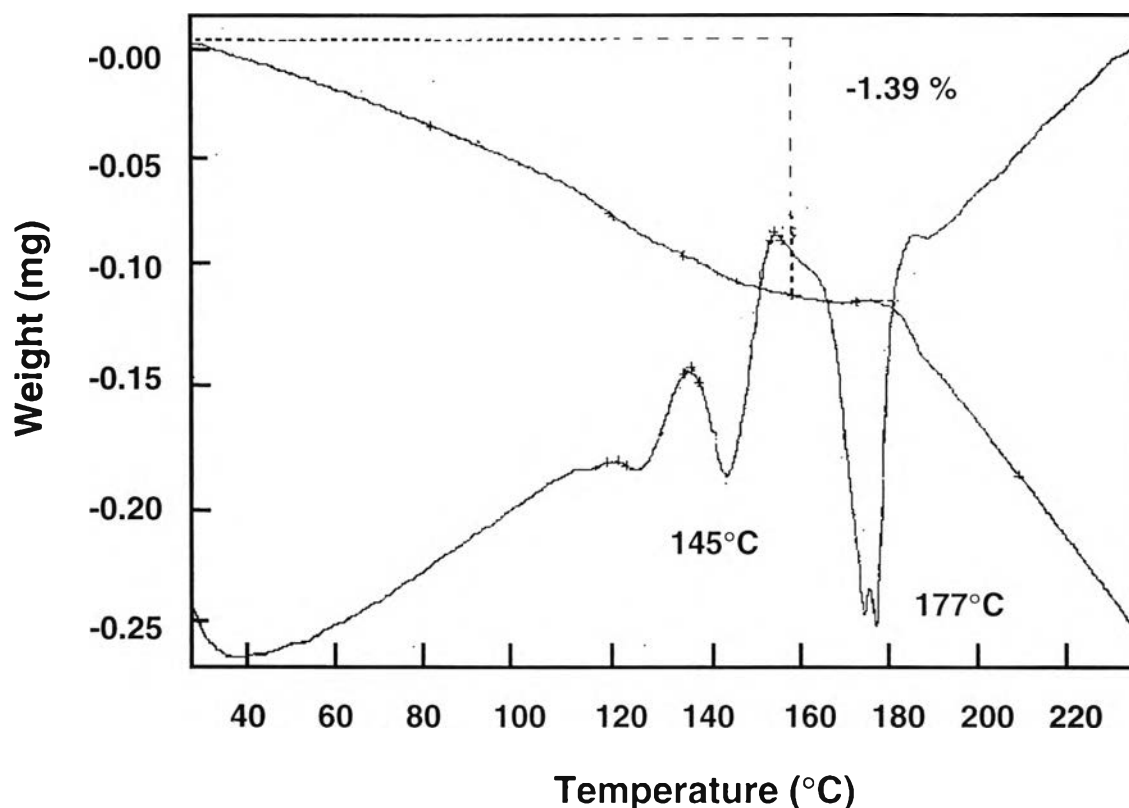Figure 4.13. FT-IR of DCA-PVC adduct prepared from guest free DCA-dioxane.

Figure 4.14. TG/DTA thermogram of DCA-PVC adduct.

DTA of DCA-trichloethylene shows the similar pattern to that of DCA-PVC having the significant peak at 153 °C as shown in Figure 4.9. At this temperature the weight loss is found to be 3.40% referring to the evaporation of trichloethylene. However, in the case of DCA-PVC, PVC cannot be degraded at the releasing temperature (Figure 4.14). As a result, the weight loss is only 0.6%. This implies that PVC and trichloroethylene may be included in DCA with the same level of thermal stability. The major peaks of the XRD patterns of both cases also confirm that the DCA-PVC and DCA-trichloroethylene have the same host-guest structure as shown in Figure 4.15.
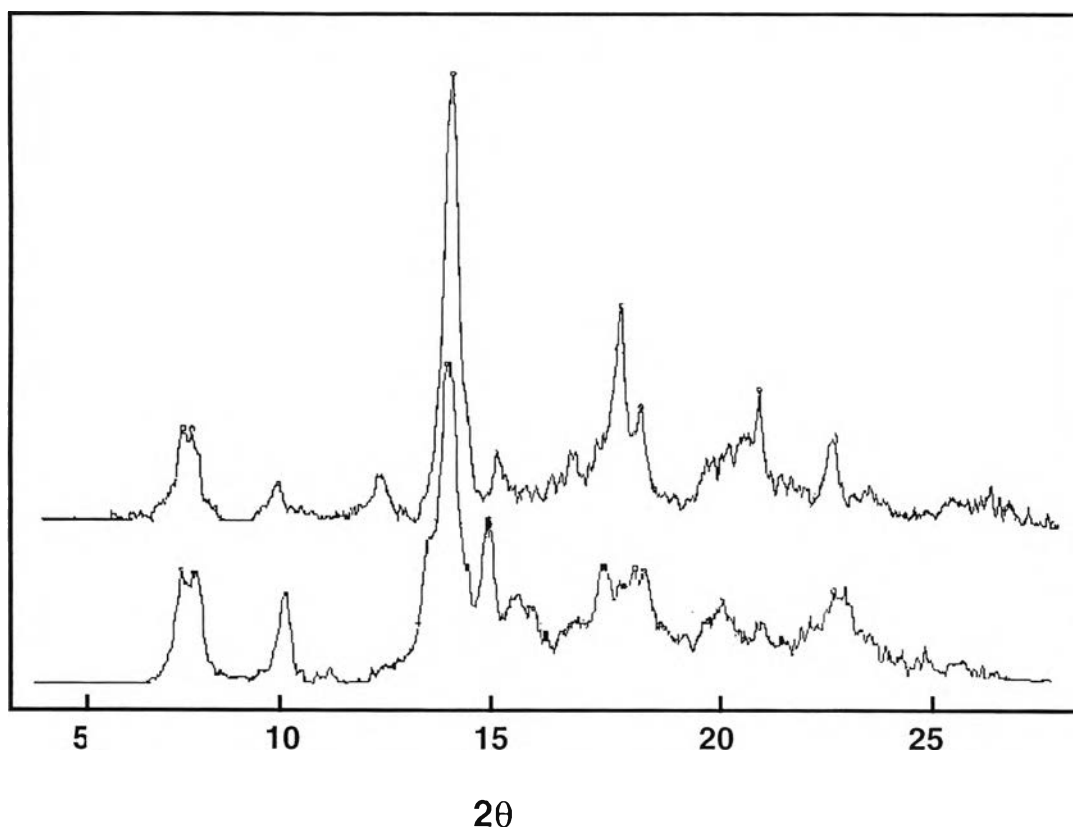
Figure 4.15. XRD patterns of intercalated guest free DCA from dioxane with trichloroethylene (top) and DCA-PVC adduct (bottom).

In order to study the propagating radical, ESR technique was used to investigate the radical during postpolymerization. The guest free DCA and liquefied VCM were added in ESR tube and sealed under vacuum. The irradiation dose to initiate reactive species is 2 Mrad. ESR spectrum of DCA-VCM system was measured under liquid nitrogen after irradiation as shown in Figure 4.16. The ESR results show two peaks, the first peak at 2.0097G is assigned to the background signal from the radical belongs to the sample tube, while board peak at 2.0221G is assigned to the propagating radical of VCM.
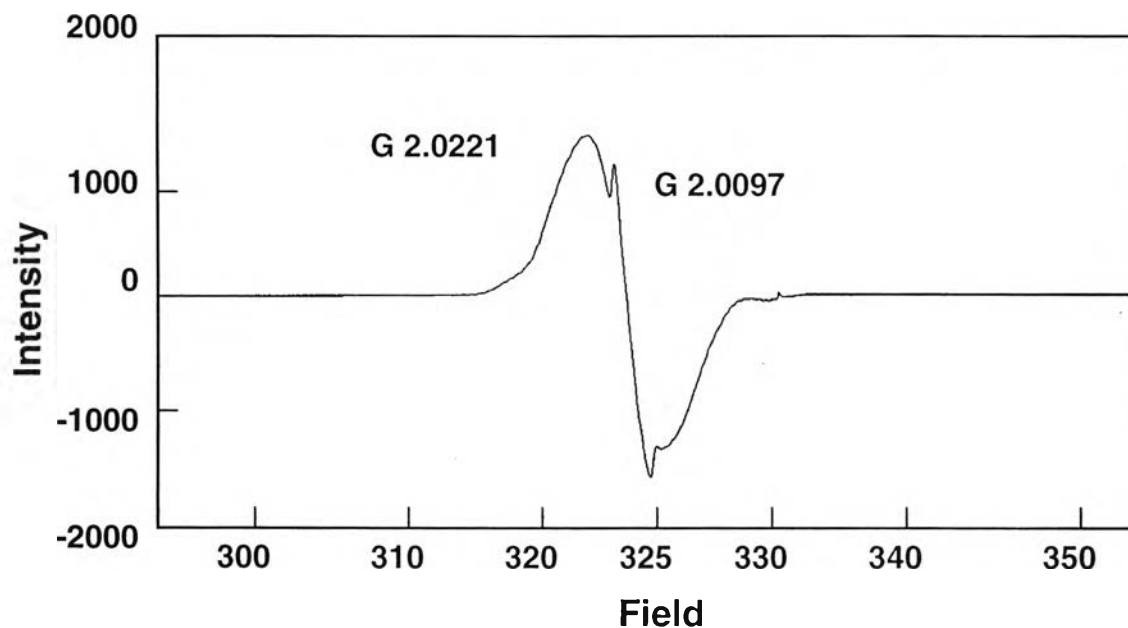
Figure 4.16. ESR spectrum of DCA-VCM adduct, γ-ray irradiated at -78 °C and measured at -197 °C.

Generally, Very board signal can be assigned to the polyenyl radical ($-CH_2-CH^*-(CH=CH)_n-CH_2-$). The radical may be produced by dehydrochlorination of poly(vinyl chloride). The ESR spectrum was observed 4 months after irradiation. The stability of the propagating radicals can be explained by the restricted mobility of PVC molecule within the DCA channel. Also, the coupling of the propagating radical with that in another channel is prevented by the channel walls. The result also indicates that the polymerization of vinyl chloride monomer in the DCA channel proceeds via free radical polymerization. Tsutsumi *et al.* reported that the polymerization in DCA channel is a living radical polymerization. Comparing to DCA-VCM case, after post polymerization for 4 months, the radical can be detected by ESR, which suggest that the polymerization of the DCA-VCM adduct is indeed living radical polymerization.

## 4.4 Study on microstructure of resulting polymers

Figure 4.17 shows the IR spectra of the obtained products from inclusion polymerization, which DCA-VCM were prepared from two types of

guest free DCA, i.e. guest free DCA from DCA-dioxane and guest free DCA from DCA-ethyl acetate. Comparing the FT-IR spectrum of the PVC obtained by the inclusion polymerization to the commercial PVC, the resulting polymer can be concluded as PVC. It should be noted that there are some differences on these spectra, especially in the band around 1250 cm$^{-1}$, which is assigned to the vibration mode of methine (CH). The PVC from the inclusion polymerization shows two bands at 1257cm$^{-1}$ and 1228 cm$^{-1}$ while the commercial PVC shows the methine (CH) broad band at 1250 cm$^{-1}$. This indicates that the resulting polymer may have higher degree of crystalinity due to the regularity. There is no difference between FT-IR spectra of the PVC from different guest free DCA. These results indicate that the provided channels form ethyl acetate and dioxane may have similar shape and size.
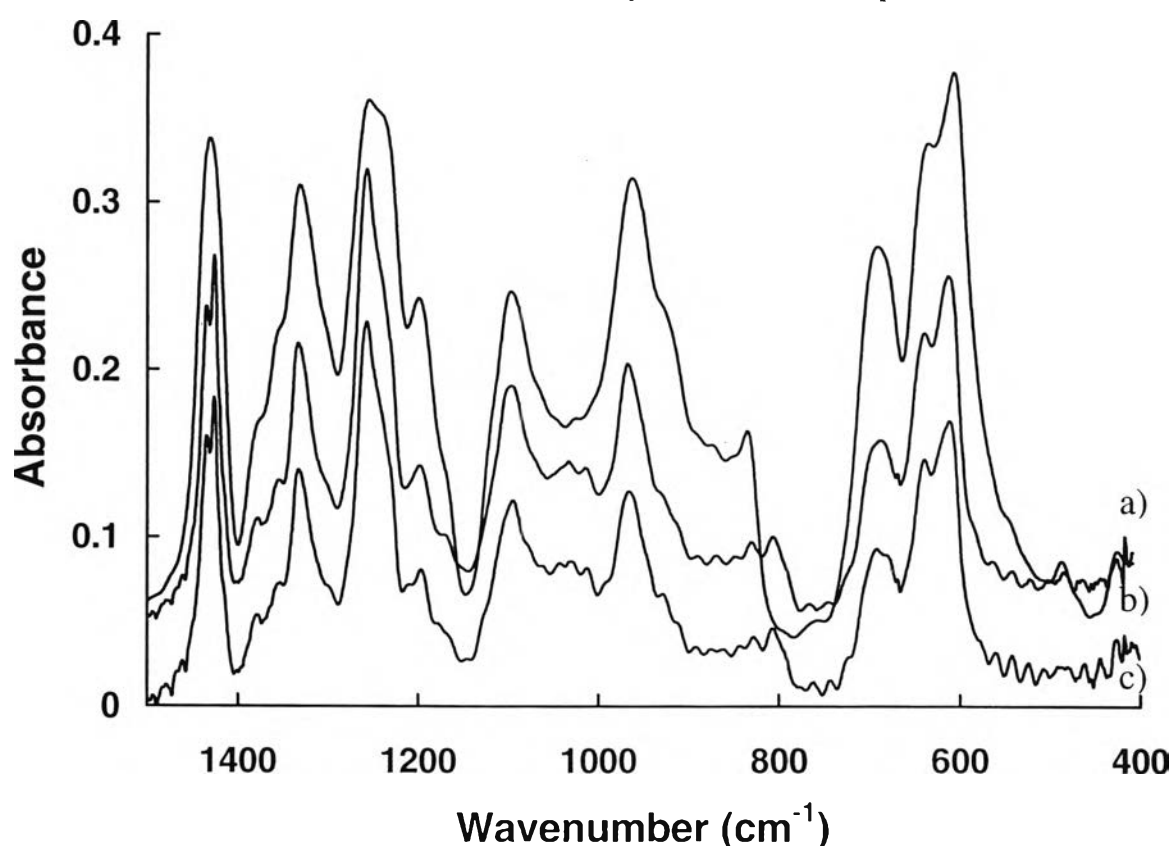


Figure 4.17. FT-IR of a) the commercial poly(vinyl chloride), b) the inclusion polymerization product obtained from guest free DCA prepared form DCA-ethyl acetate, and c) obtained from guest free DCA prepared by DCA-dioxane.
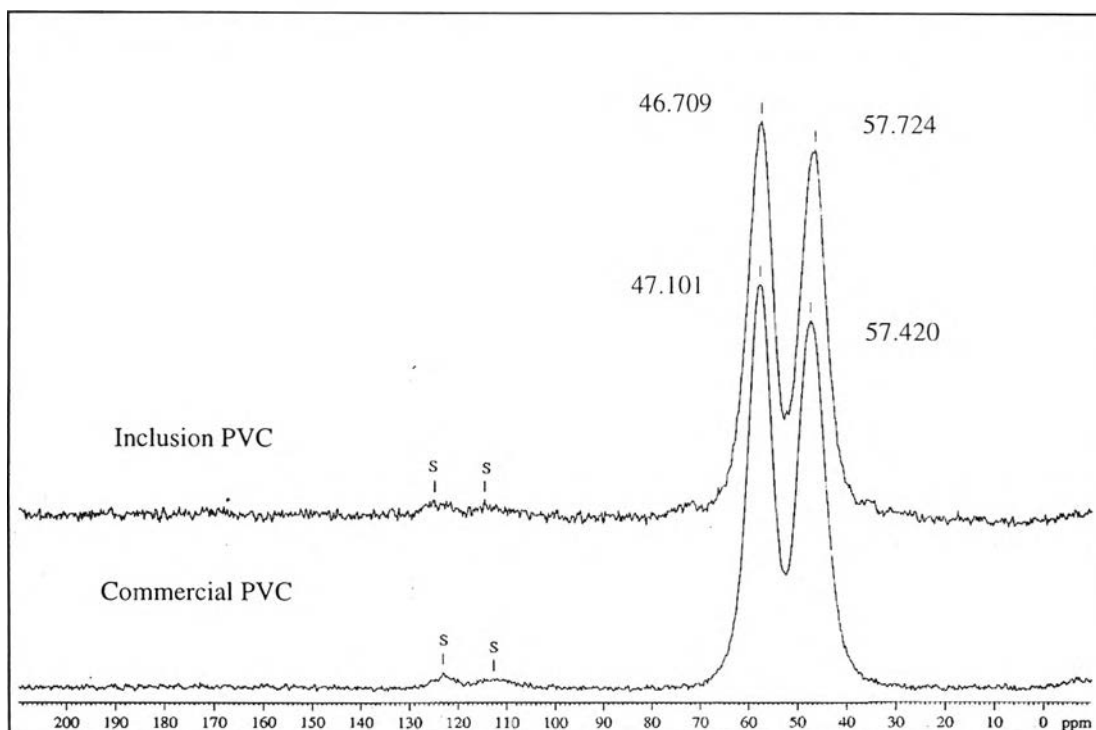
Figure 4.18. Solid state $^{13}$C NMR spectra of poly(vinyl chloride) prepared by inclusion PVC using DCA as a host and the commercial PVC.

The resulting polymer from inclusion polymerization using DCA as a host was measured by solid state $^{13}$C NMR and compared to the commercial PVC as shown in Figure 4.18. Only two resonances were observed. One is around 47 ppm, which is assigned to $CH_2$, and another peak is around 57 ppm, which is assigned to CHCl. This result also strong supports that the obtained polymer is PVC. Unfortunately, due to the broadness of the resonance the stereoregularity of the polymer could not be determined.

Thermal stability study by DSC (Figure 4.19) shows that the glass transition temperature (Tg) of the obtained PVC is slightly higher than that of the commercial PVC. However, in the case of the obtained PVC, the range of Tg peak is broader than the commercial PVC, which may due to the broad distribution of the regularity in the product.
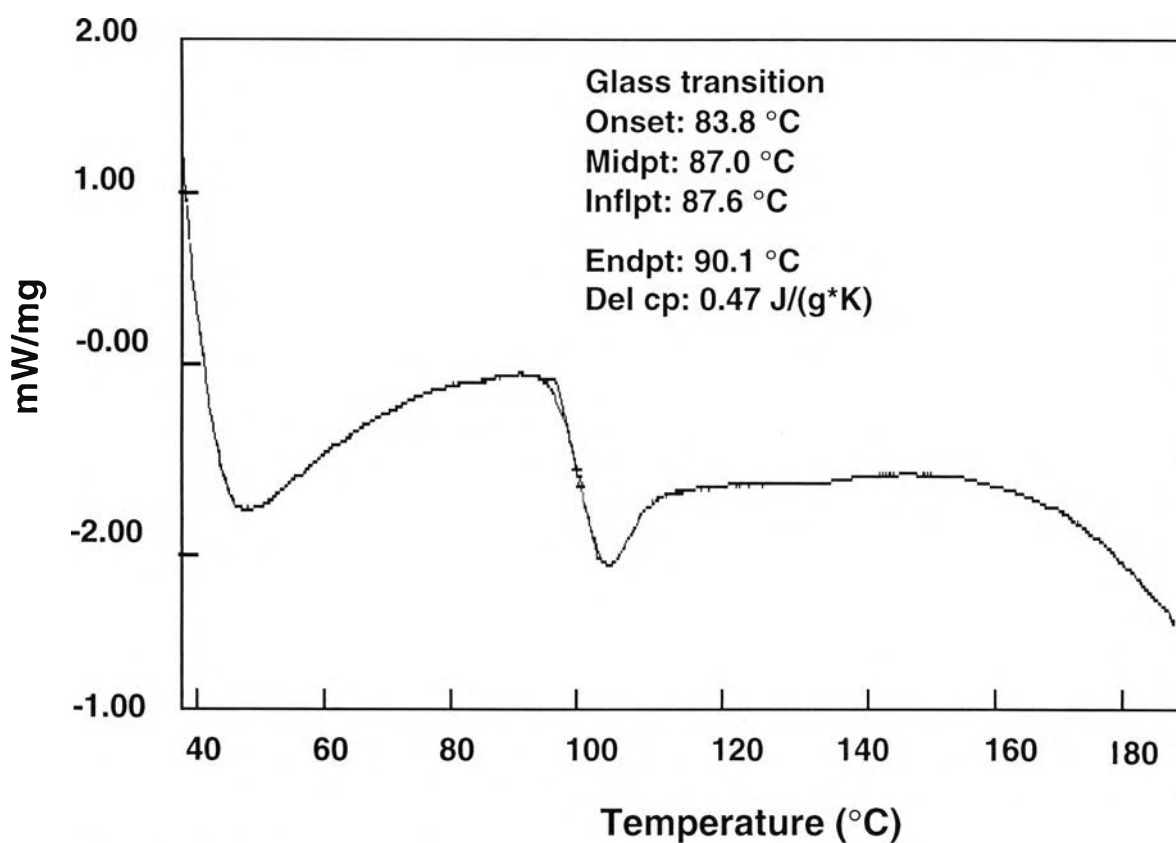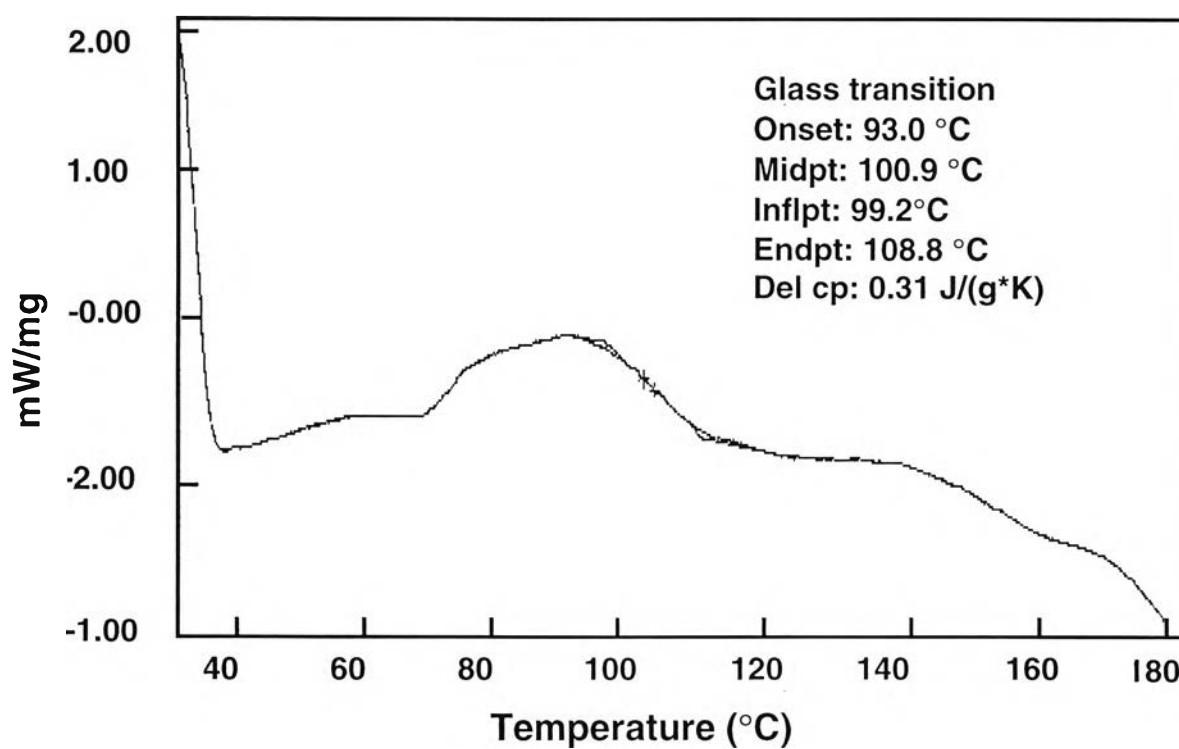
Figure 4.19*a*.  DSC of the commercial PVC.



Figure 4.19*b*.  DSC of the obtained PVC.

Solubility is another approach to evaluate the differences in the structure between the obtained PVC and the commercial one. Various solvents are used for the PVC solubility study, i.e. tetrahydrofuran, cyclohexanone, dimethylsulfoxide (DMSO), and benzene-acetone mixture. The solubility testing results are summarized in Table 2.

The solubility test indicates that the obtained PVC is more difficult to dissolve in good solvents for commercial PVC, except for cyclohexanone and DMSO at elevated temperature. Obviously, the obtained PVC took longer time to dissolve comparing to the commercial PVC. Yoshii *et al.* reported that syndiotactic PVC prepared by inclusion polymerization using urea as a host molecule is insoluble in all of solvents in Table 2. This suggests that the obtained PVC might have some level of stereoregularity different from either the commercial PVC or the inclusion polymerization using urea as the host.

Table 4.2. Solubility of the obtained PVC and the commercial PVC in various solvents

| Solvent | Solubility at room temperature | | Solubility at boiling point temperature | |
|---|---|---|---|---|
| | Commercial PVC | Inclusion PVC | Commercial PVC | Inclusion PVC |
| Tetrahydrofuran | √ | × | √ | × |
| Cyclohexanone | × | × | √ | √ |
| DMSO | × | × | √ | √ |
| Benzene-acetone mixture | × | × | √ | × |

√ = Soluble and × = insoluble

Here, ESR measurement was conducted on the PVC. Both the commercial PVC and obtained PVC from inclusion polymerization were

directly irradiated with γ-ray at 1 Mrad in ESR vacuum tubes in liquid nitrogen to initiate free radicals on the polymer chain. The measurement temperatures are 187 K and 273 K. The ESR spectra of the obtained PVC and the commercial PVC at 187 K and 273 K are shown in Figure 4.20.

There are some differences in the ESR spectra between commercial PVC and the inclusion polymerized PVC. If free radicals created on the polymer chain by irradiation have different environment owing to the structure of polymer itself, the obtained spectra will be different. As shown in Figure 4.21, the spectra obtained at 183 K are similar to each other. However, when the temperature is increased to 273 K, a shoulder peak on 2350 G appears. This can be explained as follows: at 183 K, the free radical movement is rather restricted, which makes frequency of the free radicals be the same reflecting its immediate neighboring environment. However, at 273 K, the movement of the radicals is relatively free and the shoulder peak appeared. This implies that the microstructure of the obtained PVC shows some differences in regularity.
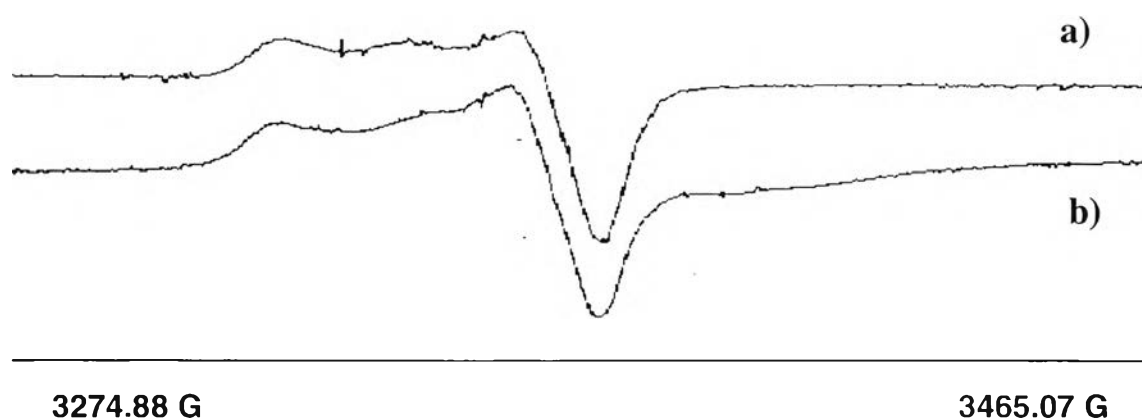


**3274.88 G**                                              **3465.07 G**

Figure 4.20a. ESR spectra at 183 K of irradiated PVC, a) the obtained PVC, and b) the commercial PVC.

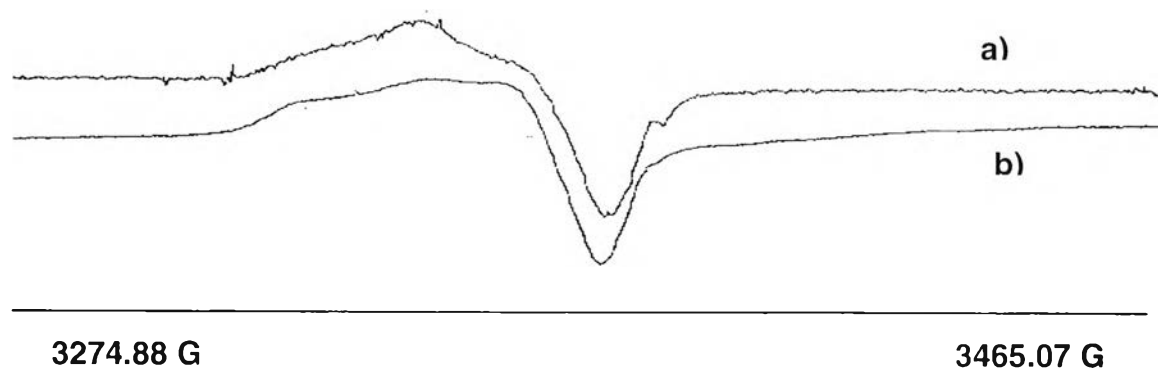**3274.88 G**                                        **3465.07 G**

Figure 4.20*b*.  ESR spectra at 273 K of irradiated PVC, a) the obtained PVC, and b) the commercial PVC.