จุฬาลงกรณ์มหาวิทยาลัย

ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย
เรื่อง

แนวทางใหม่เพื่อการสังเคราะห์พอลิเมอร์ชั้นสูงโดยการควบคุมโครงสร้างเคมีสามมิติด้วยเทคนิคการเกิดปฏิกิริยาพอลิเมอร์ด้วยสารประกอบอินคลูชั่น

โดย

สุวบุญ จิรชาญชัย

มกราคม 2542

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ชื่อโครงการวิจัย แนวทางใหม่เพื่อการสังเคราะห์พอลิเมอร์ชั้นสูงโดยการควบคุมโครงสร้างเคมีสามมิติด้วยเทคนิคการเกิดปฏิกิริยาพอลิเมอร์ด้วยสารประกอบอินคลูชั่น

ชื่อผู้วิจัย สุวบุญ จิรชาญชัย

เดือนและปีที่ทำวิจัยเสร็จ มกราคม 2542

บทคัดย่อ

สารประกอบอินคลูชั่นระหว่างสารประกอบหลักดีออกซิคอลิค เอซิด (DCA) และไวนิลคลอไรด์มอนอเมอร์ (VCM) ซึ่งทำหน้าที่เป็นสารประกอบรองได้ถูกเตรียมขึ้นด้วยวิธีการดูดซับเข้าในผลึก DCA ที่ปราศจากสารรองจำพวกตัวทำละลายอยู่ในผลึก สารประกอบ DCA ที่ปราศจากตัวทำละลายเตรียมได้จาก DCA และตัวทำละลายชุดหนึ่ง ได้แก่ เอธิลอาเซเตท ไดออกเซน ออร์โธและพาราไซลีน การวิเคราะห์สารด้วยการหักเห X-ray กล้องจุลทรรศน์ FT-IR และเทคนิคการวิเคราะห์ด้วยความร้อน แสดงผลว่าไวนิลคลอไรด์มอนอเมอร์ถูกตรึงอยู่อย่างเสถียรในผลึก DCA และพบว่าค่าการคายตัวของสารประกอบรองปรากฏที่ 40-60 องศาเซลเซียส ปฏิกิริยาการเกิดพอลิเมอร์สามารถทำได้สำเร็จโดยการใช้วิธีการฉายรังสีโดยให้ปริมาณการฉายรังสีรวมที่ค่า 20 กิโลเกรย์ และตามด้วยการต่อปฏิกิริยาพอลิเมอร์ที่อุณหภูมิ –15 องศาเซลเซียส เป็นเวลา 2 วัน จากการวิเคราะห์เชิงโครงสร้างพบว่าสารที่ได้เป็น พอลิไวนิลคลอไรด์ (PVC) โดยที่มีอุณหภูมิสถานะคล้ายแก้วสูงกว่าพอลิไวนิลคลอไรด์ที่มีจำหน่ายอยู่ประมาณ 8-10 องศาเซลเซียส ผลการวิเคราะห์ด้วย FT-IR บ่งให้เห็นว่า PVC ที่ได้จากการสังเคราะห์มีส่วนที่เป็นระเบียบเชิงโครงสร้างสามมิติอยู่ในระหว่างสายใยพอลิเมอร์

Project Title : A New Approach for the Synthesis of Advanced Polymers by Stereochemically Controlled Structure Using Inclusion Polymerization Technique

Name of the Investigators : Suwabun Chirachanchai

Year : January 1999

Abstract

Inclusion compound of deoxycholic acid (DCA) host molecule and vinyl chloride monomer (VCM) guest molecule is prepared from solvent free DCA crystal via guest insertion technique. Solvent free DCA inclusion compound is achieved from a series of DCA-solvent guest, i.e., ethylacetate, dioxane, *o*- and *p*-xylene. X-ray diffraction, FT-IR and thermal analysis results indicate that vinyl chloride monomer is entrapped and stabilized in DCA crystal in solvent free DCA. Guest releasing peak of DCA-VCM is confirmed at ca. 40-60 °C. Inclusion polymerization is accomplished from the γ-radiation for total dose 20 KGy, followed by post polymerization at –15 °C for two days. The obtained product is confirmed to be polyvinyl chloride by structural analysis. Glass transition temperature of the obtained product is 8-10 °C higher than the commercial one, while characteristic peaks at 1500-1100 cm^{-1}studied by FT-IR show the sharp peaks of which imply that the obtained PVC contains stereoregularity portion in the polymer chain.

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CHAPTER 1

Introduction

1. The Concept of Host-Guest, or Inclusion Compound

Inclusion compound is known as the molecular assembly of which can be formed either by the macrocyclic of host molecules, e.g. calixarenes, crown ether, or cyclodextrin or the gathering of groups of molecules, e.g. urea, steroid. As a result, host molecules supply the concave framework for guest molecules. Host and guest molecules, thus, incorporate to each other by secondary valence forces or physical entrapment owing to the specific structure of the framework fitting to the guest molecules[1].

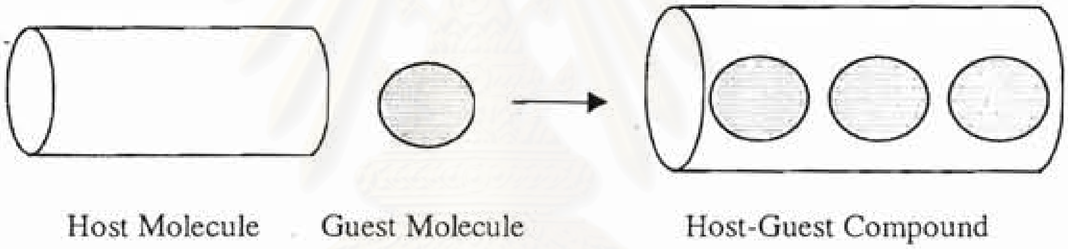


Figure 1. Concept of inclusion compound and host-guest formation.

Inclusion compound has received much attention to open up a wide range of applications, such as stabilization for unstable species, separation for chemical isomers or metal ions, co-catalyst for phase-transfer systems.

One of the most interesting applications in the viewpoint of polymer synthesis is the inclusion polymerization. Here, the host molecule forms as a molecular assembly and includes monomer molecule as a guest. Through supramolecular structure of the host, the entrapped guest monomer is forced to align in an order and the monomer guest molecules lost their degree of freedom in rotation or movement contrary to the case of monomer in conventional solution. Miyata et al.[2] proposed that the space provided to the monomer for the inclusion polymerization is 10^{-8} order smaller than the normal polymerization in solution as shown in schematic draw (Figure 2).

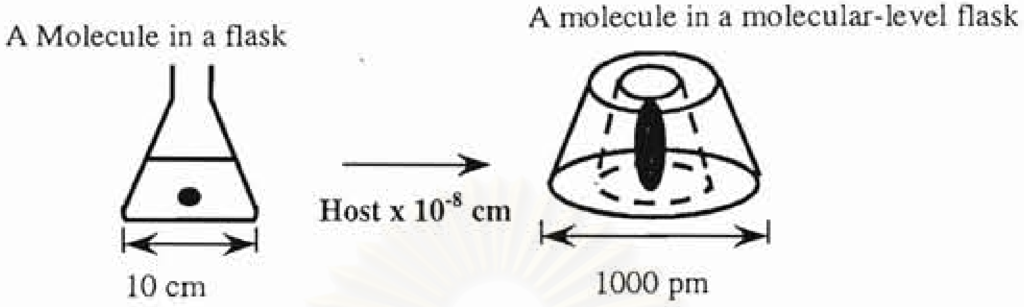


Figure 2. Relationship between container (host) and content (guest).

Thus, inclusion polymerization can be claimed as a space-dependent reaction, which can contribute the stereoregularity polymer corresponding to the low-dimensionality spaces provided from the host molecular assembly[3] (Figure 3).

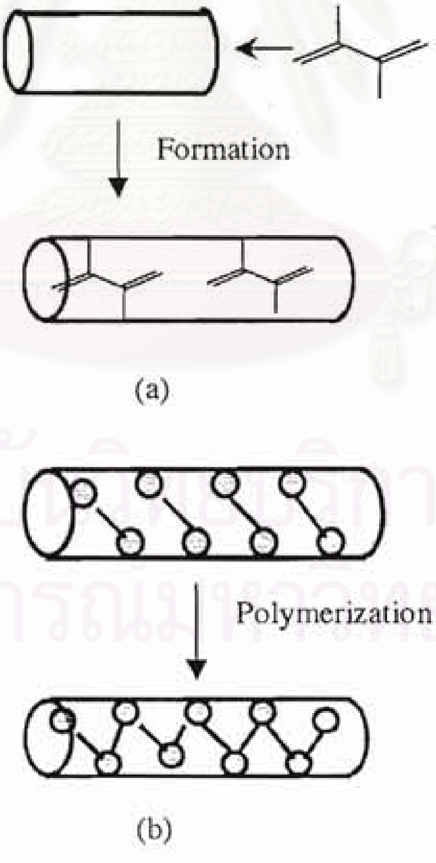


Figure 3. (a) Formation of host-monomer inclusion compound, and (b) polymerization of monomer in low dimensional space controlled by host structure.

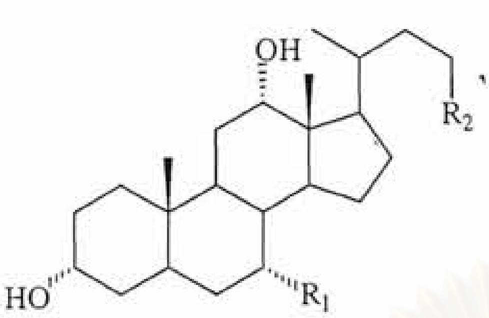
2. Historical and Development

Inclusion phenomenon was firstly reported by W. Schlenk in 1940. The concept of inclusion polymerization was then proven when Clasen[4] (1956) applied urea and thiourea as a host molecule for butadiene monomer and proceeded the polymerization in room temperature for the nine months of a long period time. Brown and White[5] adopted γ-rays for the polymerization to find the stereoregularity polymer in a good yield in 1960. Meanwhile, C.J. Pedersen reported the alkaline and alkaline earth metal interaction with crown ether of which can be proven by the analytical techniques. Hydrotriphenylene was also recognized as a host compound for diene polymerization by Farina et al.[6] in 1964.

However, the inclusion phenomenon was not as much recognized until in the year 1987, when D.J. Cram, J.M. Lehn and C.J. Pedersen were awarded the Nobel Prize for their carriers and scientific fundamental researches to establish inclusion chemistry. With the development of the analytical instruments, understanding of inclusion chemistry is grown up rapidly and has received very much attention to concern as a molecular assembly or supramolecular chemistry to be an extended area in polymer science. In 1990, Miyata et al. reported the first case of guest responsive system as found in cholic acid host molecular assembly and solvent guests by single crystal X-ray analysis[7].

Inclusion polymerization is known as a strategy toward low-dimensionality architectures by controlling the space for monomer in the polymerization. Urea and thiourea are one of the interesting compound to form host-guest compound and provide the inclusion polymerization as seen in the case of acrylonitrile[8], 1,3-butadiene[9], aclolein[10]. Steroids (Figure 4), such as cholic acid, deoxycholic acid, and other derivatives are also known as hosts for inclusion polymerization.

Tsutsumi et al. showed that 1-chlorobutadiene which has bulky group of chlorine atom can be polymerized successfully to obtain the high regularity polymer by using the canal of deoxycholic acid (DCA) [11]. In 1993, methyl cholate is reported to be one-dimensional inclusion polymerization for diene and vinyl monomers[12].



$R_1 = H, R_2 = COOH$: deoxycholic acid
$R_1 = OH, R_2 = COOH$; cholic acid
$R_1 = OH, R_2 = COOCH_3$; methyl cholate

Figure 4. Cholic acid steroid compounds and its derivatives.

At the moment, though inclusion polymerization process has been established, the composition of monomer and host in the canal or channel, the relationship between the monomer radicals and polymerization, including the mobility change of monomer and the development to control the molecular weight, are still not clarified. Miyata et al. focused on the molecular structure of host-guest compound in the series of cholic derivatives and proposed that the understanding of molecular structure help the molecular design for inclusion polymerization.

3. General Processes of Inclusion Polymerization

Inclusion polymerization consists of three steps (Figure 5), which are;

3.1 Inclusion compound formation between host and monomer molecules
3.2 Polymerization and post polymerization of inclusion compound
3.3 Reprecipitation or seperation of the polymer

The formation of the inclusion compound from the monomer and the host can be proceeded by recrystallization the host and the guest molecules. In some cases, it is also possible to form host-guest molecules by the absorption technique, i.e., immersing host molecules in the guest solution. However, it is important that the technique require the guest molecules as a liquid. Structural analysis of the inclusion compound can be done by Fourier transform infrared spectroscopy (FTIR) or nuclear magnetic resonance (^{1}H-NMR). Depending on the type of the hosts and guest molecules, inclusion compound forms in various ratios of host to guest, such as; 1:1, 2:1, 3:1, or 1:2, 1:3 etc., which can be quantitative by thermogravimetry analysis.

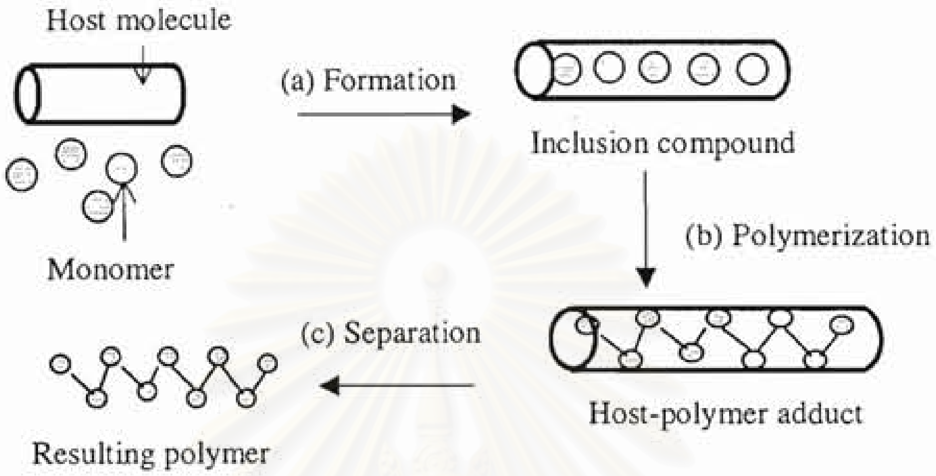


Figure 5. Steps for inclusion polymerization, (a) formation, (b) polymerization, and (c) separation.

The polymerization process can be achieved by various mechanisms, such as thermal polymerization, radiation polymerization, etc. In either case, radical polymerization is expected to generate among the monomers inside the host cavity with or without the initiator. The most efficient way to proceed the reaction is the irradiation by γ-ray. The generation of radical species to form stereoregularity polymer can be observed by electron spin resonance (ESR) in which each of the radical can be evaluated for the result of polymerization. Practically, after irradiation, radical polymerization is allowed proceeding in low temperature for a long period time, e.g. 2—5 days. In this step, radical species will attack other monomers in the host channel gradually.

The final process is the separation of the resulting polymer from the host. In this step, the product from the polymerization step can be obtained by reprecipitation in organic solvent to exclude the host. The main purpose of the inclusion polymerization is to obtain a stereoregularity polymer, thus, various approaches are applied in order to study the structure of polymer such as, ^{13}C-NMR, ^{1}H-NMR, FTIR, differential scanning calorimeter (DSC).

4. Advanced Polymer and Inclusion Polymerization

Polymeric material can be concerned as a product from petrochemical raw material. Up to now, polymeric material has reached its goal for various applications as can be seen in the case of plastic, fiber, coating reagent, rubber, etc. Concerning with specific application of which required significant properties of material, such as; selectivity for separation purposes, photoresponsive and conductivity for liquid crystal appication, controlled release for drug delivery systems, biocompatibility for medical use, biodegradability for environmental friendly products, etc., conventional polymeric material shows the limit to apply as an advanced material .

There are many approaches proposed in order to develop conventional polymer to be an advanced polymeric material with the required properties suitable for each application. Addition of a specific functional group onto polymer chain is one of the approaches to achieve the advanced polymer as a functional polymer which can induce the unique properties for various applications. Utilization of biopolymer or natural abundant polymer is also concerned as a useful way to obtain biocompatibility, biodegradability polymer material. Combining the chemistry of functional polymer to a biosystem of natural polymer leads to a new area of research, so called a biomimetic polymer material.

Recently, with the development of instrumentation, the understanding of polymeric material has been revised to the fundamental theory of polymer chain and the movement of the molecules. Thus, it can be expected that with a control on the unit of polymer structure in molecular level, even conventional polymer will exhibit unique property induced by the structure. At present, there be many interesting approaches to prepare controlled structure polymer as seen in the case of enzyme catalyst polymer synthesis[13], biomimetic polymer synthesis[14] and inclusion polymerization[15].

The present work, thus, focuses on the synthesis of controlled structure polymeric material via inclusion polymerization process. Here, it should be expected that conventional polymer will show some unique properties owing to the high stereoregularity of polymer chain.

5. Deoxycholic Acid as a Host Compound

Naturally occurring steroid compounds (Figure 4), such as deoxycholic acid (DCA), cholic acid, and methyl cholate, are reported to form specific channel-type inclusion compounds with a variety of organic substances[16] for nearly three decades. Specific properties of cholic acid and its derivatives including deoxycholic acid can be mentioned as its high crystallinity by assembly each molecule and provide a channel for other molecules (as shown in the schematic representation, Figure 3).

DCA can be recrystallized to obtain as a crystal by most of organic solvents, especially polar solvent. However, only some particular organic solvent that DCA will form good crystal structure. Up to now, it is reported that DCA can form inclusion compound will obtain good crystal with xylene, dioxane, etc.

Though it is known that DCA can form inclusion compound, only few studies are performed on DCA and its crystal structure. Application of DCA for inclusion polymerization was constructed in the year of 1975[17]. From crystal structure analysis, Miyata et al. demonstrated that the steroid host compounds have a flexible inclusion ability for conjugated diene monomers and show high yield stereoregular polymers from a great deal of diene with bulky and/ or polar substituents that hardly seen in the case of urea derivative hosts[17-19].

6. Vinyl Chloride Monomer and Polyvinyl chloride via Inclusion Polymerization

Vinyl chloride monomer (VCM) is a product made by addition of hydrogen chloride to acetylene in petrochemical process. In ambient, VCM is gaseous (bp-13 °C) and shows no color and no odor. Toxicity of VCM causes angiosarcoma, liver cancer.

The major use of VCM is for the production of polyvinylchloride, polyvinylidine chloride and other copolymer, including chloride solvents, i.e., vinylidene chloride, trichloroethylene, and tetrachloroethylene.

Polyvinyl chloride is a polymer obtained from a typical vinyl chloride monomer, which receives much attention for tremendous applications for more than a half century. Conventional polymerization of vinyl chloride monomer, i.e. , radical polymerization, brings amorphous polyvinyl chloride with low tacticity which makes the processing of polyvinyl chloride require some specific conditions comparing to other ordinary polymer as polyethylene or polypropylene. Though polyvinyl chloride has been utilized in a large amount, less study is focused on the controlled structure to propose as a new type of material as seen in the case of isotactic polypropylene and HDPE, LLDPE.

In 1975, Yoshii et al.[20] proposed inclusion polymerization of vinyl chloride monomer. The approach is operated by using urea in low temperature (under liquid nitrogen) in order to allow the host-guest formation step proceeding. However, the ratio of host-guest and the thermal stability was not clear. It was also concluded that the overall properties, such as solubility in organic solvent, crystallinity, x-ray diffraction theta angle were shown differently from the commercial polyvinyl chloride, however, stereoregularity was not precisely reported owing to the limited technique of broadline NMR at that period.

7. The Unique of the Present Work

In the case of urea and thiourea, host-guest compound can be formed by recrystallization. However, vinyl chloride monomer, which has the boiling point -13°C, is difficult to recrystallization with urea and thiourea, which have the melting point of 132-140°C. Yoshii et al. reported the preparation of the host-guest compound, thiourea/vinyl chloride monomer, by soaking the powder of thiourea with vinyl chloride monomer under liquid nitrogen, and as a result, the formation of host-guest structure as a crystal of inclusion compound was not clear[20].

For inclusion polymerization, the most important step can be mentioned as a step for preparation a crystal of host and guest. Thus, the formation process of vinyl chloride monomer and host molecule can be mentioned as the main key.

Here, the unique of the project is to apply the stable crystal structure of steroid compound to form inclusion compound with vinyl chloride monomer via absorption technique. Deoxycholic acid is suitable for the absorption technique because the crystal of this type of compound is easy to obtain and stable even the guest molecule is excluded .

The present work proposed a possibility to apply deoxycholic acid as a host molecule providing a channel for vinyl chloride monomer. Instead of using the direct recrystalllization technique with vinyl chloride monomer which is not practical in the case, the absorption technique is used (Figure 6).

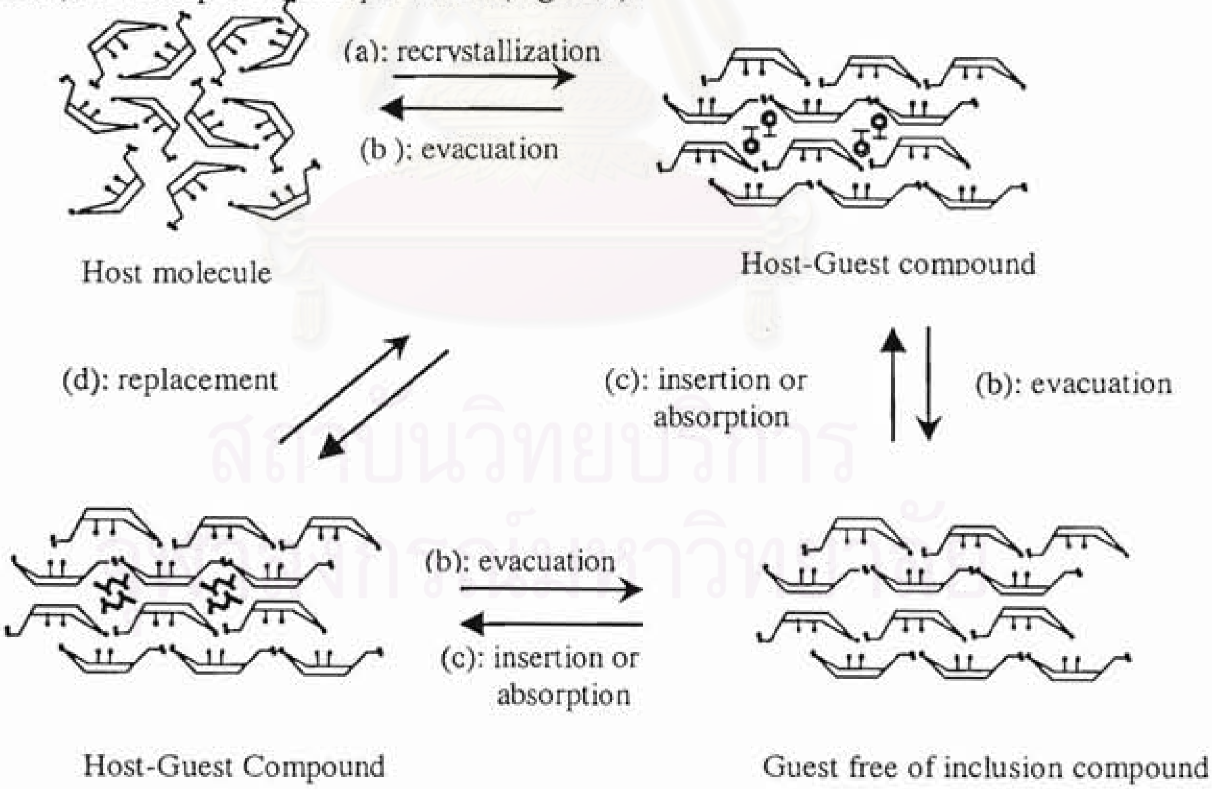


Figure 6. Preparation of inclusion compound by guest absorption into solvent free host molecules, (a) recrystallization, (b) evacuation, (c) insertion or absorption, and (d) replacement.

In the first step, DCA is dissolved with good solvents to obtain complete crystal of DCA. This crystal will contain the solvent molecule as a guest inside the molecular assembly of DCA, which can be confirmed by analytical techniques, such as IR, thermal analysis, XRD or single crystal X-ray crystallography.

Secondly, the evacuation will be operated in order to exclude guests from the host channel and the guest free inclusion compound can be prepared. In this step, thermal analysis and IR can be applied to study the completion of the guest exclusion. When crystal of DCA turns out to be guest free DCA or solvent free DCA, the IR will give the characteristic peak of only host compound, while the thermal analysis will show only melting peak of host compound.

Thirdly, the absorption of vinyl chloride monomer to host molecules under liquid nitrogen will be proceeded and the inclusion compound of deoxycholic acid and vinyl chloride will be obtained. In this step, when guest insertion occurs, the crystal of DCA will give guest-releasing peak observed by thermal analysis. The combination peak of IR spectrum also informed the existence of guest inside the obtained DCA crystal.

It should be noted that in the case of urea and thiourea, the crystal obtained from the recrystallization will be deformed as soon as the guest is taken out from the host framework which makes the absorption technique not practical. However, DCA and cholic acid (CA) are known as a unique type of host, that is, solvent guest can be penetrate inside the crystal owing to the stability of the molecular assembly of DCA and CA. Thus, it is possible to form host-guest compound by insertion or absorption technique into the guest free host molecules. As a result, guest insertion technique makes it possible to form host-guest compound and practical in the case of which the guest shows the low boiling point and to avoid recrystallization step.

8. The Goal of the Present Project

The present work is originally focused on the inclusion polymerization of VCM via an approach of steroid host compound. The goal of the present part can be concluded as,

8.1 To establish the method for the preparation of DCA and VCM as an inclusion compound.

In order to obtain inclusion compound of DCA and vinyl chloride monomer by absorption technique, stable crystal of guest free DCA host molecule has to be prepared. Here, recrystallization of DCA with good solvents (guest molecules) is an effective way to produce DCA-guest compound. Following by the evacuation procedure, the crystal of guest free DCA host compound will be obtained. DCA-VCM inclusion compound is obtained by immersing DCA into liquid VCM at low temperature (-196 °C).

In the present work, the inclusion compound of DCA with various organic solvents will be studied. In order to obtain high stability of DCA-VCM, the obtained DCA-solvent compounds will be compared for the host-guest ratio and the guest absorption ability. The present work will also cover the consideration of DCA-VCM evidence by analytical approaches.

8.2 To study on the possibility for inclusion polymerization of vinyl chloride monomer via inclusion polymerization

Up to now, there is no report about DCA-VCM inclusion polymerization. Thus, it is an important issue to show that the inclusion polymerization of VCM in DCA host compound can be accomplished. The present work applies γ-ray irradiation technique to induce radical polymerization inside the host channel. It is also important to study the effect of the amount of γ-ray energy including the post polymerization condition.

8.3 To develop the specific structure of polyvinyl chloride

The utilization of inclusion compound can be defined as an approach for topochemical polymerization. Through the polymerization in the channel of the host, which the space for monomer movement is limited, the polymerization can be expected for the stereospecific polymer products. The main idea of the present project is to apply the inclusion polymerization for VCM to obtain syndiotactic or/and isotactic polyvinyl chloride which has never been reported in any catalytic system. It should also be noted that the achievement of inclusion polymerization of vinyl chloride monomer is mainly related to the successful preparation of DCA/vinyl chloride monomer inclusion compound.

CHAPTER 2

Experimental

1. Materials

DCA (AR grade) was purchased from Nacalai Chemical, Japan and used without further purification. Dioxane, ethylacetate, *o*-xylene, *p*-xylene and trichloroethylene (HPLC grade) were purchased from Ajax chemical and used without purification. Methyl alcohol anhydrous (AR grade) was purchased from Mallinckrodt. Vinyl chloride monomer and commercial grade PVC were supplied from Thai Plastics and Chemicals Public Co., Ltd.

2. Preparation of Inclusion Compounds with Various Solvents

Dioxane, ethylacetate, *o*-xylene and *p*-xylene were applied as solvents for DCA recrystallization. DCA was dissolved in each solvent at its boiling point until clear solution and saturation obtained. The solution was cooled down slowly to room temperature to obtain colorless needle like crystal. The obtained crystal was qualitative by FT-IR to study host-guest formation. The host-guest stability was qualitatively and quantitatively studied by TGA.

3. Preparation of Solvent Free Inclusion Compound

The solvent free (or guest free) DCA was obtained by heating the DCA-solvent adducts at 140 °C for 12 hours under reduced pressure around 1020 mbar in order to remove the solvent, i.e., dioxane, THF, ethylacetate or xylene. The obtained crystals were studied by FT-IR and TGA to confirm that all the solvent molecules were removed and the crystals were guest free inclusion compound.

4. Preparation of Host-Monomer Inclusion Compound

The obtained guest free inclusion compound crystals (1.0 g) were collected in a glass tube and cooled by liquid nitrogen. Vinyl chloride monomer 2 ml. was gradually collected under liquid nitrogen . The tube was evacuated under reduced pressure and sealed. The sealed tube was allowed standing at -15 °C for 2 days to prepare DCA-VCM inclusion compound.

5. Polymerization of Host-Monomer Inclusion Compound

The prepared host-monomer inclusion compound was γ –ray irradiated (dose rate 2 Mrad/h (20 kGy/h), 1h, at –78 °C) to initiation the polymerization. After irradiation, the tube was left under -15 °C to let the postpolymerization occur for 4 days. The γ –ray irradiation was operated by courtesy of Office of Atomic Energy for Peace.

6. Separation of Polymer after Postpolymerization

After postpolymerization, the DCA-polymer adduct was poured into the excess methanol (100 ml). The separated polymer was filtered off and washed with absolute methanol repeatedly, and dried under vacuum at room temperature for a day to avoid the degradation and oxidation.

7. Measurements

7.1 Structural Analysis

Infrared spectra of DCA and various solvents as guest molecules, monomer-host adduct, polymer-host adduct, and polymer were measured by a Bruker Equinox55/S FT-IR spectrometer using KBr pellet technique. Microscope FT-IR was applied to study the inclusion compound of DCA-VCM crystal. 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 ESR measurements were performed at 187 K and 273 K.

7.2 Microstructure Analysis

Single crystallographic of DCA-solvent data and molecular packing were determined by Rigaku AFC-7R diffractometer with graphite-monochromated Mo-Kα radiation in combination with TEXAN crystallographic software package of Molecular Structure Corporation. Powder X-ray analysis was performed by Rigaku D/MAX 2000, at room temperature, to study the microstructure of the obtained crystals and the obtained polymer by using small angle (at angle range (2θ) 2°-10°) and wide angle measurement (at angle range (2θ) 3°-25°).

7.3 Thermal Stability Analysis

Thermogravimetry Analysis (TGA) and Differential Thermal Analysis (DTA) were made with a Rigaku Thermoplus Thermogravimetric and Differential Thermal Analyzer under nitrogen atmosphere at a rate of 20 mL/min. DCA with various solvent guests were analyzed at a heating rate of 10 K/min from 30 °C to 300 °C. Monomer-host adduct was observed from 10 °C to 200 °C with a heating rate of 1 K/min between 10-50°C and 10K/min between 50-200 °C. Guest releasing point was determined by Differential Scanning Calorimeter Nertzsch DSC 200. The scan was taken at 10°C/min under nitrogen atmosphere.

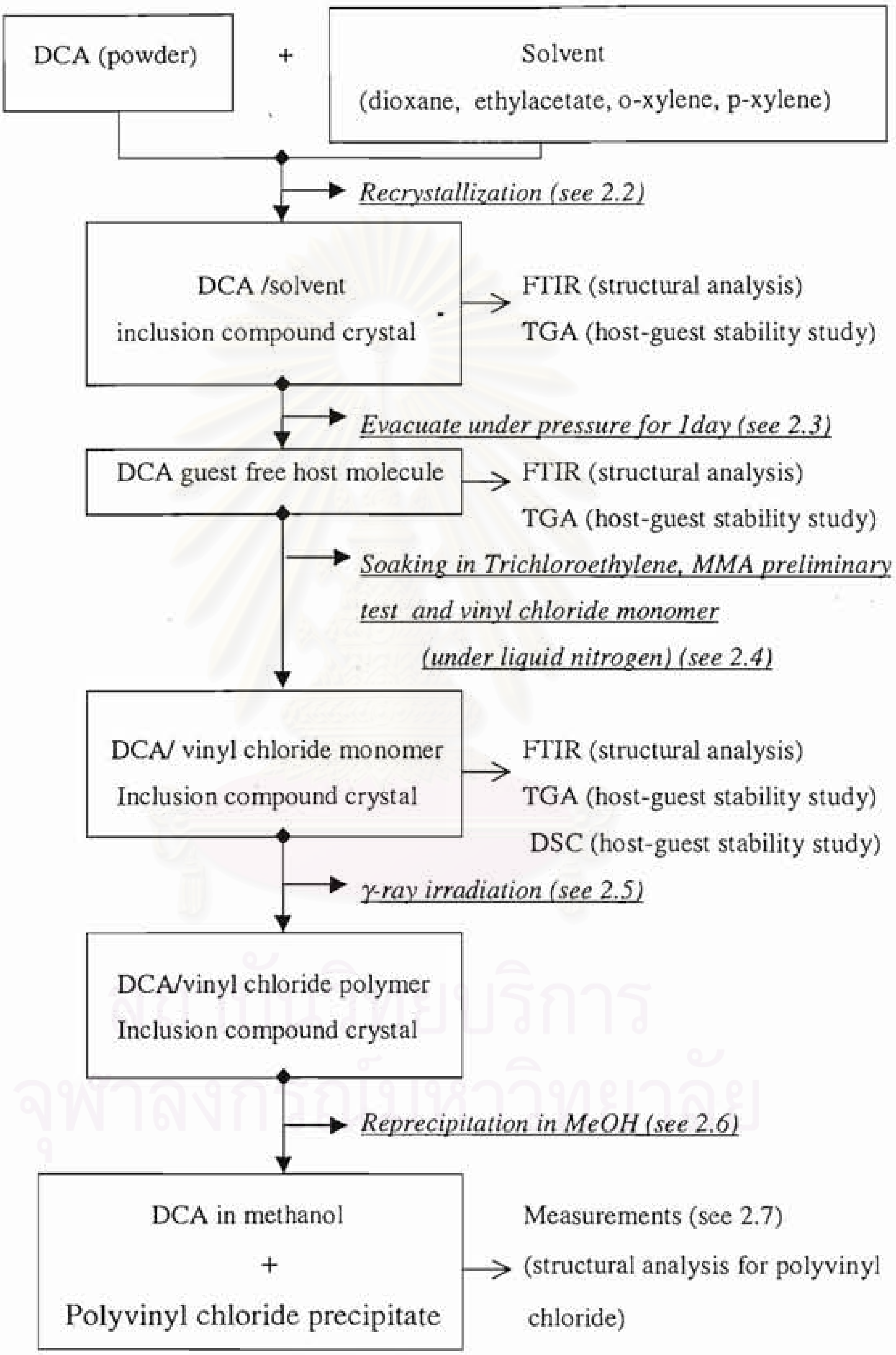


Chart 1. Overall procedures of the experiments.

CHAPTER 3

Results and Discussion

1. Properties of DCA and Various Solvents Inclusion Compounds

DCA was recrystallized with good solvents, i.e., dioxane, ethyl acetate, p-xylene and o-xylene to prepare inclusion compound crystal. The obtained needle crystals are not melt or deformed at room temperature. The obtained crystals were analyzed by FTIR and TGA techniques in order to confirm the formation of inclusion compounds.

Figure 7 shows the FT-IR of DCA which free hydroxyl group can be observed at 3552 cm^{-1}, while carbonyl of carboxylic acid shows strong peak at 1714 cm^{-1} and 1699 cm^{-1}, owing to the free carbonyl and internal hydrogen bonding.

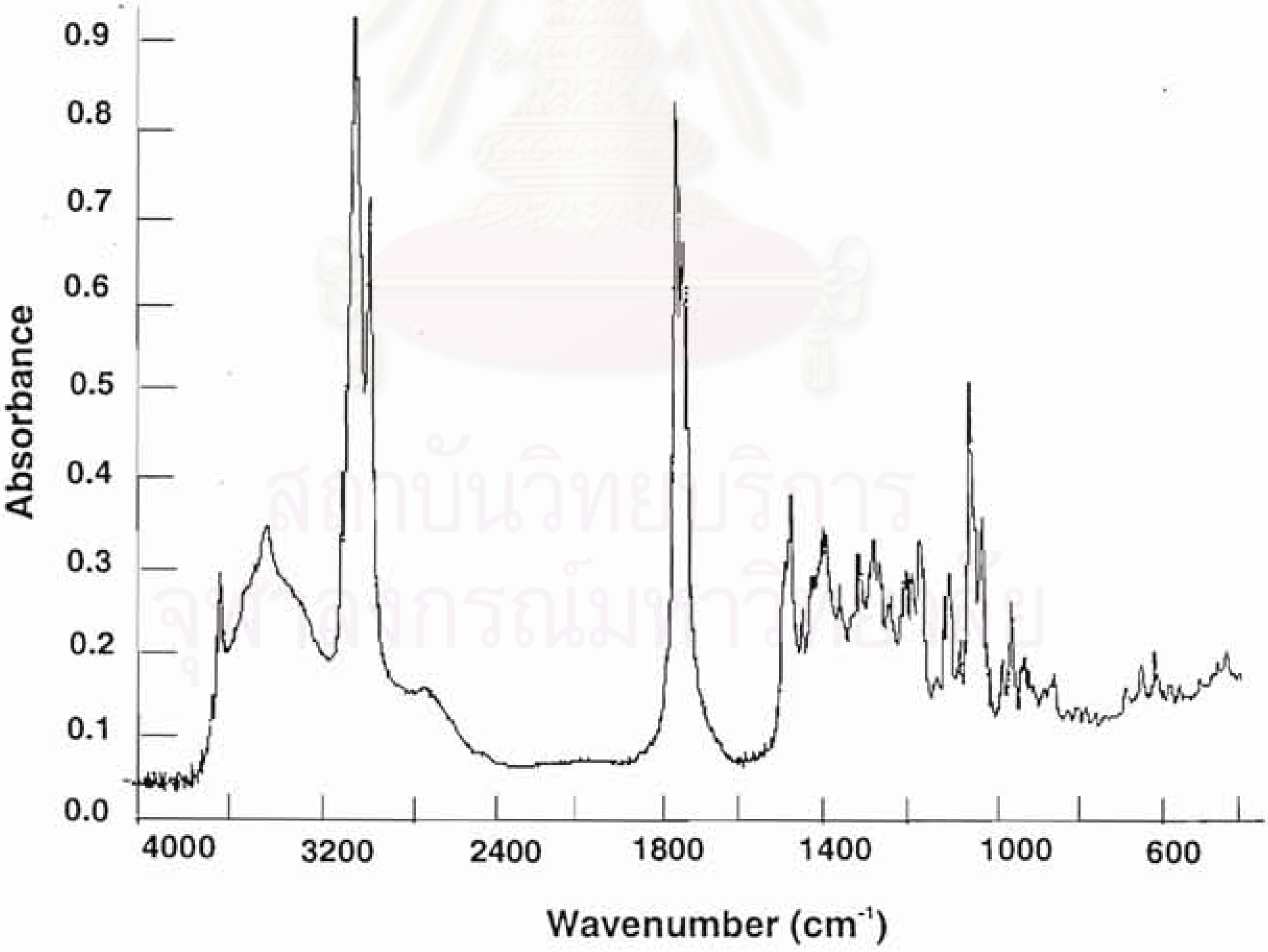


Figure 7. FTIR of DCA starting material.

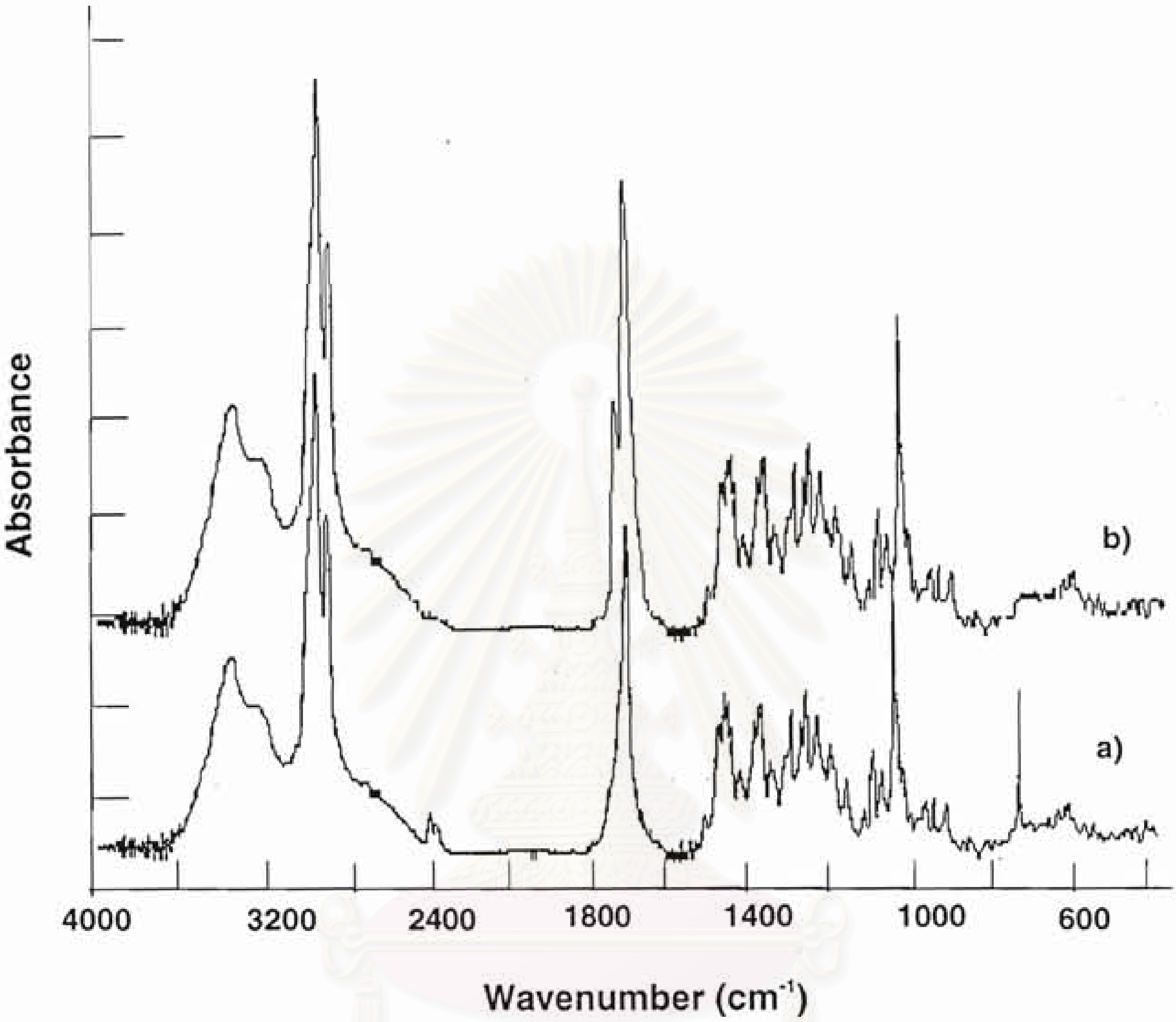


Figure 8. FTIR of a) DCA-*o*-xylene inclusion compound, and b) DCA-ethyl acetate.

However, as shown in Figures 8, and 9 when DCA was recrystalized with *o*-xylene, ethyl acetate, and dioxane, free hydroxyl group could not be observed and intermolecular hydrogen bonding of DCA shows significantly at 3200 cm^{-1}, whereas carbonyl group shows a single peak at 1693 cm^{-1}. In the case of xylene (Figure 8a), aromatic hydrocarbon peak can be observed at 941 cm^{-1}. DCA-ethyl acetate shows the significant peak of carbonyl of ester at 1742 cm^{-1} (Figure 8 b). Similarly, DCA-dioxane shows the peak of C-O-C stretching at 1121 and 1196 cm^{-1}, respectively (Figure 9).

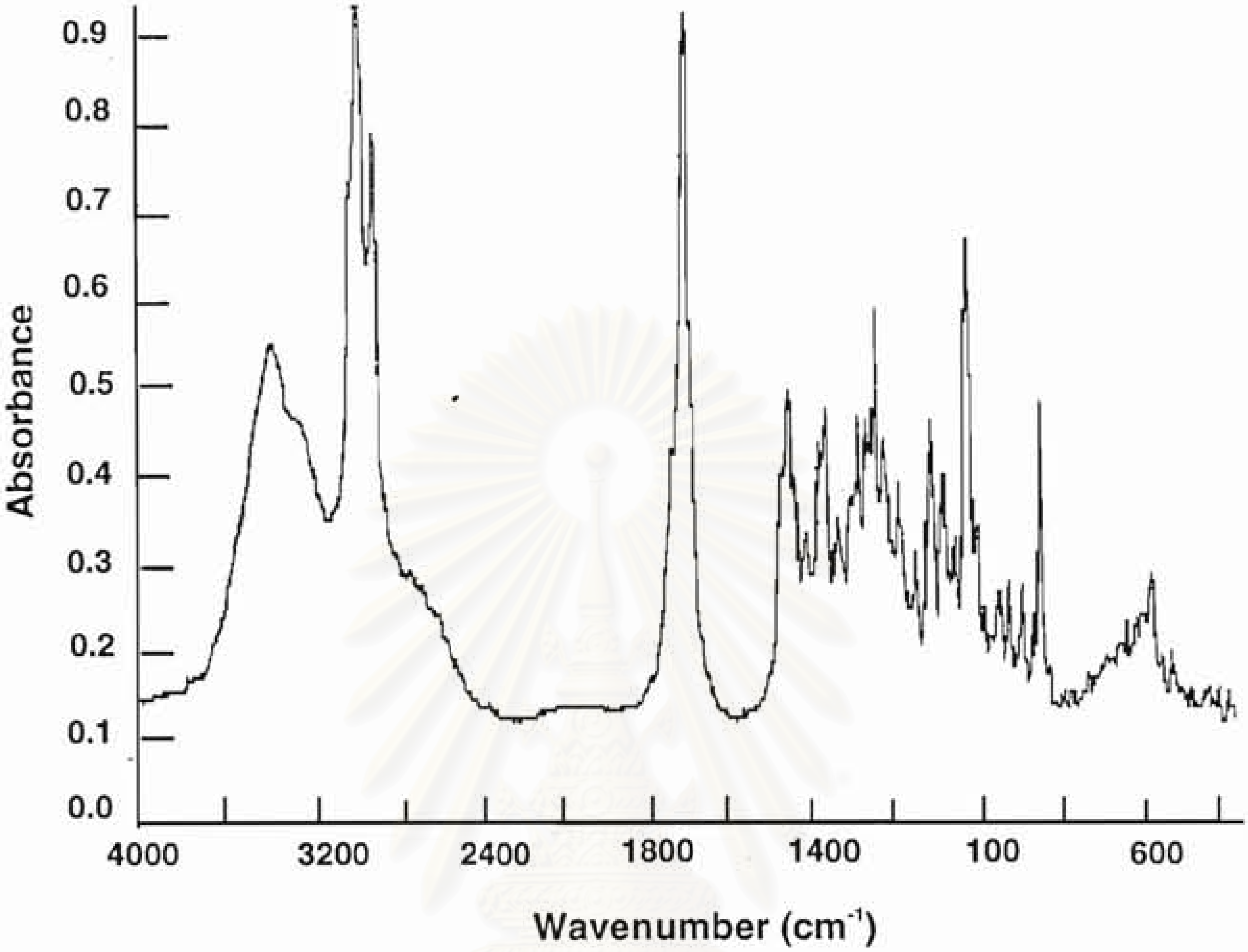


Figure 9. FTIR of DCA-dioxane inclusion compound.

2. Host-Guest ratio

Normally, guest will be stabilized in host channel and the crystal structure is maintained by the packing of host and guest. By adding the energy, e.g. thermal energy, guest will response to the circumstance and will release from the structure. Thermal gravimetry analysis will be a useful way to find the host-guest ratio by the weight loss owing to the guest-releasing peak.

Guest entrapped in DCA channel was quantitatively studied by TGA. As shown in Figure 10, in the case of DCA-ethyl acetate, the release of guest can be observed at ca. 150 °C, which is around 80°C higher than the boiling point of ethyl acetate (from Merck index; 77.1°C). Another peak is found at 170°C referring to the melting temperature of DCA crystal. Tsutsumi et al. reported[11] that when DCA formed inclusion complex with a guest of 1-chlorobutadiene, TGA shows the weight loss of the guest at 159 °C, which is higher than the boiling point of 1-chlorobutadiene for 90 °C (bp. of 1-chlorobutadiene : 65-65.8°C). Thus, it can be concluded that ethyl acetate is included and stabilized by DCA. The thermal stability of entrapped guest in DCA channel can be observed by differential thermogravimetry analysis (DTG). As shown in the Figures 11-12, each guest molecule is removed at 140-150°C at which is higher than the boiling point of *o*-xylene and dioxane for ca. 70-90 °C.

From weight loss peak, the molar ratio of host and guest can be calculated, i.e., 6.1% for ethyl acetate and 93.9% of DCA which is equal to the ratio of 6.1/88 : 93.9/391 that is 3.46:1, approximately 3:1. Figure 10 implies that ethyl acetate for 1 molecule entrapped by 3 host molecules.

Here, it should be noted that when the inclusion compound of DCA-ethyl acetate is left for a long period time (i.e., more than 1 month), guest release pattern is different. As shown in Figure 13, host guest ratio of DCA-ethylacetate is calculated to be nearly 6 host molecules to entrap one guest molecule. This may be due to the different packing and different stability of guest molecules in the host structure.

At the equilibrium time, the unstable guest in the channel is released while the stable one is still remained in the channel. This can be confirmed by single crystal X-ray crystallography as discussed in the *next section, Single crystal analysis of DCA with particular solvents.*

For DCA-o-xylene, guest releasing peak imply that host guest ratio is (88.38/391): (11.62/106) approximately 2 hosts for 1 guest (Figure 11). Similarly, Figure 12 implies that host guest ratio is 2.5 hosts to one guest.

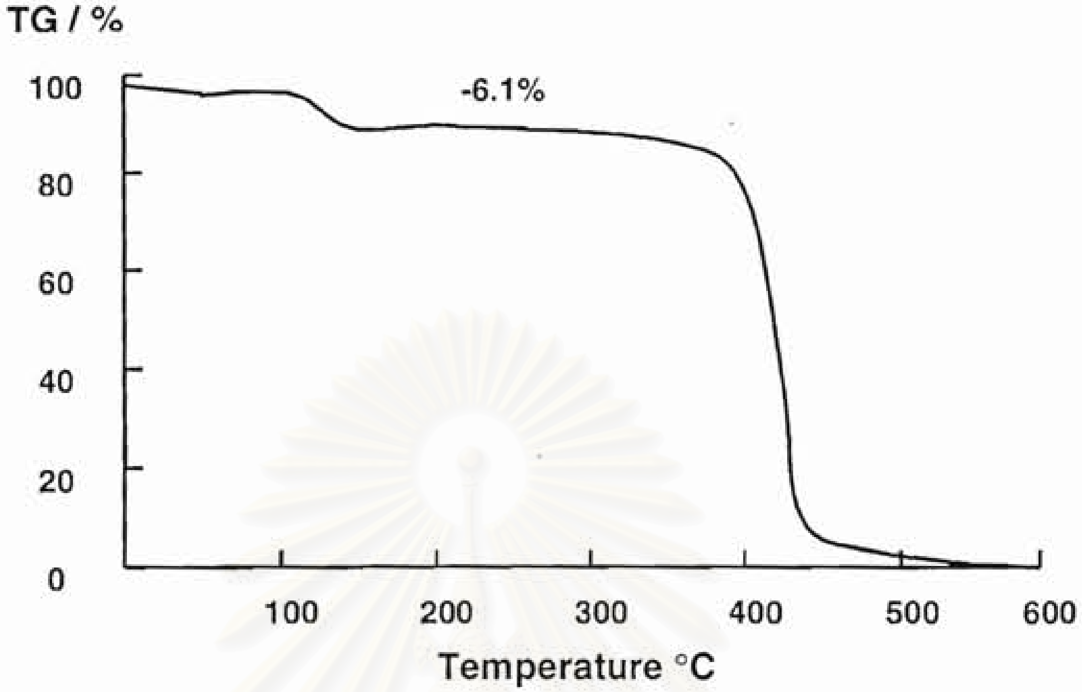


Figure 10. Thermal stability of DCA-ethyl acetate after a week. From the weight loss peak, host:guest ratio can be calculated to be 3:1.

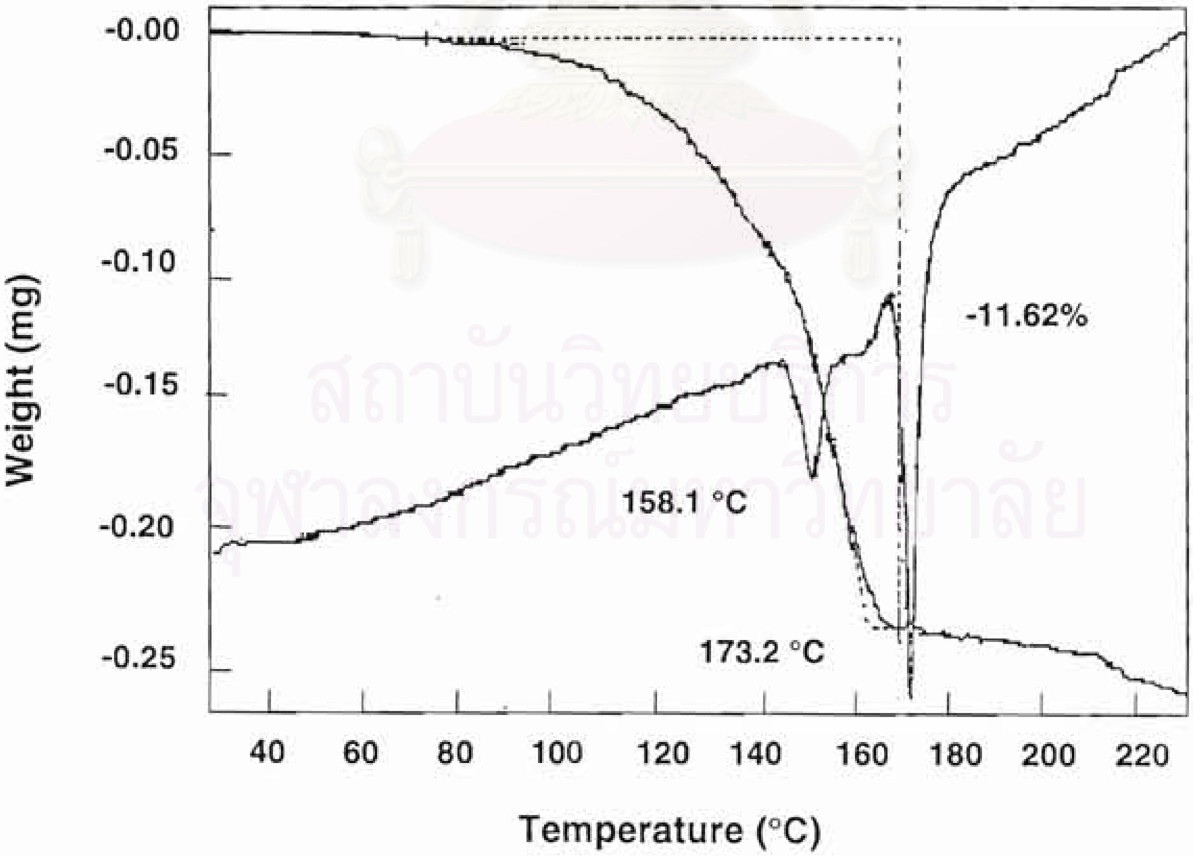


Figure 11. Thermal stability of DCA-*o*-xylene inclusion compound.

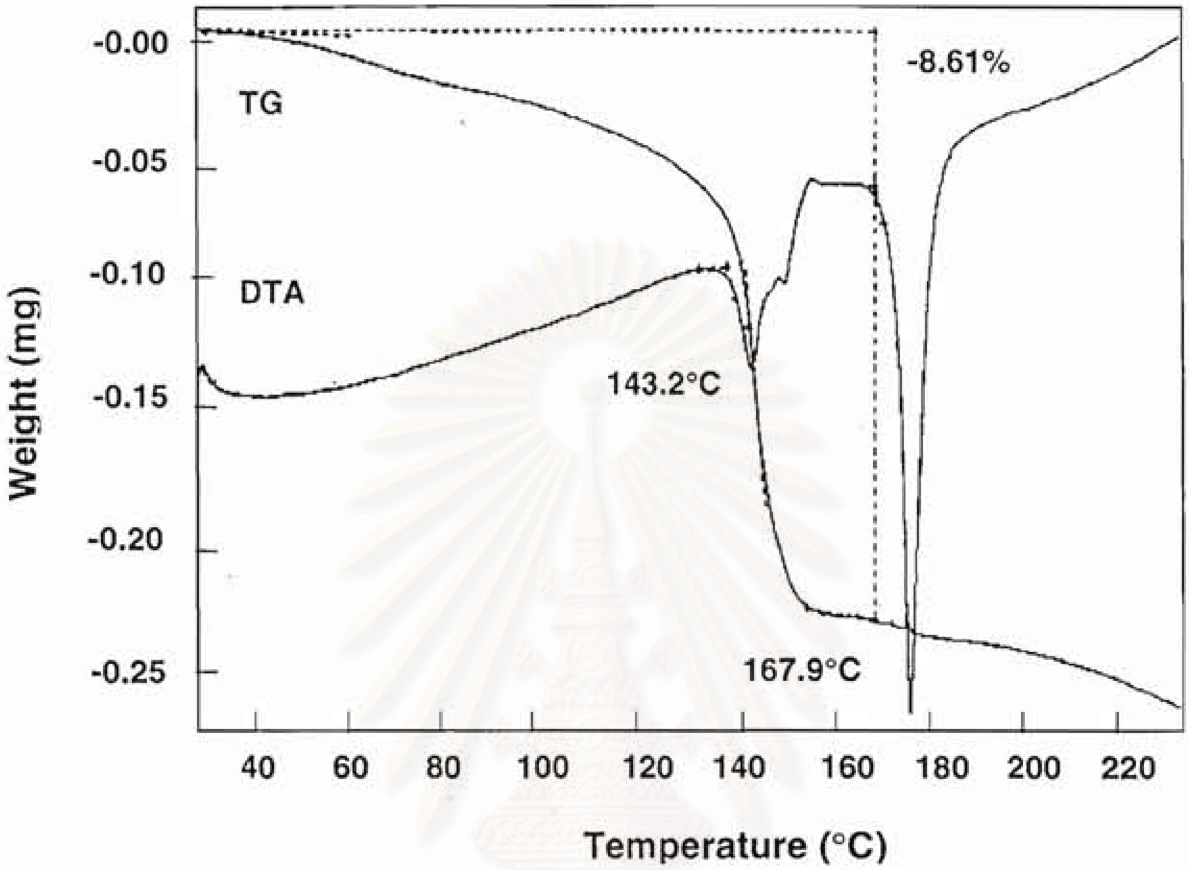


Figure 12. Thermal stability of DCA-dioxane inclusion compound.

TG/DTA diagrams show the peaks in two separate regions related to the guest releasing peak besides melting peak of DCAat 170°C. In the case of DCA-dioxane and DCA-ethylacetate TG/DTA shows two peaks to guest releasing, which is around 140°~160°. This may be due to the evaporation of the guest molecules from the different region inside the channel of DCA. It can be mentioned that the inner region of the DCA channel stabilized guest molecules much more than the outer region of the DCA channel. The weight loss of the guest releasing peaks can be calculated as a molar ratio of host and guest.

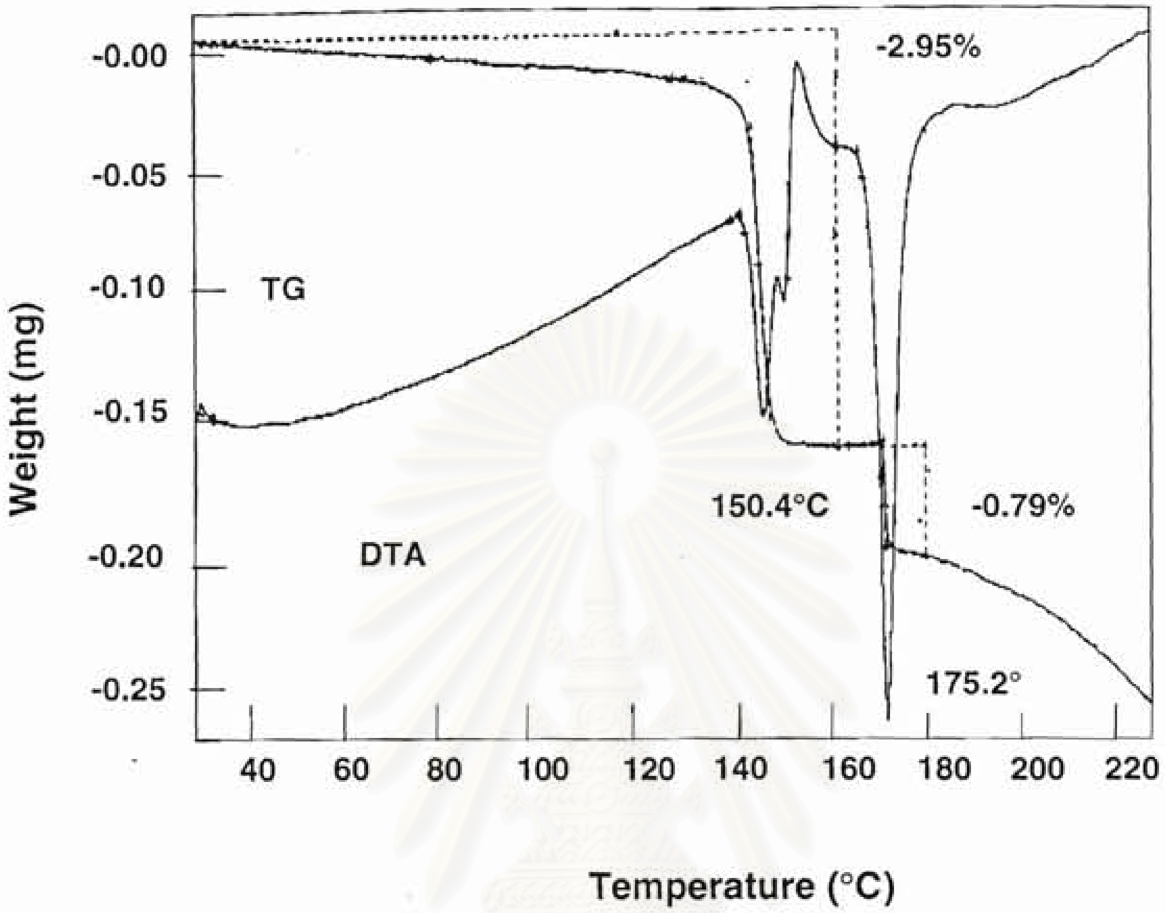


Figure 13. Thermal stability of DCA-ethyl acetate after more than two months, from the weight loss peak, host:guest ratio can be calculated to be 6:1.

3. Single Crystal Analysis of DCA with Particular Solvents.

DCA (Figure 14), Cholic acid (CA) and its derivatives such as methyl cholate[12], 3-epiursodeoxycholic acid[21] have been reported in terms of crystallographic view to demonstrate the molecular assemblies when inclusion compound was formed. Cerini et al reported that DCA forms inclusion compound with *o*-xylene or *p*-xylene as a monoclinic type ($P2_1$). Usually, DCA forms inclusion compounds in layer crystal form in orthorhombic, monoclinic, tetragonal system, while it forms in helical form in hexagonal system[22].

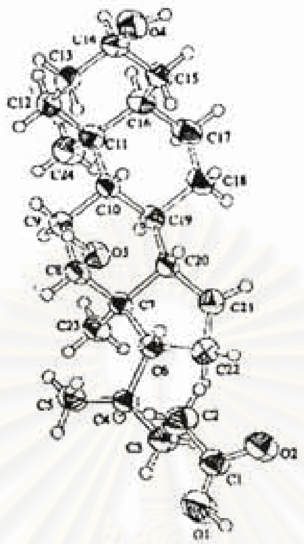
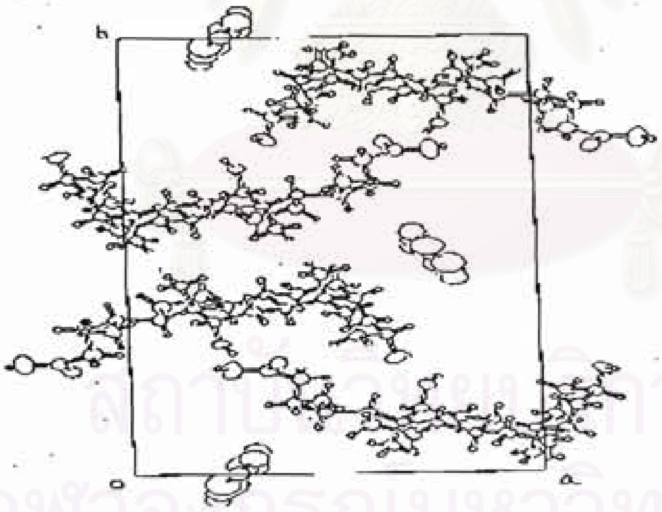


Figure 14. Orthep plot of deoxycholic acid molecule.



- a = 13.577 ºA
- b = 25.698 ºA
- c = 7.2402 ºA

Figure 15. Single crystal analysis of DCA with ethyl acetate, while ethyl acetate molecule is represented by guest packing model.

It should be noted that, when the crystal of DCA-ethyl acetate is left for a long period time, DCA-ethyl acetate shows unique property different from other DCA-solvents system. It is found that the DCA-ethyl acetate after long period time shows ethyl acetate in bilayer form of orthorhombic system, while the host guest ratio is not 3:1 but rather bigger ratio (Figure 15). Single crystal analysis is much more difficult to determine for each repeating structure unit including the position of guest when the unit cell becomes larger owing to the large number of guests to one host.

When the host guest ratio is complicated , the data base for analysis is tremendous amount. Owing to the limitation of single crystal analysis data base the position of guest can be estimated only for overall structure but can not be exactly determined for the guest structure, the position and the ratio to host molecules. Especially, in this case, the electron density of ethyl acetate guest molecules is not strong enough to detect the correct position in DCA channels, which may be due to the disordering of ethyl acetate guest molecules. However, for the overall structure, it is found that ethyl acetate is arranged in DCA channel as a one-dimensional chain along the *c*-axis as shown in Figure 16.

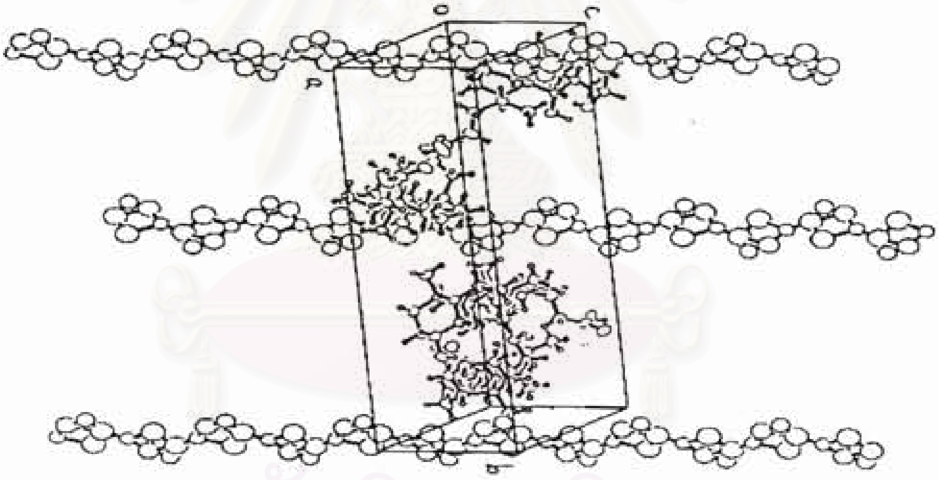


Figure 16. One-dimensional chain of guest molecules along c-axis by using chain model for ethyl acetate guest.

DCA-dioxane is another interesting compound. After long period, host:guest ratio is changed from 2.7 to 2.3. Here, the study on single crystal X-ray crystallography implied that the system is unique and quite different from those of the reported DCA-xylene by Cerrini et al[23]. and DCA-ethyl acetate by Nassimbeni et al[24]. DCA-dioxane crystal shows host guest ratio be not simple as an integral number to one host molecule. In this case, The host guest ratio can be explained as approximately 24 guests to 10 host at equilibrium time. Thus, the determination of host and guest molecules in crystal structure is difficult owing to the limitation of the X-ray analysis program.

By using Texan software combining with the electron density data in the unit cell, it can be approximately evaluated that molecular structure of DCA-dioxane can either be monoclinic or orthorhombic as concluded in Table 1. In the case of orthorhombic system, the molecular assembly is shown in Figure 17.

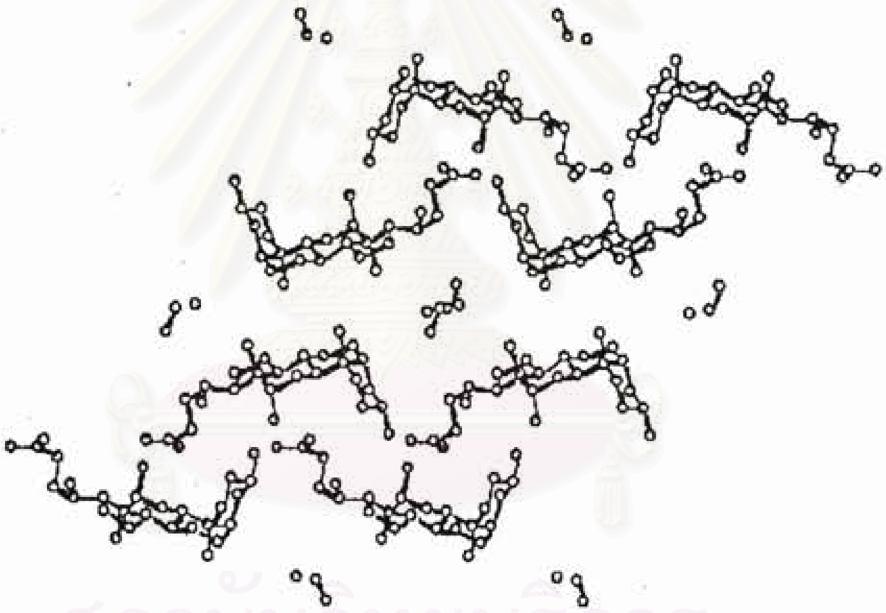


Figure 17. Single crystal of DCA-dioxane host guest compound, while dioxane guest is shown as a group of atoms due to the limitation of guest determination by X-ray crystallography.

Table 1. Summary data of DCA-dioxane crystal when it is monoclinic or orthorhombic system

	Preliminary test	Monoclinic	Orthorhombic
Space group	-	$P2_1$	$P2_12_12_1$
a	13.459	13.491	13.490
b	26.558	7.6272	7.6270
c	7.275	26.580	26.549
α (°A)	90.0603	90.000	90.000
ß (°A)	90.2170	89.973	90.000
γ (°A)	89.9589	90.000	90.000

Figure 18 shows the schematic drawing of DCA-dioxane adduct to simplify the system, which is not integral ratio of host and guest. In the case of it can be expected that guest alignment is overlapping in the host channel. Nasimbeni et al reported that guest molecules in host channel can be disordered in both dynamic and static type. In DCA-dioxane, it may be due to the guest disordering which rather be a static disorder owing to the high stability of the crystal in the ambient pressure and temperature.

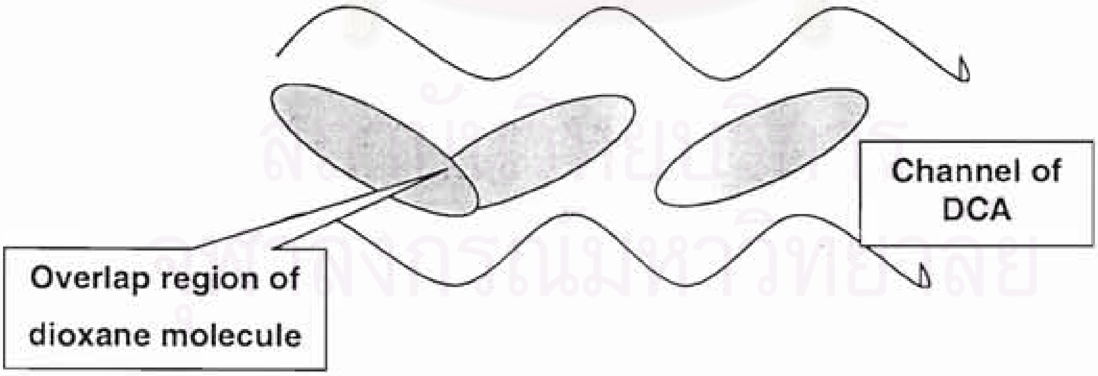


Figure 18. Schematic representation of dioxane guest overlapping in DCA channel.

4. Thermal Stability and the Effect to Host-Guest Ratio

As mentioned in the previous section, in the case of DCA-ethyl acetate, the obtained crystal shows host guest ratio in the range of 3:1, however, after the crystal is left for a long period, host guest ratio is changed to 6:1. This may be due to the stability of guest in the channel. After long period, the dynamic guest can be excluded from the channel while the static guest is still maintained. As a result, the host guest ratio is changed to stabilize at 6:1 ratio. The molar ratio between host and guest and guest releasing point are summarized in Table 2.

Table 2. 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

5. Solvent Free (Guest Free) DCA and Its Properties

The unique feature of DCA in the inclusion compound application is the stability of guest free DCA crystal. Hence, host guest compound can be prepared by guest absorption method, which is very useful for the guest that can not be directly recrystallized with DCA. The structural analysis of guest free DCA is done by FTIR.

As shown in Figure 19, DCA-*o*-xylene crystal can be completely removed guest to form guest free DCA crystal as confirmed by FT-IR.

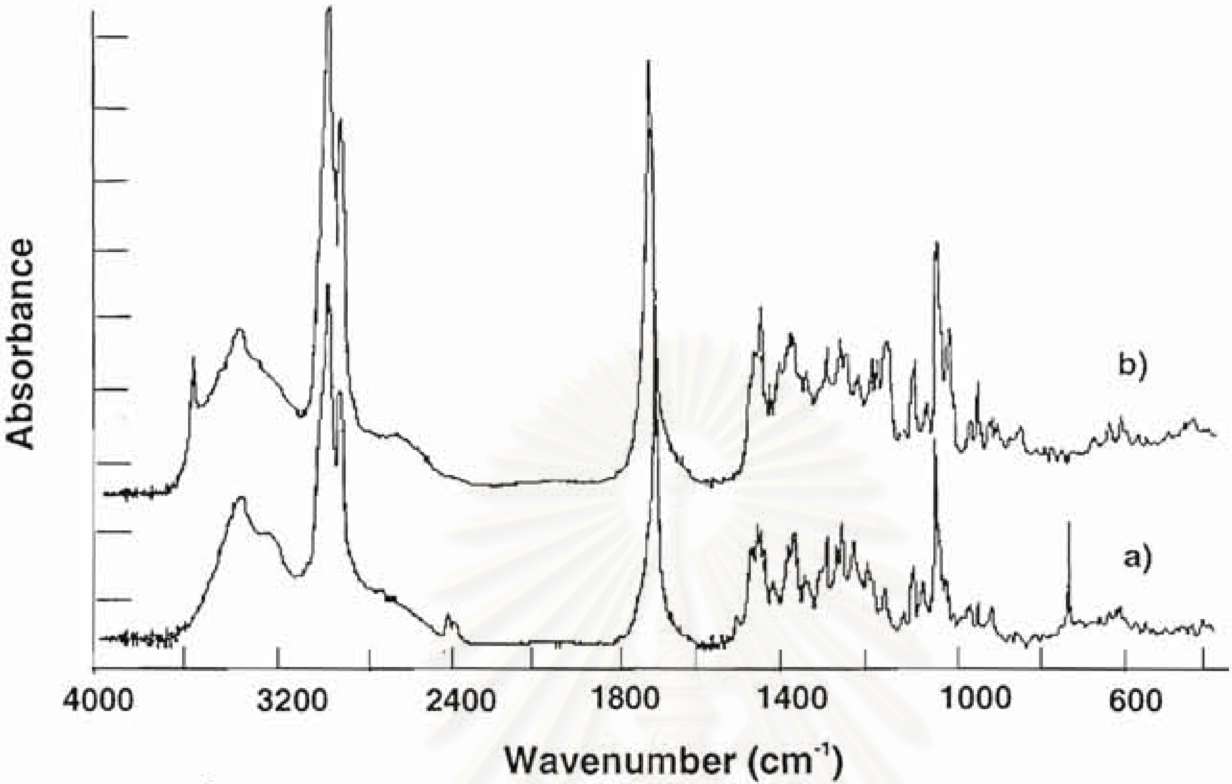


Figure 19. FT-IR of a) DCA-*o*-xylene inclusion compound, and b) after evacuation under pressure for a day at 140 °C.

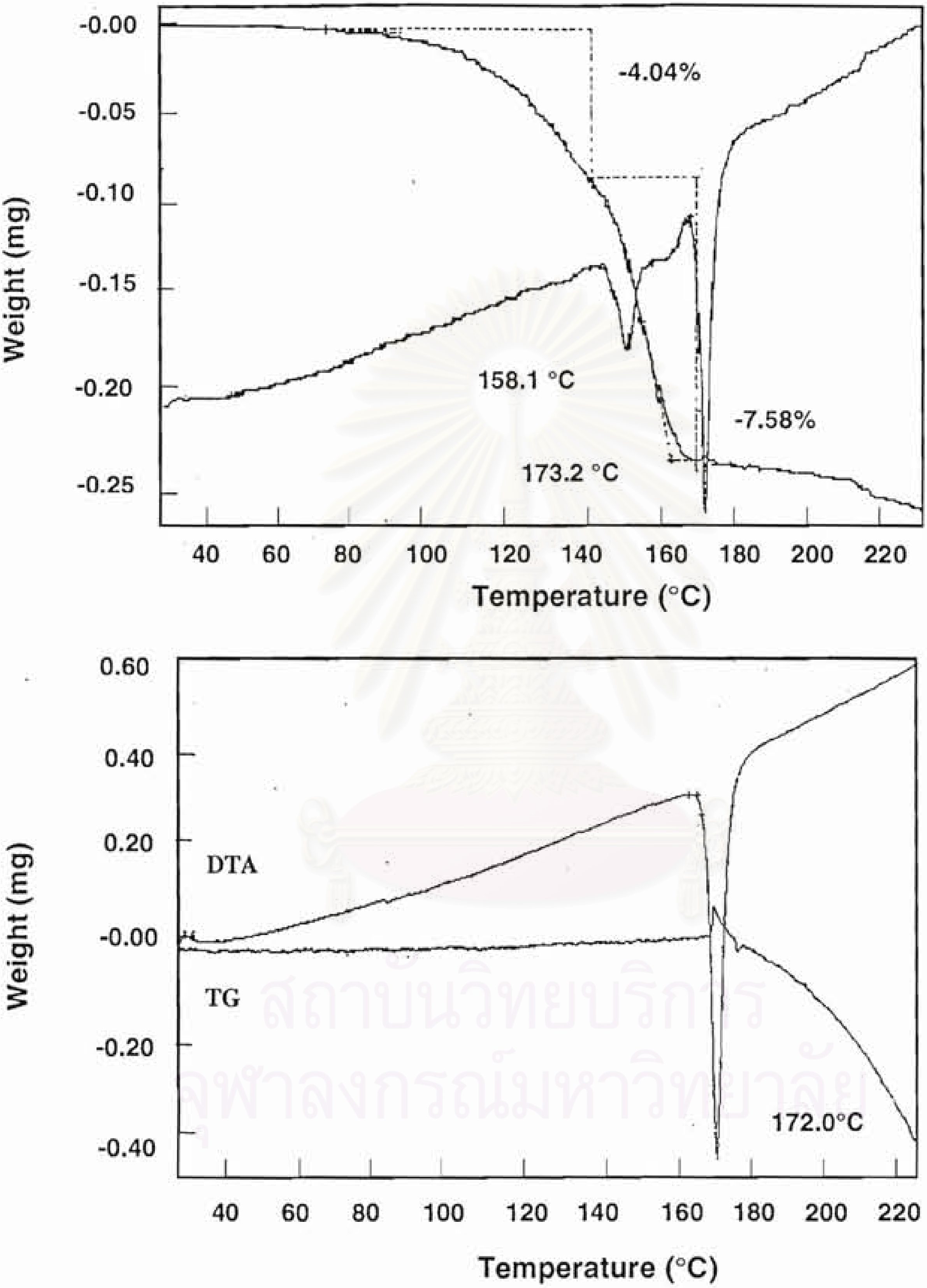


Figure 20. Thermal stability of DCA-*o*-xylene (top), and after exclusion *o*-xylene to be a guest free DCA (bottom).

When DCA-*o*-xylene crystal was vacuum dried, TGA shows the same peak as same as DCA, suggesting that the crystal is guest free DCA inclusion compound (Figures 19 and 20).

Similarly, in the case of other solvents; dioxane, and ethyl acetate, the solvent free DCA inclusion compounds were achieved and can be confirmed by TGA (Figure 21-22). FT-IR appears to be as DCA starting material, which also supports that guest removal is successful.

XRD study is another alternative way to confirm guest free DCA. Here, the results also support that the removal of guest *o*-xylene from DCA-*o*-xylene is successful as shown in Figure 23. It should be noted that the XRD pattern of DCA starting material and the solvent free DCA is similar. Guest movement and intercalation system is found in most cases of cholic acid and its derivative host compounds. Miyata et al. reported that the inclusion crystal of cholic acid with a former guest would allow the latter guest intercalated by a movement of guest. XRD study shows that cholic acid will allow the crystal layer slide without losing their crystalinity or changing to amorphous[25].

However, the solvent free DCA is maintained in crystal form while the starting material, which is the powder. In the present case, DCA with guest is found to be a transparent crystal and the crystal structure is maintained even after evacuation guest to obtain the blank solvent free (or guest free) DCA. In this step, the crystal appears to be a white needle crystal. XRD pattern shows that the white needle crystals lose their crystallinity and changes to the original amorphous structure (Figure 23).

After the guest free DCA is immersed with another guest, XRD pattern shows that the crystal pattern is appeared again related to the type of the guest (*see DCA inclusion compound adduct by absorption technique; DCA-trichloroethylene, Figure 28*). This implies that the amorphous structure of DCA host can change to the crystal structure by guest absorption. The XRD pattern informs that after guest absorption DCA host will arrange the packing to be a high crystallinity again.

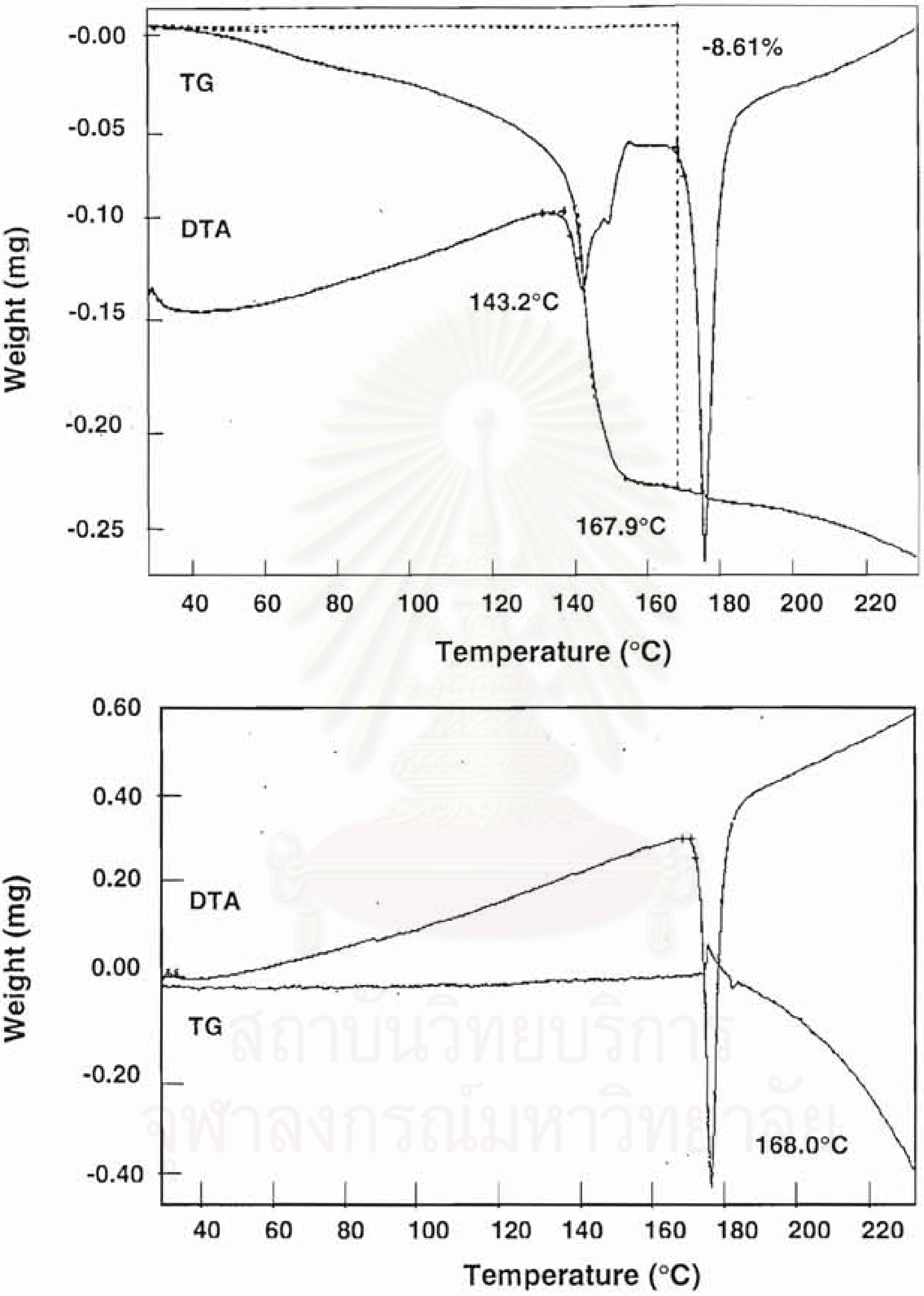


Figure 21. Thermal stability of DCA-dioxane (top), and after exclusion dioxane to be a guest free DCA (bottom).

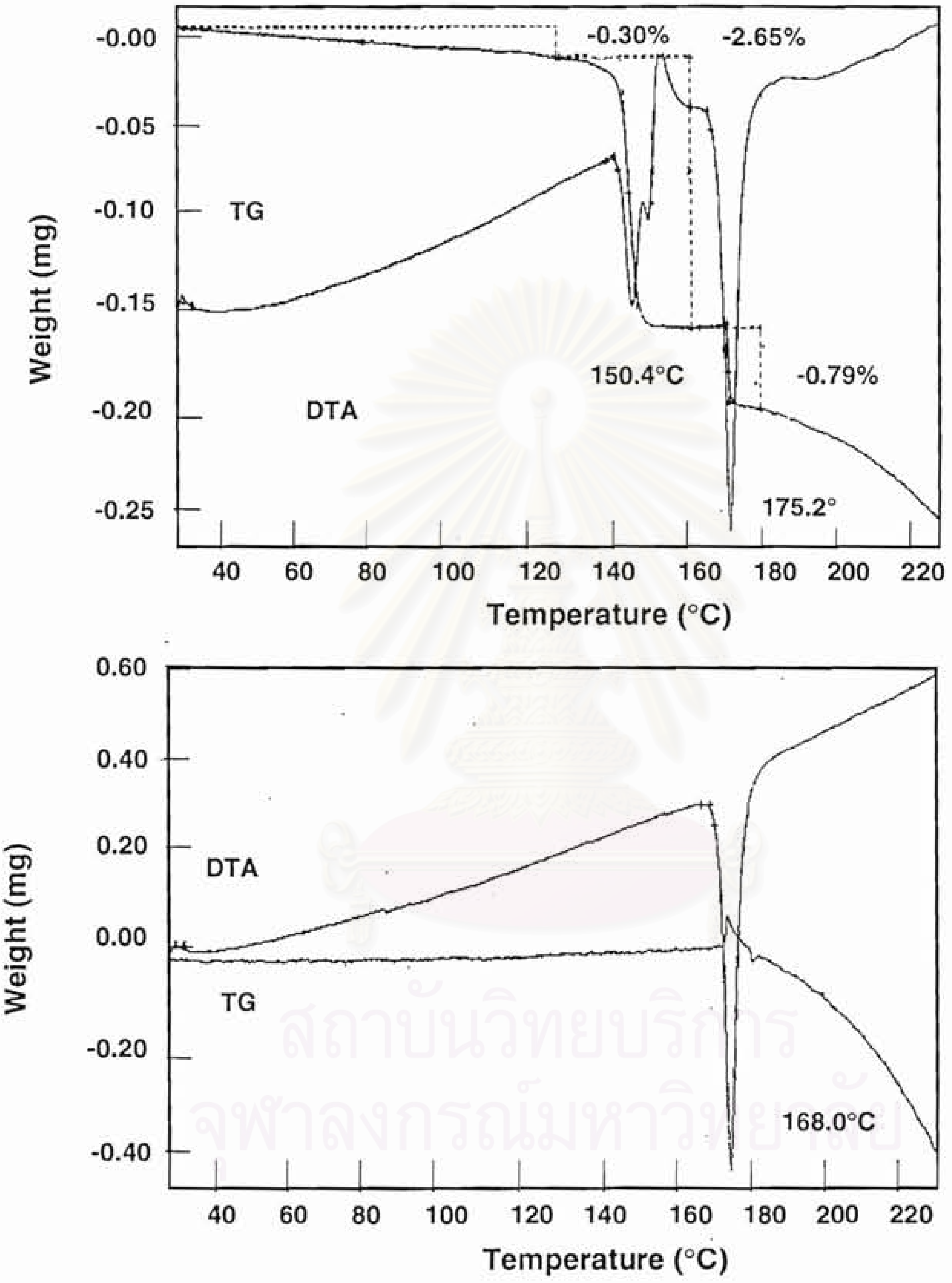


Figure 22. Thermal stability of DCA-ethylacetate (top), and after exclusion ethyl acetate to be a guest free DCA (bottom).

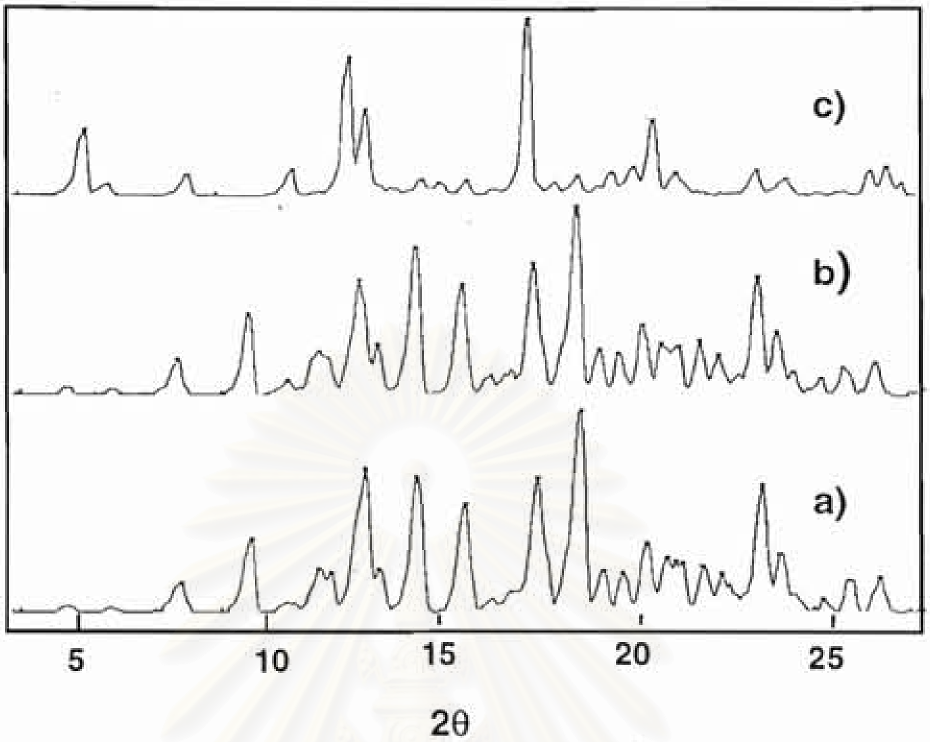


Figure 23. XRD pattern of a) DCA, b) solvent free DCA after exclusion *o*-xylene, and c) DCA-*o*-xylene.

6. DCA Inclusion Compound by Absorption Technique; DCA-trichloroethylene System as a Model for DCA-VCM

Owing to the property of vinyl chloride monomer for its volatility and the low boiling point (-13.4°C), the preparation of inclusion compound via recrystallization of DCA/ vinyl chloride monomer can not be achieved by the ordinary recrystallization procedure. Yoshii et al.[20] reported the preparation of urea/vinyl chloride monomer by mixing urea and vinyl chloride monomer in low temperature for a period of 50 hours and claimed as an inclusion complex. However, the stability of the host-guest compound and the ratio between host and guest were not mentioned.

It should be noted here that DCA host compound is an inclusion compound that can form stable host crystal and prepared as a guest free host crystal via vacuum drying of the crystal of DCA-guest compound. Tsutsumi et al.[11] proposed the preparation of monomer-DCA adduct by the chemisorption of the monomer into guest free inclusion compound of DCA, so called insertion technique. 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 DCA host molecule, the insertion 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, the crystals have to be kept in low temperature. Thus, it is very difficult to study for the structural analysis and thermal properties of DCA-VCM by FT-IR and TGA techniques.

In preliminary studies, trichloroethylene that has the structure similar to vinyl chloride monomer is applied as the guest molecule. Here, methyl methacrylate is (MMA) also used for reference study since it is easy to handle.

Firstly, DCA guest free crystal was prepared via vacuum drying DCA/ethyl acetate crystal. The obtained crystal was then left in MMA or ethyl acetate for the insertion process. The guest absorption behavior was observed by FT-IR, TGA and XRD.

In the case of DCA-MMA system, as shown in Figure 24, the hydrogen bond of DCA and the fingerprints are changed indicating that the insertion of MMA is successful. Figure 25 shows the stability of MMA in DCA. Here, the MMA weight loss peak for 8% is appeared at 170 °C relating to the period of soaking temperature.

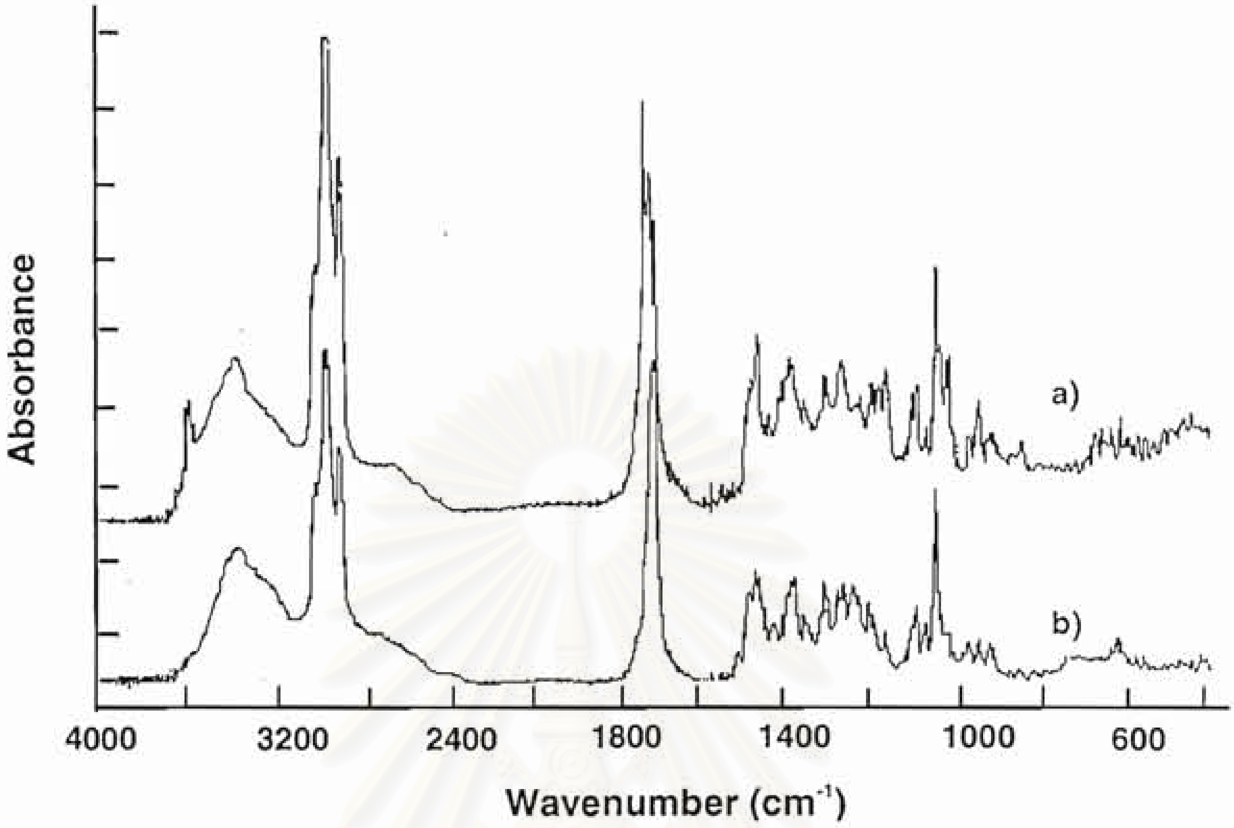


Figure 24. FT-IR of a) solvent free DCA obtained from DCA-*o*-xylene, and b) DCA-MMA after MMA absorption for over 3 days.

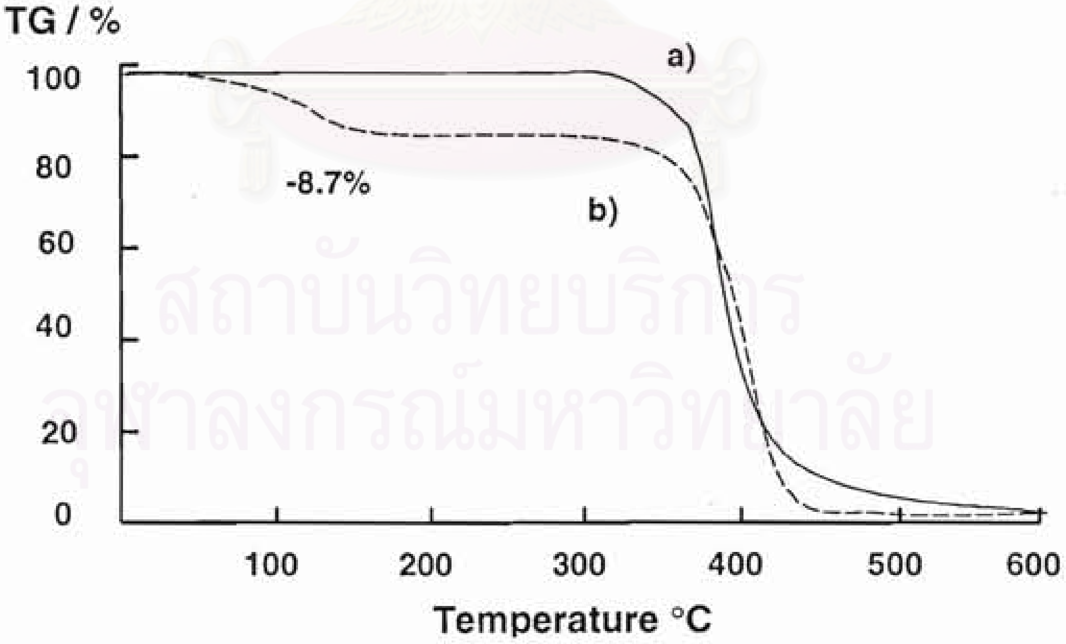


Figure 25. Thermal stability of a) guest free DCA crystal (obtained from DCA-*o*-xylene), and b) DCA-MMA after MMA absorption for over 3 days

The absorption behavior of trichloroethylene was also studied. FT-IR confirms the hydrogen bonding of DCA and guest peaks referring to trichloroethylene (Figure 26).

Thermal analysis (Figure 27) indicates that in either case the trichloroethylene guest is included in the DCA host cavity with the weight percent of (6-8%) and is stable at the temperature of 170-190 °C.

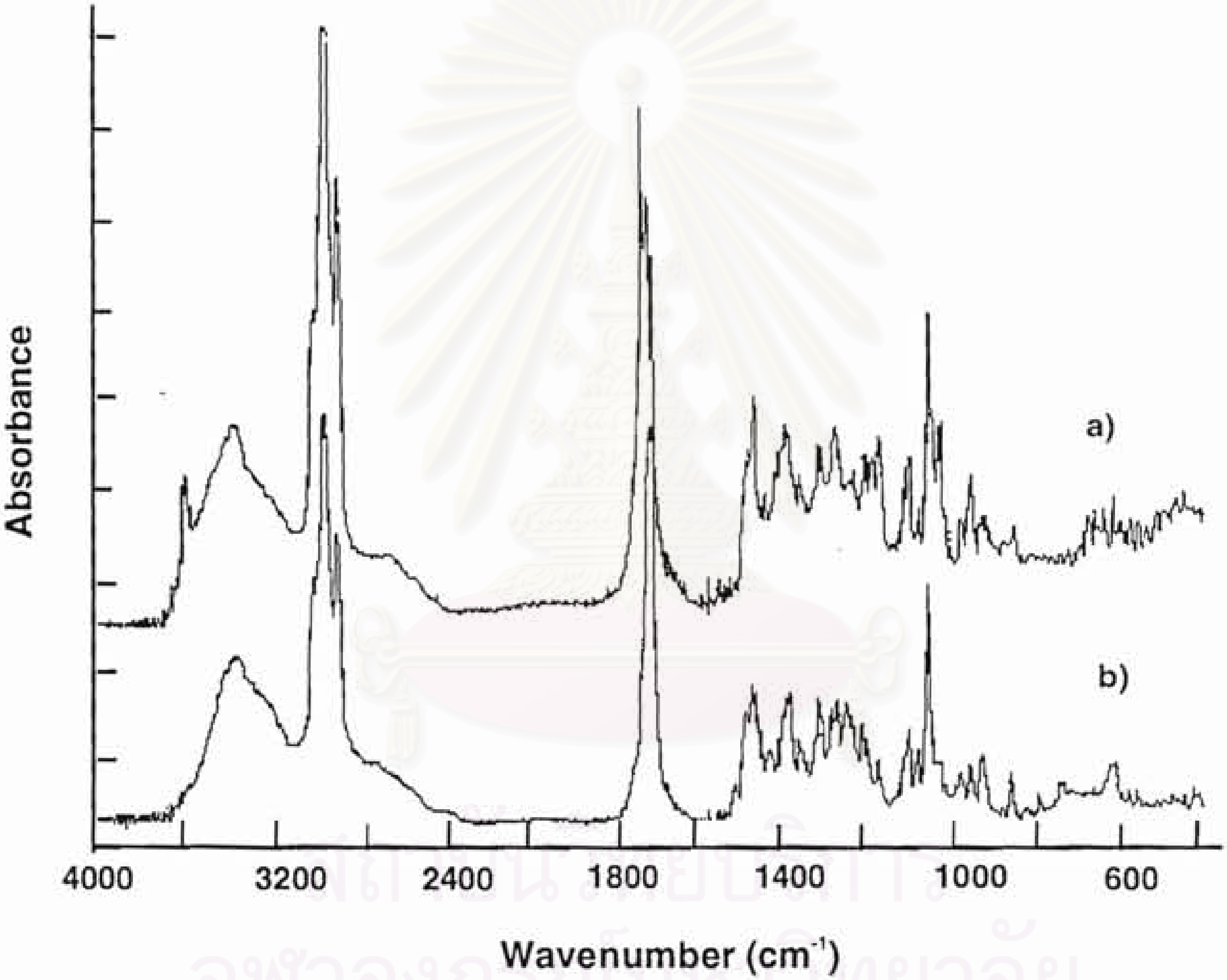


Figure 26. FT-IR of a) solvent free DCA prepared from DCA-o-xylene, and b) after immersion in trichloroethylene for 3 days.

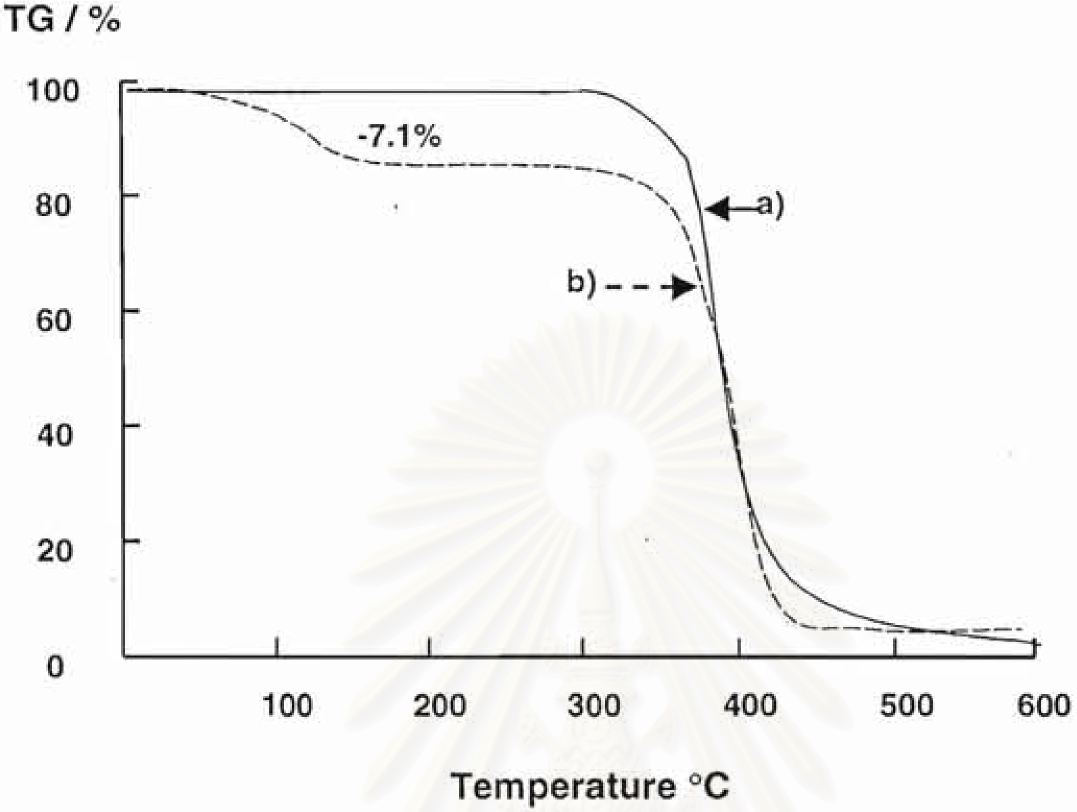


Figure 27. Thermal stability of a) guest free DCA crystal (obtained from DCA-*o*-xylene), and b) after soaking in trichloroethylene at room temperature for over 3 days.

XRD pattern indicates that DCA entraps trichloroethylene with a certain crystal structure (Figure 28). It is confirmed that DCA starting material shows the same XRD pattern with guest free DCA. This implies that though opaque needle crystal is obtained after exclusion guest out completely, the microstructure of the solvent free crystal is amorphous. 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 crystal structure again.

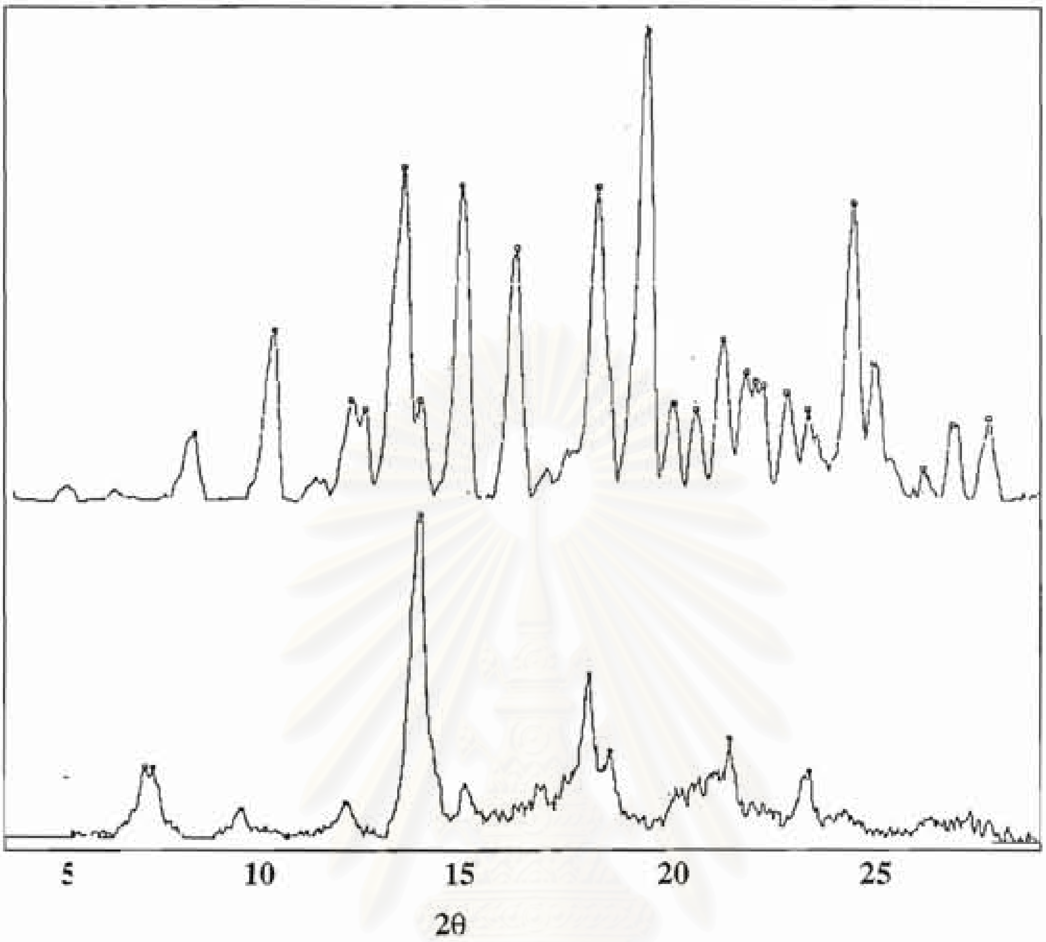


Figure 28. XRD pattern of solvent free DCA, (top) and DCA-trichloroethylene (bottom).

7. DCA-VCM Host-Guest Compound, Properties and Structural Analysis

Owing to the instability of VCM, it is difficult to study DCA-VCM host guest compound obtained from intercalation method by normal analytical approaches such as FTIR, TG/DTA. An attempt to study the absorption of vinyl chloride monomer into the DCA guest free host is done. As mentioned in previous section, the crystal has to be kept in low temperature owing to the volatility of vinyl chloride monomer, thus, microscope FT-IR technique is applied to observe DCA-VCM directly without grinding DCA-VCM to prepare as a KBr pellet to avoid the guest evaporation.

Vinyl chloride monomer was cooled in a glass tube within liquid nitrogen. The guest free DCA crystal obtained from recrystallization by *o*-xylene were left with liquid nitrogen to progress insertion process for two days in vacuum atmosphere.

Microscope FT-IR (Figure 29) shows that DCA forms the inclusion compound with VCM which can be concluded by considering the characteristic referring to changing of DCA characteric peaks, i.e., OH peak at peaks at 3600 and singlet peak at 1700 cm^{-1} (see in Figure 7).

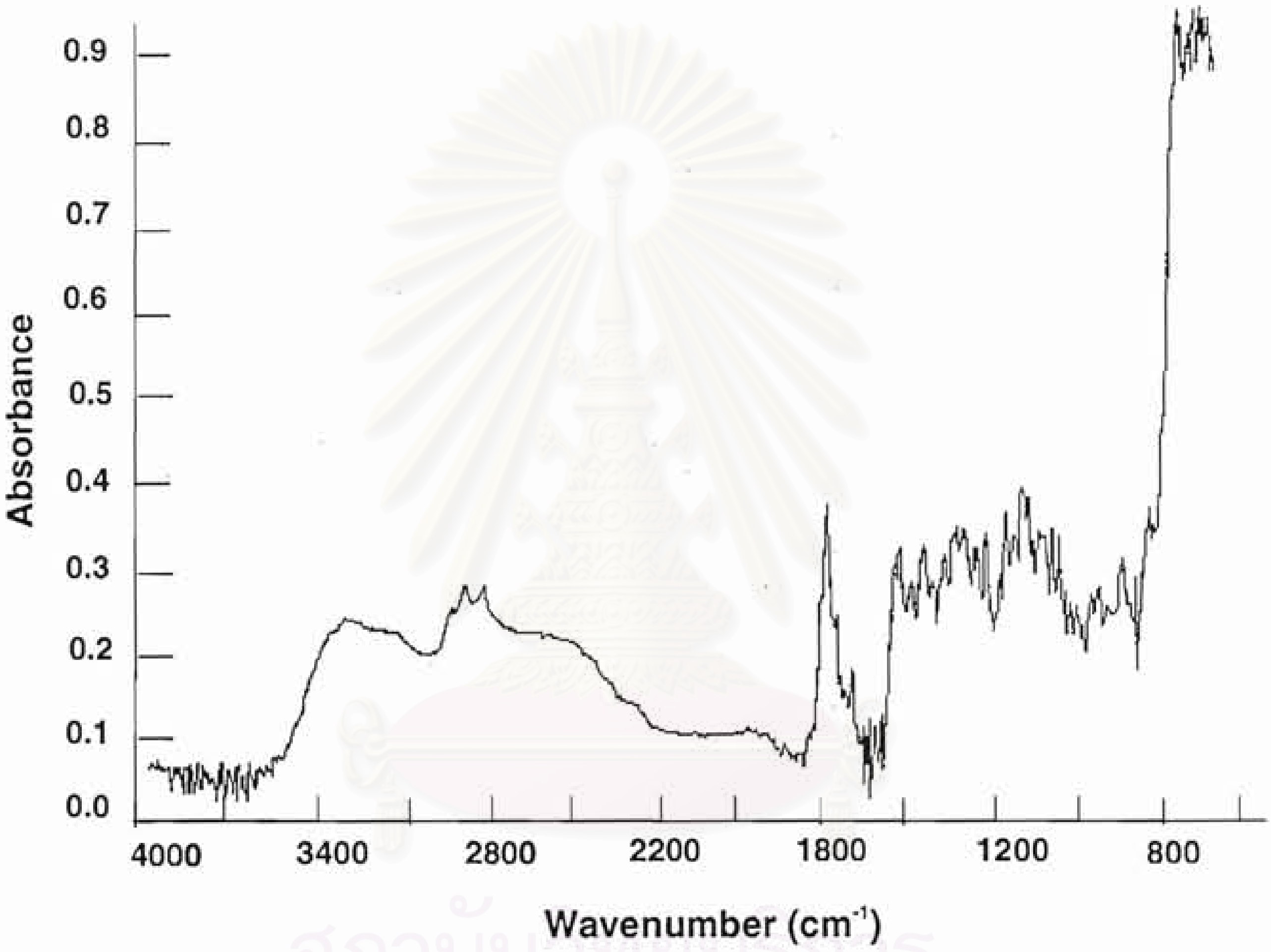


Figure 29. Microscope FT-IR of DCA crystal after immersion in liquidified VCM for over 3 days.

Low temperature DSC was also applied to observed the DCA-VCM formation. As shown in Figure 31, the DSC analysis of the DCA-VCM adduct was carried out from –20 to 200 °C to define the VCM releasing point of the DCA-VCM. It is found that VCM releasing point of the DCA-VCM adduct is broad in the range of 40-60°C.

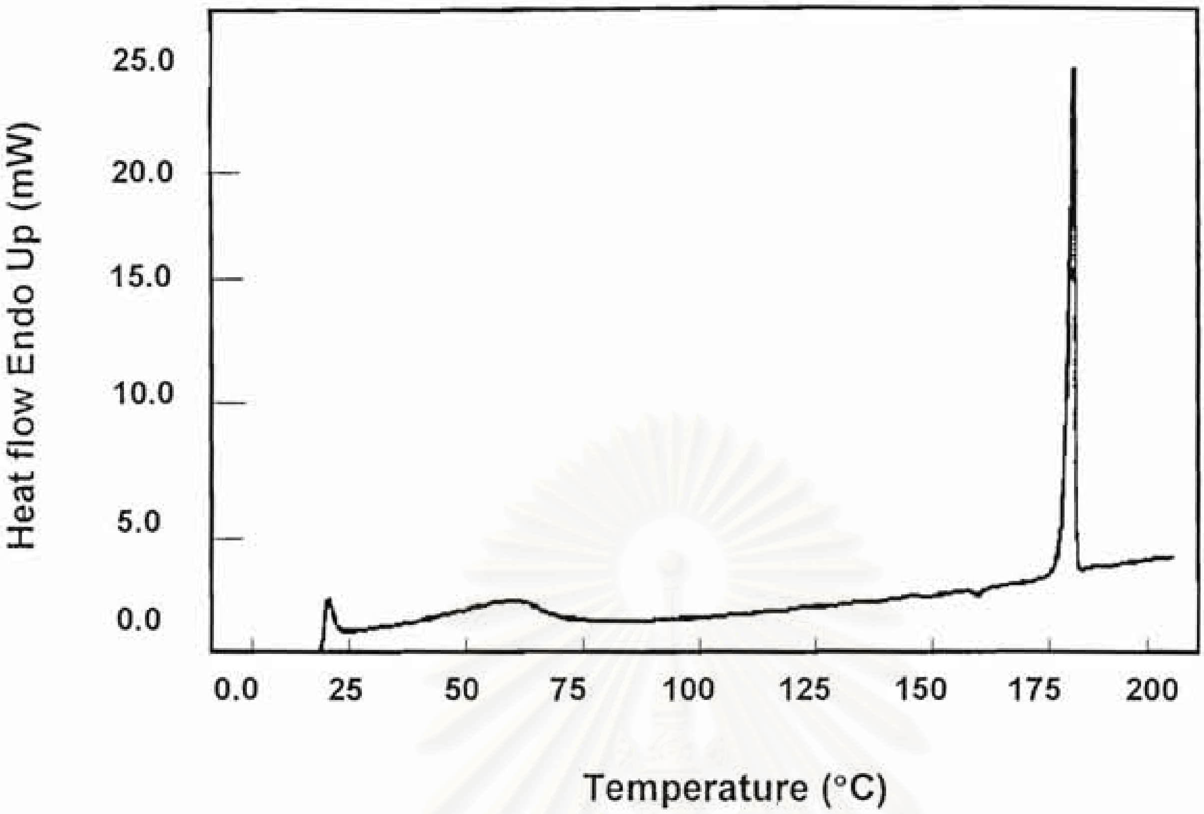


Figure 30. DSC thermogram of DCA after immersion in liquidified VCM for over 3 days.

8. Effect of γ-ray on the Inclusion Polymerization of DCA-VCM

Table 3. Amount of γ -ray and the induced polymer properties.

γ-ray	Mn	Mw	MWD	%yield PVC/CA (g/mol)
10	2808	7322	2.61	4.54
20	2809	7178	2.55	7.77
30	4926	14304	2.9	59.53
40	-	-	-	86.84

It is known that inclusion polymerization be effected by the host channel and the energy level of γ-ray to accelerate the inclusion polymerization, here, the effect of γ-ray on the inclusion polymerization was studied by varying the amount of γ-ray.

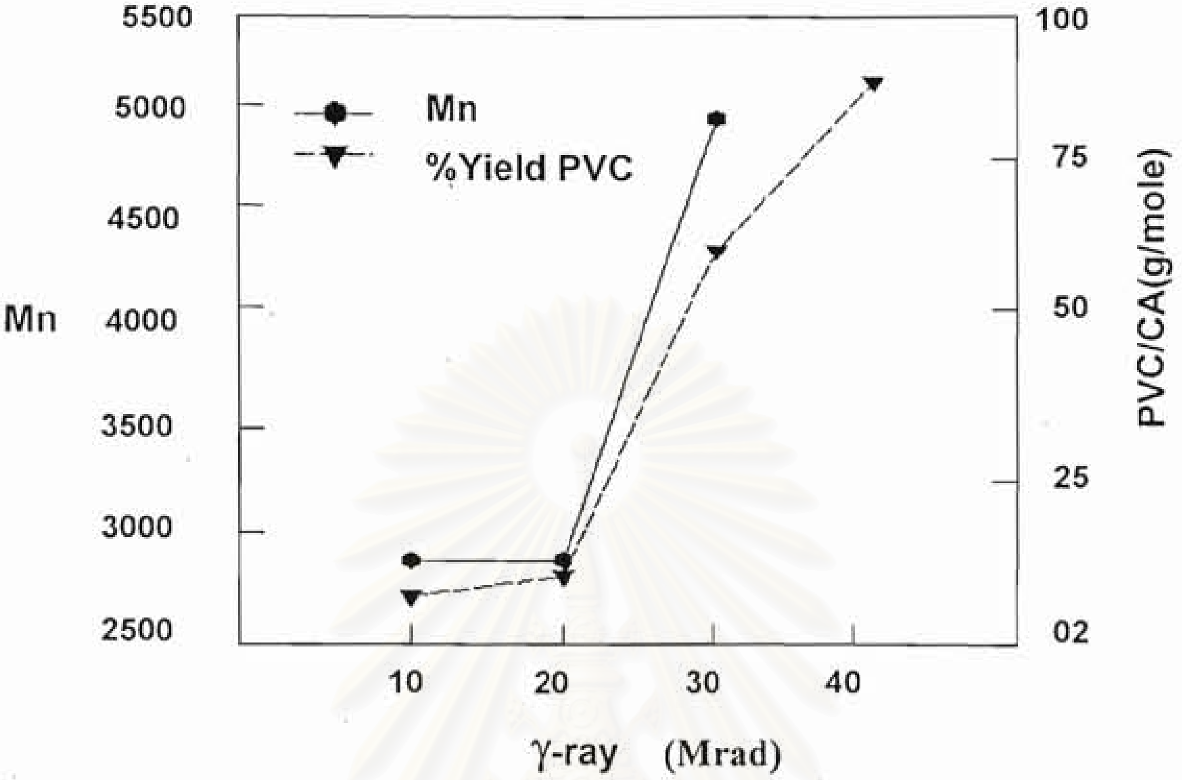


Figure 31. Effect of γ-ray on inclusion polymerization of DCA-VCM.

As the amount of γ-ray increased, the high molecular weight polymer was obtained with the high yield, however, the distribution of polymer species is also increased significantly (Table 3 and Figure 31). These results can be referred to the effect of γ-ray that it is not only on the production of the radical species to enhance the polymerization but also the degradation of polymer chains. It is found that the yield of PVC was as high as 80% yield when the amount of γ-ray was 40 Mrad.

9. DCA-VCM Inclusion Polymerization and Study on the Resulting Polymer

After irradiation, DCA-VCM crystals are expected to change to DCA-PVC crystals. Thermal stability study on the DCA-VCM after irradiation indicates that the releasing point of the obtained product from the host is at 145 °C (Figure 31). It is found that guest releasing temperature is rather high than PVC. This may be related to the consumed energy to exclude the guest from the packing layer of DCA host. FT-IR of the iradiated crystal (Figure 32) implies that DCA entrapes a gues. However, the guest peaks can not be clarified as a PVC until purification on the irradiated host-VCM adduct were done.

In order to confirm the successful of inclusion polymerization for the DCA-VCM host-guest compound to obtain PVC. The obtained crystals were analyzed after the washing thoroughly with methanol to exclude DCA host. It is found that white precipitate was appeared when DCA-VCM crystal were washed with methanol. The amount of the obtained PVC is found to be 10 mg for each 1.0 g of DCA inclusion crystal as confirmed by the weight measurement before and after irradiation process. The white precipitate was collected to analyze the structure.

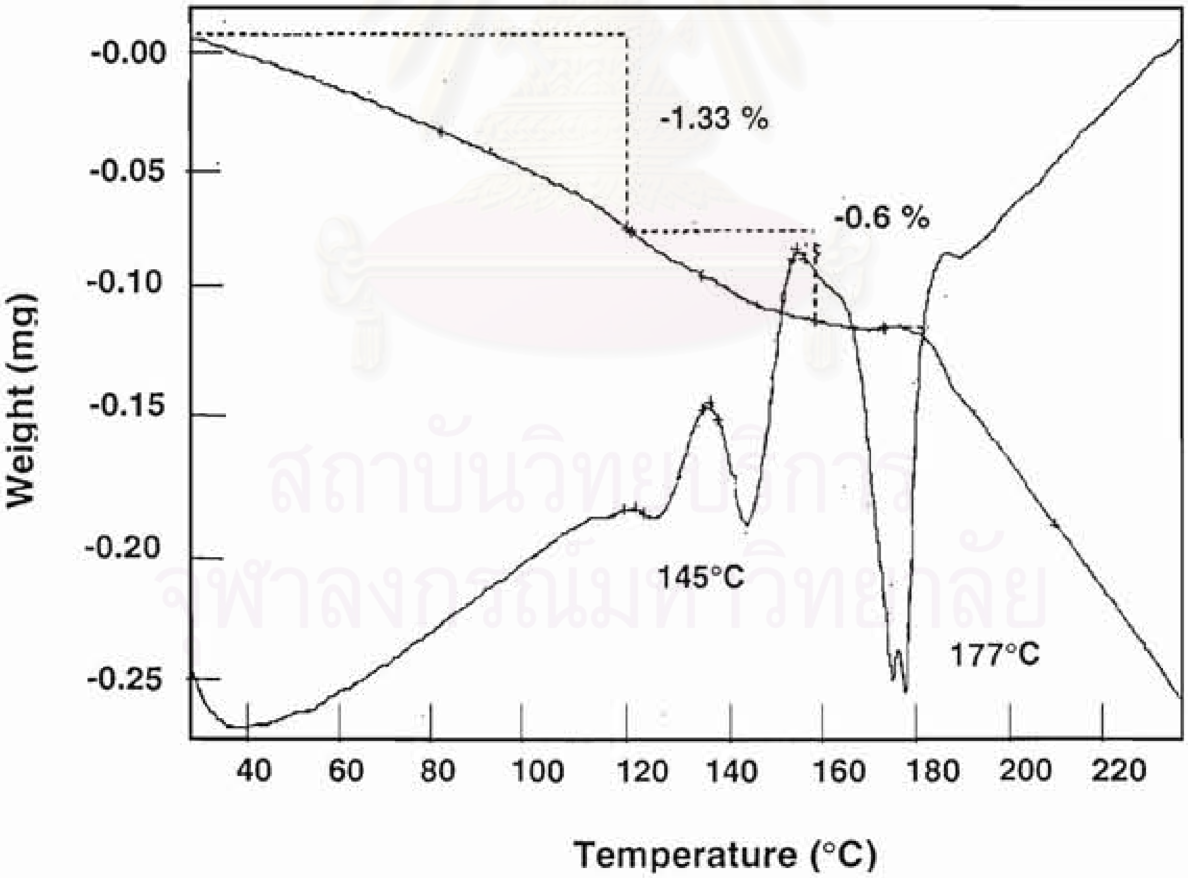


Figure 32. TG/DTA of DCA-VCM resulting crystal after irradiation.

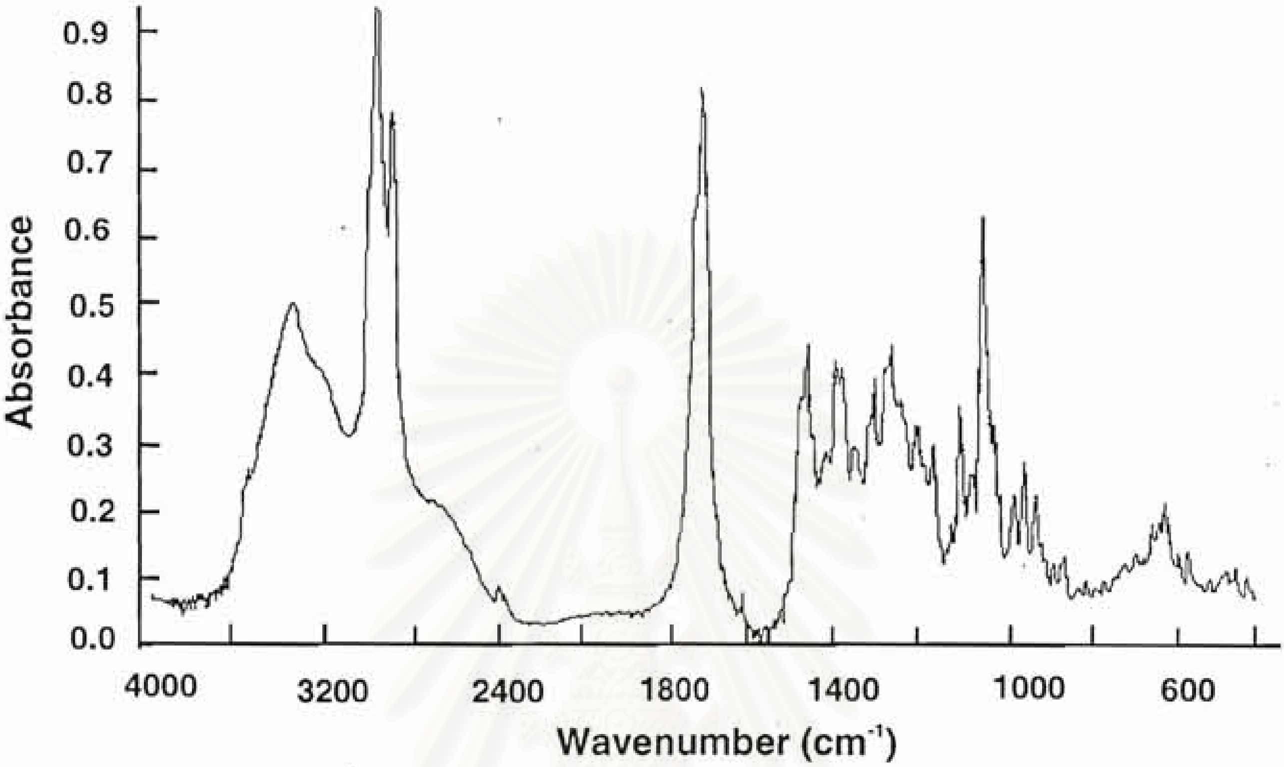


Figure 33. FT-IR of DCA-VCM resulting crystal after irradiation.

Comparing the FT-IR spectrum (Figure 33) of the PVC obtained by the inclusion polymerization to the commercial poly(vinyl chloride), the resulting polymer can be concluded as poly(vinyl chloride). It should be noted that there are some differences of 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 sharp peak while the commercial PVC shows the methine (CH) broad peak at 1250 cm^{-1}. Moreover, other observed peaks are relatively sharp peak comparing to the peaks of he commercial one. These sharp peaks indicates that the resulting polymer may have specific structure owing to the higher regularity than the commercial PVC.

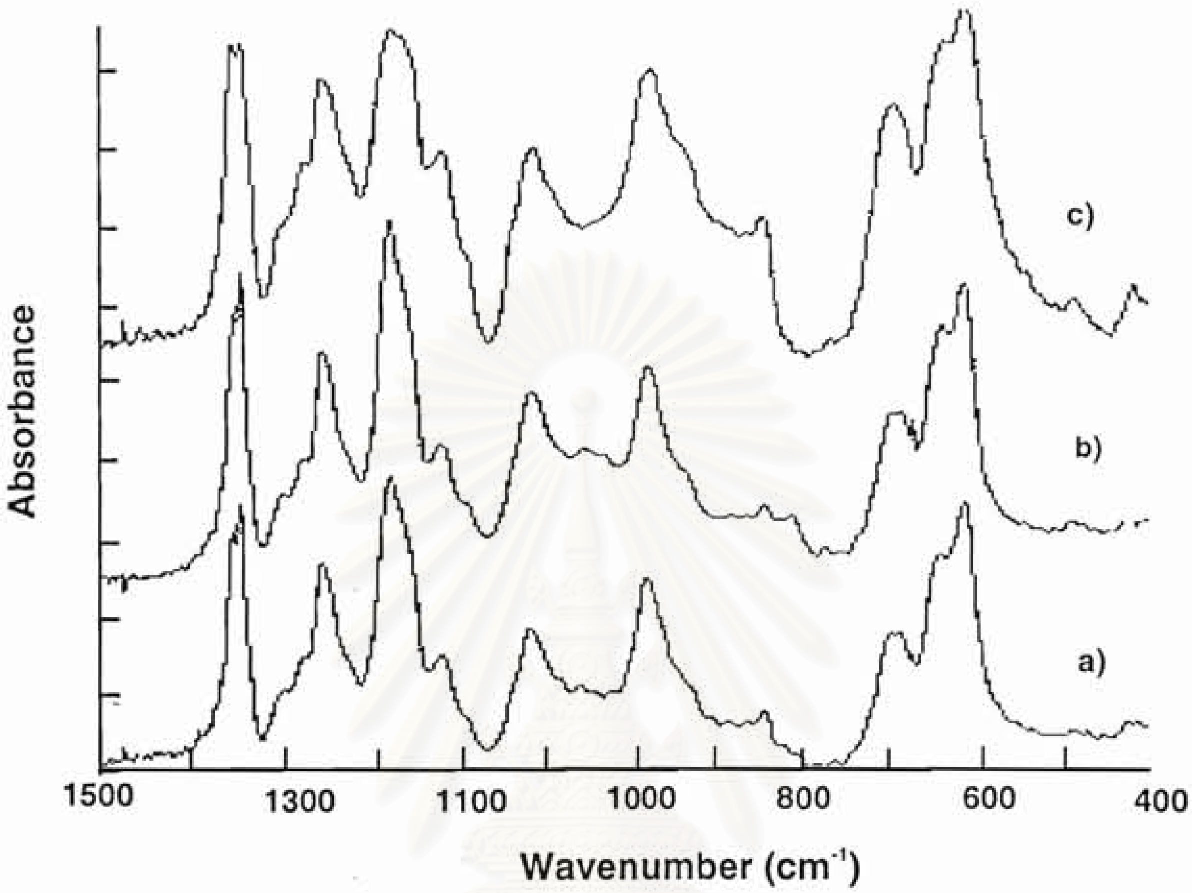


Figure 34. FT-IR of a) the obtained product after washing the irradiated DCA-VCM prepared from DCA-dioxane, b) the obtained product after washing the irradiated DCA-VCM prepared from DCA-ethyl acetate, and c) commercial PVC.

It should be noted that two types of solvent free DCA (Figure 33 a and b) give the similar result of the product PVC. This means that the channels provided from both solvents contribute no different for VCM alignment in the channel.

Thermal stability study by DSC shows that the glass transition temperature (Tg) of the obtained PVC is at 101° (Figure 35) which is slightly higher than that of commercial PVC (at 87°)(Figure 34).

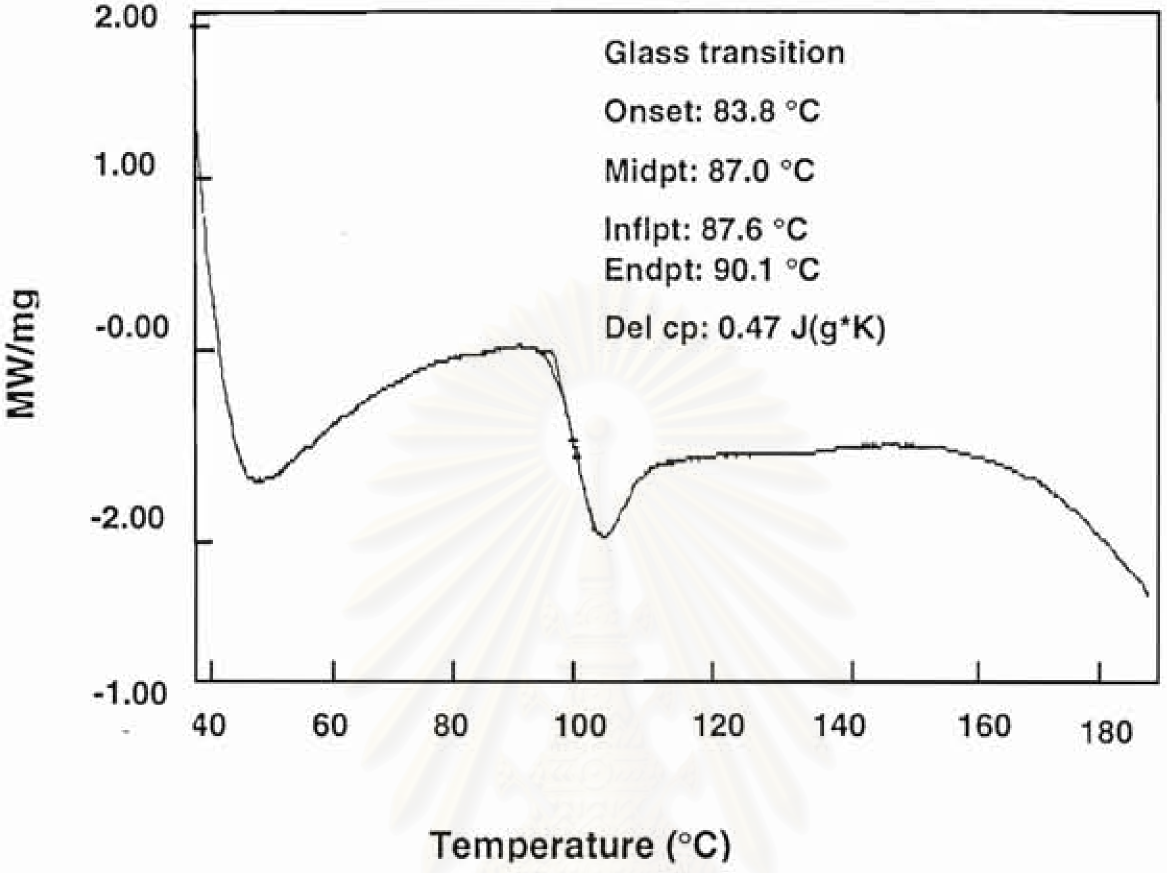


Figure 35. DSC thermogram of the commercial PVC.

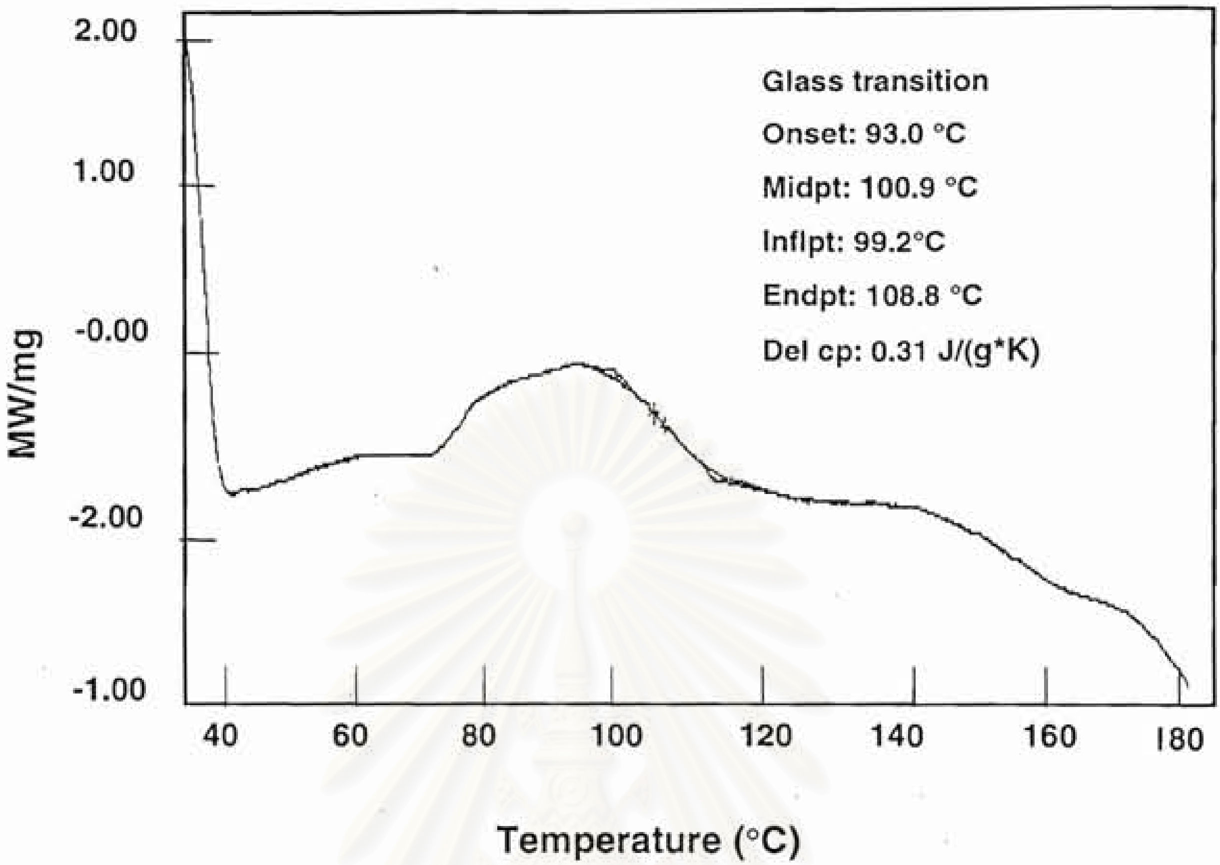


Figure 36. DSC thermogram of the obtained product from irradiated DCA-VCM.

However, in the case of the obtained PVC, the range of Tg is broader than the commercial one, which may be due to the broad distribution of the regularity in the product. The obtained PVC does not show the melting temperature, which indicates that it may not be the complete crystalline polymer.

Solubility is another approach to evaluate the differences in structure between the obtained PVC and the commercial PVC. Certain solvents are used for the study on solubility, i.e. tetrehydrofuran, cyclohexanone, and benzene-acetone mixture. The solubility testing results are summarized in Table 3.

Table 4. 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	√	x	√	×
Cyclohexanone	×	×	√	√
Benzene-acetone mixture	×	×	√	×

√ = Soluble and × = insoluble

The solubility testing indicates that the obtained PVC is more difficult to dissolve in good solvents for PVC, except for cyclohexanone at elevated temperature. 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 3[20]. This can be concluded that the obtained PVC may have some level of stereoregularity different from either the commercial PVC or the obtained PVC from urea host.

Here, ESR measurement was conducted. The ESR spectra of the obtained PVC and the commercial PVC at 187 K and 273 K are shown in Figure 36 and 37, respectively.

There are some different parts in ESR spectra between commercial PVC and the inclusion polymerized PVC. Here, if free radicals created on the polymer chain by irradiation have different environment of polymer chain, the obtained ESR pattern will be different. As shown in Figure 6, the spectra obtained at 183 K are similar to each other. However, when the temperature is increased to 273K, a shoulder peak on 2350 G appears (Figure 37). This can be explained as follows, at 183 K, the free radicals movement is rather restricted, which makes the position that the appeared free radicals created be the same. However, at 273 K, the movement of the radicals is more freely than at 183 K and the shoulder peak is appeared. This can be concluded that the microstructure of the obtained PVC shows some differences in the regularity.

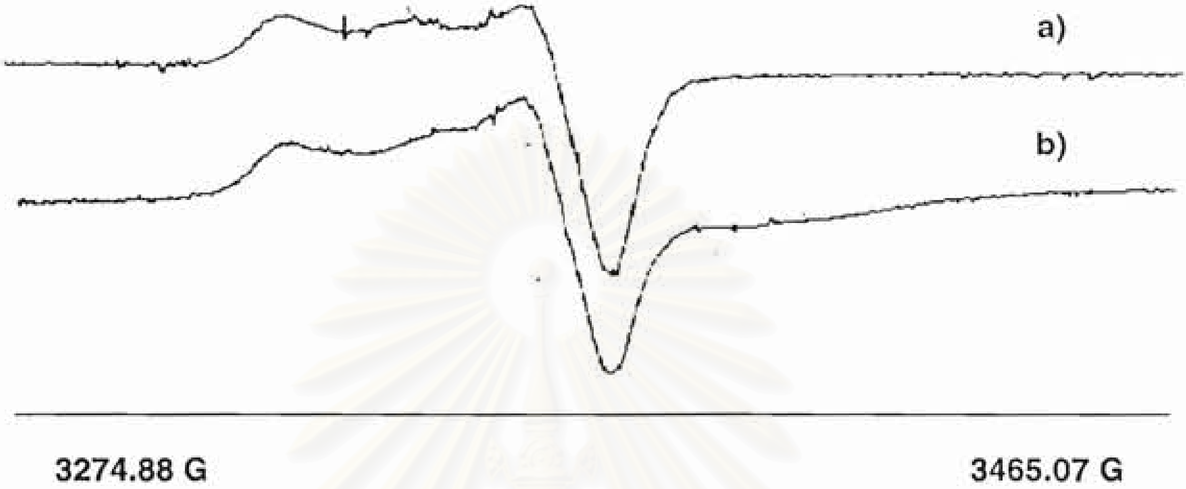


Figure 37. ESR spectra at 183 K of irradiated PVC, a) the obtained product from irradiated DCA-VCM, and b) the commercial PVC.

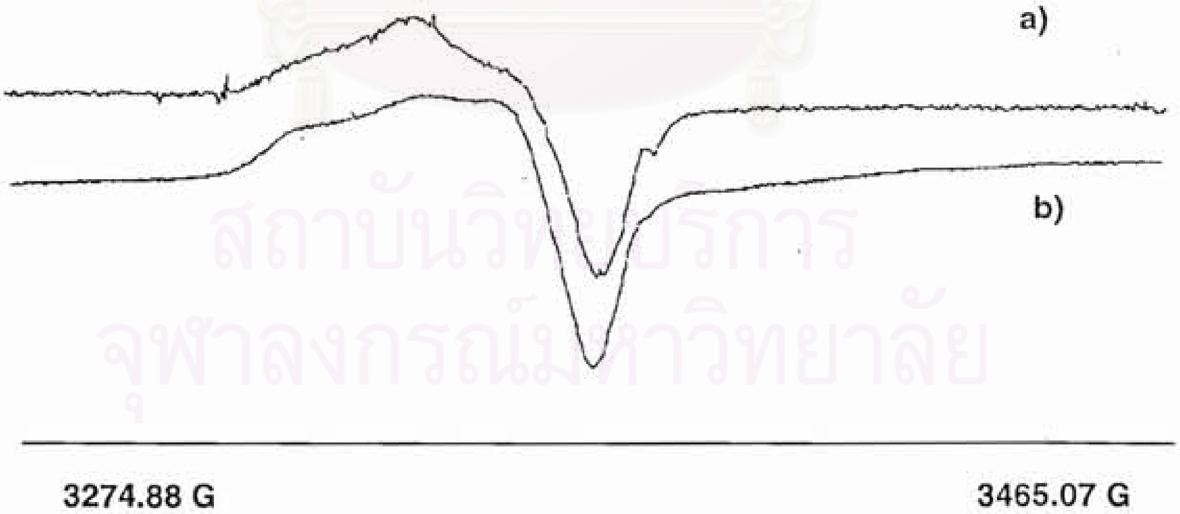


Figure 38. ESR spectra at 273 K of irradiated PVC, a) the obtained product from irradiated DCA-VCM, and b) the commercial PVC.

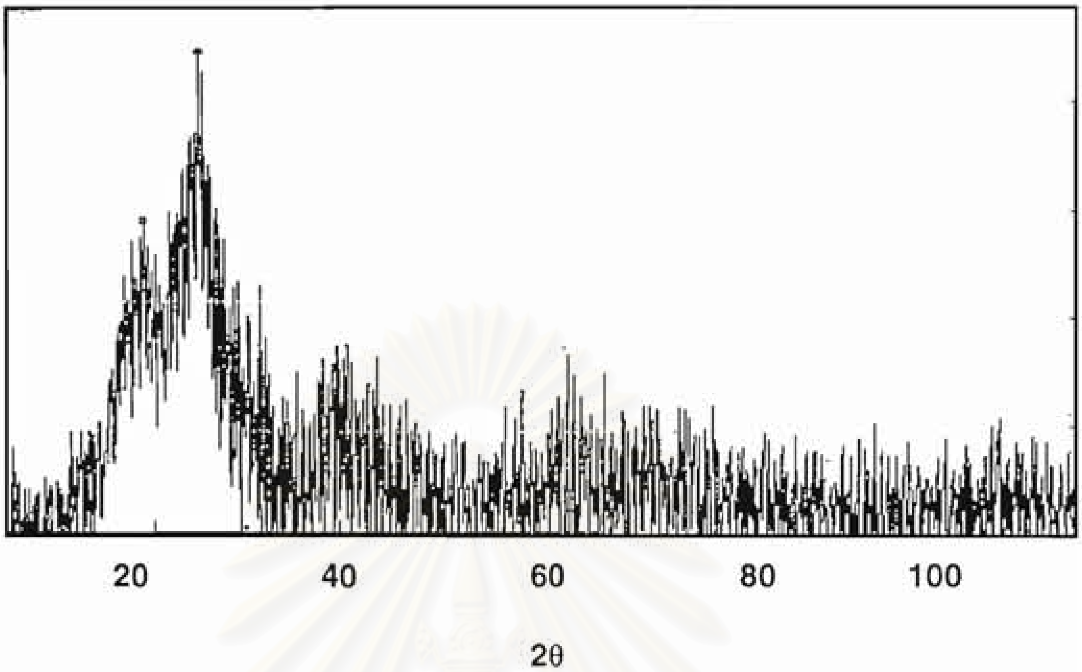


Figure 39 XRD pattern of the commercial PVC.

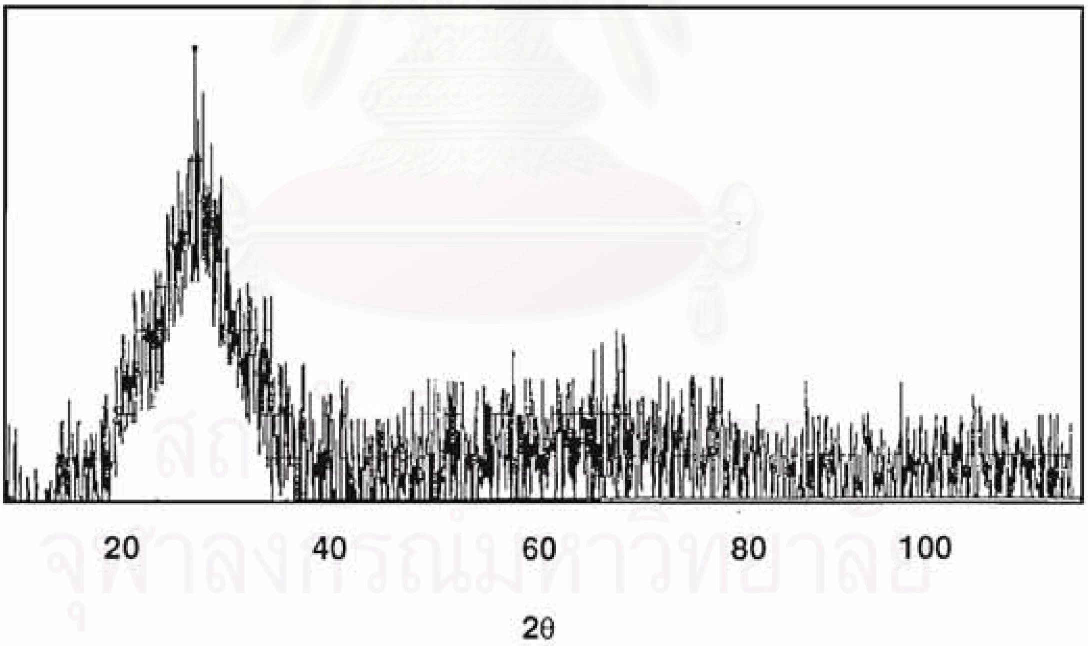


Figure 40 XRD pattern of the obtaining PVC.

Structural analysis was also done by XRD. As shown in Figure 38 and 39, the obtained polymer shows one major peak at 30° and a slight peak at 70°, while the commercial PVC shows the peak at 20°, 30° and sub peaks at 40° and 80°. This implies that the structure of the obtained product be more regularity. However, the broadening of the peaks in all ranges informs that the regularity of the obtained polymer is still based on the amorphous phase.

With specific software, the XRD analysis can be evaluated for the amorphous phase and crystalline phase to determine the degree of the crystallinity in the overall polymer chain. However, when there is no concerned with the broadening of the peaks, for the obtained polymer, by using Braggs' Law, the spacings of groups of atoms can be calculated to get the average distances of 0.4~0.5 nm.

In order to clarify the crystallinity and the regularity, another approach can be proposed. Generally, regularity of the polymer effects the solubility of the polymer in good solvents at a certain temperature, i.e., the higher regularity with high molecular weight, the solubility will be decreased and tends to precipitate out from the system. Thus, it can be expected that the obtained polymer can be extensively studied in the stereoregularity and the degree of crystallinity.

CHAPTER 4

Conclusions

Although polyvinyl chloride has been known for over 3 decades, the development of polyvinyl chloride did not received much attention. This due to the preparation process, which is a radical polymerization of vinyl chloride monomer, limits the polyvinyl chloride about its property and the stereospecific structure to be only random polymer and as an amorphous structure. However, inclusion polymerization is an alternative way to propose as a space dependent radical polymerization to obtain a controlled structure of polyvinyl chloride.

DCA is found to be a useful host compound owing to two main reasons. Firstly, DCA can be prepared as a solvent free DCA host structure, which is very stable in the form of opaque needles-like crystal. Secondly, DCA solvent free host will allow another guest molecule to penetrate inside and, thus, DCA-VCM can be prepared successfully by guest absorption technique.

Radical polymerization by γ-radiation is proven to generate PVC from the DCA-VCM. Structural analysis of the resulting polymer based on stereospecific structure concluded that the obtained PVC is found to be a mixture of stereoregularity products. It is to our interest in the future work to focus on the purification of the product by using critical solubility technique in order to separate each fraction of the polymer out from the mixtures.

The present work will be extended for structural analysis by XRD and NMR technique, especially 13C-NMR solid state in order to clarify the structure of the obtained product. In this step, it is important to separate each molecular weight fraction by precipitation in the solvent technique.

CHAPTER 5

Future Aspects

DCA can be prepared as an inclusion compound with many types of solvents. It is an interesting issue to focus the type of inclusion crystal in order to clarify guest channel in the cavity of DCA. In the present work, we found that DCA can entrap some guest in a stable manner, however, there are some particular guests, such as dioxane or ethyl acetate that guest will be decreased after long period of time. The obtained product was characterized from various approaches to study the specific property of the polymer. Here, we concluded that there are some properties differed from the commercial PVC. FT-IR, thermal analysis and ESR study implied that the obtained product shows some different property from the commercial PVC. However, the results also implied that the obtained PVC is the mixture of the stereoregularity polymer. In order to characterize the specific structure, NMR technique is another useful approach for the study. Here, the obtained product should be reprecipitate and fractional separated to collect each level of the molecular weight related to the structure. Thus, in the future work, it is our interest to study the structure in details by using XRD and NMR including molecular weight study by using GPC technique.

Concerning with the channel of the host, the present work is also attractive to us to clarify the size and specific structure for the VCM guest molecules. We propose that the inclusion polymerization of VCM should be studied by using another steroid derivatives, such as; cholic acid host system. The merit of cholic acid is also on the point that the inclusion compound with VCM can be prepared by absorption technique. Here, we expect that cholic acid will give different structure of the channel which leads to the understanding of host channel and guest stability by comparing to DCA system. The inclusion polymerization in Cholic acid is also interesting issues for the stereoregularity polymer.

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Structural Investigation of Radiation-Induced Urea Canal Polymerization of 1,3-Butadiene

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ABSTRACT: The formation of a highly trans-1,4-tactic polymer by the radiation-induced canal polymerization of 1,3-butadiene in the urea adduct was examined by structural viewpoints based mainly upon crystal structure analyses of the monomer–urea adduct and the polymer–urea adduct of 1,3-butadiene. Crystals of the monomer–urea adduct are orthorhombic $P2_12_12_1$ with cell dimensions of a = 8.20, b = 14.20, and c = 11.00 Å at −120°. The unit cell contains two urea canals along the c axis, and the canals are slightly deformed from regular hexagonal prisms owing to the inclusion mode of the monomer molecules. The monomer molecules are aligned in the canals at an interval of 7.27 Å along the canal axis so as to be favorable to trans-1,4 polymerization. Crystals of the polymer–urea adduct are hexagonal $P6_122$ with a = b = 8.22, and c = 11.01 Å and one urea canal per unit cell, and the urea canals have pure hexagonal prismlike cavities. The polymer chains are included in the canals with an identity period of 4.84 Å. Since the difference between the canal shapes of both adducts is small, single crystals of the monomer–urea adduct can transform into single crystals of the polymer–urea adduct by irradiation. However, since the canal polymerization requires considerable shortening of the monomer interval (from 7.27 to 4.84 Å per monomer molecule), the polymerization must produce some amount of vacancies in the canals, and thus some extent of urea (about 30%) which cannot accommodate the polymer chains crystallizes into usual tetragonal crystals. The characteristics of the canal-polymerized polymer were examined by infrared absorption, X-ray diffraction, DSC measurement, and electron microscopy.

In previous papers,[1,2] the highly trans-1,4 tactic polymerization of 2,3-dimethylbutadiene and 2,3-dichlorobutadiene by γ-ray irradiation in the thiourea canals (adducts) was supported by structural evidences based upon crystal-structure analyses of the monomer–thiourea adducts, polymer–thiourea adducts, and resulting polymers of both dienes. The formation of a urea adduct with 1,3-butadiene was reported by Clasen,[3] and the radiation-induced urea canal polymerization of 1,3-butadiene was found by White[4] to produce an extremely regular trans-1,4 polymer. However, as was pointed out previously,[2] structures of adducts of urea or thiourea with polymerizable monomers and hence the details of the mode of canal polymerization are by no means the same but are peculiar to each monomer. The present paper is concerned from structural viewpoints with the characteristics of the urea canal polymerization and the resulting polymer of 1,3-butadiene.

Experimental Section

Samples. Samples used in the present study were prepared in the following way.

needlelike crystal of monomer–urea adduct

| canal polymerization
| (γ-ray irradiation at −78°)

needlelike crystal of polymer–urea adduct

| polymer crystallization
| (removal of urea with water)

uniaxially oriented fibrous polymer

Monomer–Urea Adduct. A 40% saturated urea–2-propanol solution at 30° (25 ml) with a trace (5 μl) of methanol was cooled to −78° in an ampoule. Precooled butadiene (3 ml) was added to the solution and sealed *in vacuo* at −78°. Precipitated urea crystals in the ampoule were dissolved by elevating the temperature and the ampoule was cooled slowly (1°/15 min) to −40° and was stored. Needlelike crystals about 0.3 mm in diameter and 20 mm in length which are suitable for X-ray study were thus obtained. After removal of the mother liquid, the ampoule was sealed again. Polycrystalline monomer–urea adduct was also prepared by the method of White.[4] Since the adduct dissociated immediately above about −20°, it was handled in a Dry Ice box.

Polymer–Urea Adduct. The monomer–urea adduct was irradiated at −78° by γ-rays from a cobalt-60 source of the Radiation Laboratory of Osaka University. The irradiation dose rate and total dosage were 2×10^3 or 5×10^5 rad/hr and 1.2×10^6 or 1.5×10^7 rad, respectively. Single crystals of the monomer–urea adduct were transformed into the polymer–urea adduct preserving the original crystal shape. The polymer–urea adduct decomposed at 142°.

Polymer Samples. The polymer–urea adduct was washed with water at 25 or 100° in order to remove urea. From single crystals of the polymer–urea adduct, uniaxially oriented fibrous polymer samples were directly obtained. They were dried *in vacuo*. No other treatments, such as recrystallization, fractionation, and annealing, were made for the polymer samples. When the irradiated adduct was warmed slowly to room temperature, more tight fibrous samples were obtained; probably the postpolymerization progressed during the warming. As reference polymer samples, 90 and 98% *trans*-1,4-polybutadiene prepared by the use of VCl_3-$Al(Et)_3$ catalyst were used.

X-Ray Diffraction. Throughout the present study, nickel-filtered Cu *K*α radiation was used. Rotation photographs and equiinclination Weissenberg photographs about the needle axis (c axis) were taken for the monomer–urea adduct and polymer–urea adduct. Especially, the photographs of the monomer–urea adduct were taken at −120°. At that temperature the canal polymerization by X-rays was substantially suppressed during exposure of one photograph. Reflection intensities estimated by comparison with a standard intensity scale were corrected for Lorentz-polarization factors. A fiber photograph of the canal-polymerized polymer was taken with a cylindrical camera. Figures 1a–c show the rotation photographs of the monomer–urea and polymer–urea adducts and the fiber photograph, respectively.

Small-angle X-ray diffraction photographs of the polymer–urea adduct, the canal-polymerized polymer, and the 90% trans-1,4 polymer were taken using a Rigaku-Denki small-angle X-ray diffractometer with a pin-hole optics.

DSC Measurement. DSC measurements were made for the polymer–urea adduct and the canal-polymerized polymers on a Rigaku-Denki YDS differential scanning calorimeter. The scans were taken at a speed of 15°/min and the scanning range of 25–160°. The instrument was calibrated with the calorimetric standard benzoic acid.

Infrared Spectrum. Infrared spectra of the polycrystalline polymer–urea adduct and the polymers were obtained using the KBr disk technique. Uniaxially oriented polymer films of 15–20 μm thicknesses were prepared from the canal-polymerized fibrous polymer samples by rolling along the fiber direction, and their infrared dichroisms were measured with a Hitachi EPI2 microscopic spectrometer.

Results and Discussion

Monomer–Urea Adduct. The X-ray diffraction patterns of the monomer–urea adduct suggested to us that the

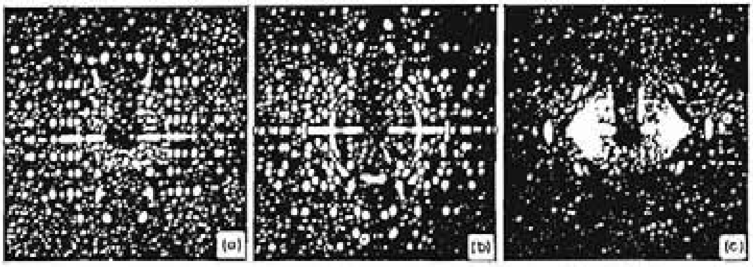

Figure 1. (a) X-Ray rotation photograph of the monomer–urea adduct taken at −120°. The rotation axis is the canal axis. (b) X-Ray rotation photograph of the polymer–urea adduct taken at room temperature. (c) X-Ray fiber photograph of the polymer obtained from the polymer–urea adduct.

gross structure of the adduct was similar to that of the well-known *n*-paraffin–urea adducts of hexagonal system $P6_122$ with cell dimensions of $a = b = 8.223$ and $c = 11.005$ Å, in which six urea (host) molecules per unit cell form the honeycomb-like canal having a cavity of about 5-Å diameter along the *c* axis.[3] However, the crystal symmetry (orthorhombic $P2_12_12_1$) of the monomer–urea adduct was certainly different from the usual hexagonal $P6_122$. (It should be noted that from the X-ray measurement the monomer–urea adduct crystals found often appeared as microscopic twinned crystals, which were composed of three orthorhombic crystals rotating every 120° about the canal axis, with a hexagonal symmetry.) The crystallographic data are shown in Table I. Since the *b* dimension, 14.20 Å, is just $3^{1/2}$ times the *a* dimension, 8.20 Å, this orthorhombic cell must contain two urea canals, i.e., 12 urea molecules. The appearance of the orthorhombic symmetry instead of the hexagonal symmetry should be ascribable to a slight deformation of the urea canals from regular hexagonal canals due to a definite angular disposition of butadiene (guest) molecules about the canal axis as in the case of 2,3-dimethylbutadiene–thiourea adduct.[2] The deformed thiourea canals with the monoclinic symmetry $P2_1/a$ in the 2,3-dimethylbutadiene–thiourea adduct were revealed to retain substantially the canal structure of thiourea molecules in the well-known rhombohedral adduct ($R\bar{3}c$).[6] Similarly, the deformed urea canals with the orthorhombic symmetry $P2_12_12_1$ can retain essentially the urea-canal structure of the hexagonal adduct as shown later. In the first step of structure analysis, the mole ratio of the host to the guest had to be decided. The X-ray rotation photograph (Figure 1a) showed an extra layer line whose periodicity does not correspond to the periodicity along the *c* axis of the crystal, and this layer line should be attributed to scatterings by the guest molecules. The identity period, c_m, of the extra layer line, 7.27 Å, indicates the interval of monomer molecules in the canal. The ratio of the *c* dimension (period of the urea canal, 11.00 Å) to c_m is expressed approximately by $2c = 3c_m$, i.e., approximately three monomer molecules exist in a length of twice the urea-canal period. Therefore, the orthorhombic cell contains 12 urea molecules and 3.02 monomer molecules; the mole ratio is thus approximately 4:1 but exactly 3.97:1 (Clasen[3] reported the mole ratio of 4.2:1 by measurement of the dissociation pressure of the adduct). The monomer packing in the urea canal having the interval of 7.27 Å could be realized as shown in the side view in Figure 3 or Figure 10, when the molecular dimensions of butadiene determined by Almenninger, *et al.*,[7] and the normal van der Waals radii were used. In the case of 2,3-dimethylbutadiene–thiourea adduct, the mole ratio of host to guest is rationally 3:1, and the guest molecules take definite dispositions to the host molecules.[2] On the other hand, in the butadiene–urea adduct, the mole ratio is irrational and hence the array of guest molecules in each canal seems to take an uncertain level to the framework of the host. If that is so, guest molecules give independent streak-like layer lines, l_m, in the rotation photograph, except the equatorial layer line, in which host and guest molecules are coherent in X-ray scatterings. In order to confirm this packing of guest molecules, a calculation of cylindrically averaged diffraction intensities about the canal axis, which should be compared with the rotation photograph, was done using eq 1 for the array of butadiene molecules located as in Figure 3 or Figure 10.

Table I

Crystallographic Data for the Monomer–Urea and Polymer–Urea Adducts of 1,3-Butadiene

	Monomer–urea adduct	Polymer–urea adduct
Crystal system	Orthorhombic	Hexagonal
Space group	$P2_12_12_1$	$P6_122$
Cell dimensions, Å	$a = 8.20 \pm 0.02$ $b = \sqrt{3}a =$ 14.20 ± 0.03 $c = 11.00 \pm 0.03$ (at −120°)	$a = b = 8.22 \pm 0.01$ $c = 11.01 \pm 0.02$
Number of host–guest molecules per cell (mole ratio)	12–3.02 (3.97)	6–2.28* (2.63)*

* Ideal adduct, in which canals are filled with endless polymer chains.

$$I(R, l_m/c_m) = \sum_j \sum_{j'} f_j f_{j'} J_0(2\pi R r_{jj'}) \exp[2\pi i l_m (z_j - z_{j'})/c_m] = \sum_j f_j^2 + 2\sum_{j>j'} \sum f_j f_{j'} J_0(2\pi R r_{jj'}) \cos(2\pi l_m z_{jj'}/c_m) \quad (1)$$

$R = [(2 \sin \theta/\lambda)^2 - (l_m/c_m)^2]^{1/2}$; θ, Bragg angle; λ, wavelength; l_m, order of layer line of the monomer; c_m, monomer interval along the canal axis; f_j, atomic scattering factor of *j*th atom; J_0, Bessel function of zeroth order; $r_{jj'}$ and $z_{jj'}$, radial and axial components of interatomic distance between *j* and *j'*th atoms in the monomer molecule. Figure 2 (top) shows the calculated intensities. The result gave the strong extra layer line of 7.27 Å (first layer line) and the scarcely detectable second layer line as observed experimentally.

The structure of urea canal was determined by the least-squares refinement with data of $F(hk1) - F(hk5)$. Subse-

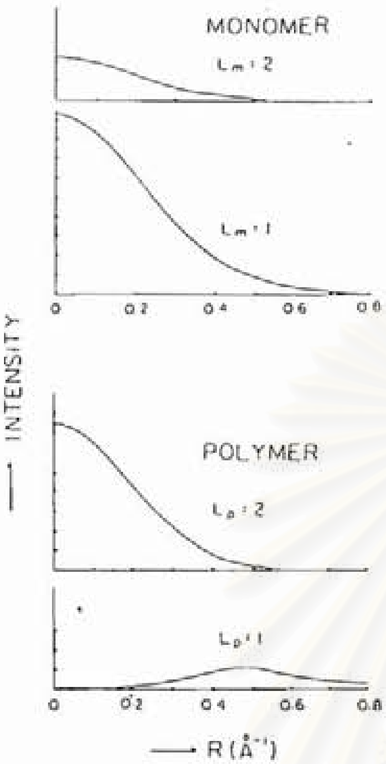

Figure 2. Calculated cylindrically averaged X-ray diffraction intensities of extra layer lines for the monomer-urea adduct (top) and the polymer-urea adduct (bottom).

quently, the angular position of guest molecule about the canal axis was determined by the least-squares refinement with $F(hk0)$, where xy coordinates and thermal parameters of urea molecules were fixed as obtained from the consideration of $F(hk1)$ − $F(hk5)$. The final atomic coordinates and thermal parameters are shown in Table II. Table III lists the observed and calculated structure factors (see paragraph at end of paper regarding supplementary material). The discrepancy factor R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.094 for all observed reflections. The crystal structure is shown in Figure 3. The averaged bond lengths and bond angles for three nonequivalent urea molecules are as follows: C–O, 1.30 Å; C–N, 1.35 Å; O–C–N, 123°; N–C–N, 118.5°. Though the canals are slightly deformed from regular hexagonal prisms, the scheme of N–H ··· O hydrogen bondings between urea molecules is the same as that in the hexagonal adduct, *i.e.*, the framework of canal is composed of three interpenetrating helices of urea molecules with the same sense (either right-handed or left-handed helices). There are 12 independent N–H ··· O hydrogen bond distances; they are ranged from 2.82 to 3.08 Å and are averaged to be 2.99 Å.

The guest molecules are included with a definite angular disposition about the canal axis and have cross-sectional dimensions of 3.8 × 5.4 Å^2 about the canal axis. Therefore, the deformation of the urea canals seems to be quite reasonable. However, as shown in the end view in Figure 3, the cavity of the canal has a slight allowance for oscillation of guest molecules about the canal axis. Also, since the canal axis is in accordance with a twofold screw axis in the $P2_12_12_1$ crystal, the guest molecules might be arranged statistically turning 180° about the canal axis in canal by canal.

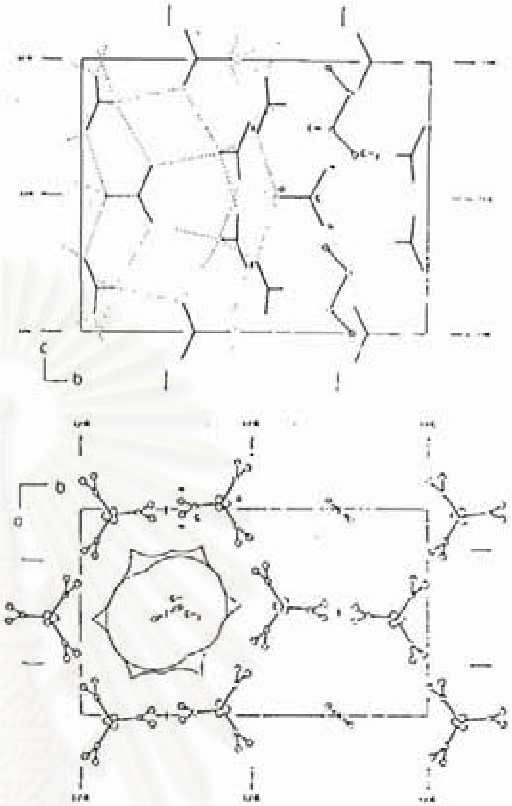

Figure 3. Crystal structure of the monomer-urea adduct. In the left part of the side view (top), the N–H ··· O hydrogen bonding scheme is indicated by broken lines, and in the right part the included monomer molecules are shown. The relative heights of monomer molecules to urea molecules are arbitrary as shown in the text.

Polymer–Urea Adduct. The procedure of structure analysis of the polymer–urea adduct was similar to that of the monomer–urea adduct. The polymer–urea adduct belongs to the hexagonal system $P6_122$. The cell dimensions are shown in Table I. Table IV lists the atomic coordinates and thermal parameters. Table V is the list of observed and calculated structure factors (see paragraph at end of paper regarding supplementary material). The final R factor was 0.11. The crystal structure is shown in Figure 4. The structure of urea canal is substantially the same as that of the *n*-paraffin–urea adduct:[5] C–O, 1.27 Å; C–N, 1.35 Å; O–C–N, 119.7°; N–C–N, 120.6°, and two kinds of N–H ··· O hydrogen bond distances are 2.98 and 3.00 Å. The canal is a regular hexagonal prism. The orthorhombic symmetry in the monomer–urea adduct disappears by transformation from the monomer–urea adduct into the polymer–urea adduct. However, since the deformation due to the transformation is small, crystals of the polymer–urea adduct can retain the single-crystal habit.

One problem about the polymer chains in the canals should be noted. The molecular chains of *trans*-1,4-polybutadiene in the low-temperature crystalline form take the T-S-trans-S̄ (T, trans; S, skew) conformation with an identity period of 4.83 Å.[8] In the rotation photograph of the

Table II
Atomic Coordinates and Thermal Parameters
for the Monomer-Urea Adduct

Atom	x	y	z	B, Å²
O(1)	0.0090	0.0937	0.1559	4.15
C(1)	0.1431	0.0462	0.1616	3.02
N(11)	0.1994	0.0110	0.2672	2.93
N(12)	0.2276	0.0438	0.0585	4.08
O(2)	0.0554	0.0967	0.8402	4.27
C(2)	−0.0754	0.0438	0.8421	4.08
N(21)	−0.1617	0.0360	0.9462	4.21
N(22)	−0.1307	0.0036	0.7155	4.19
O(3)	0.0295	0.0725	0.5005	5.48
C(3)	0.0118	0.1642	0.4997	3.36
N(31)	0.0391	0.2108	0.5029	5.26
N(32)	−0.0282	0.2054	0.3941	4.54
H(11)	0.286	−0.038	0.283	4.85
H(12)	0.146	0.013	0.348	4.65
H(13)	0.332	0.016	0.044	3.13
H(14)	0.187	0.067	0.981	3.55
H(21)	−0.267	0.008	0.954	4.32
H(22)	−0.125	0.067	0.020	3.06
H(23)	−0.222	−0.045	0.722	4.18
H(24)	−0.078	0.001	0.654	4.54
H(31)	0.044	0.281	0.616	4.23
H(32)	0.070	0.182	0.691	3.53
H(33)	−0.053	0.275	0.373	4.34
H(34)	−0.048	0.177	0.310	3.71
C(G1)	0.524	0.207	0.000[a]	8.60
C(G2)	0.510	0.219	0.219[a]	8.65
H(G1)[b]	0.501	0.243	−0.094[a]	8.60
H(G2)[b]	0.569	0.139	0.009[a]	8.60
H(G3)[b]	0.557	0.153	0.231[a]	8.60

[a] Arbitrary values relative to the host molecules as shown in the text. [b] Parameters of hydrogen atoms in the guest molecule were assumed. Equivalent positions are (x, y, z), $(\frac{1}{2} + x, \bar{y}, \frac{1}{2} - z)$, $(\bar{x}, \frac{1}{2} - y, \frac{1}{2} + z)$, and $(\frac{1}{2} - x, \frac{1}{2} + y, \bar{z})$.

polymer-urea adduct (Figure 1b), we observed a very weak layer line with a period of 2.42 Å corresponding to the second layer line for the above molecular chain. In the pure hexagonal canal, the polymer chains must orient statistically about the canal axis, since the polymer chain axis is in accordance with a sixfold screw axis in the $P6_122$ crystal. Two assumptions of free rotating polymer chains (time averaged or space averaged) about the chain axis and of randomly disposed chains in six equivalent sites were examined for the T-S-trans-$\bar{S}$ polymer chain. For the free-rotating model, the structure factor of the equator is expressed as eq 2.

$$F(hk0) = F_{\text{urea}}(hk0) + F_{\text{polymer}}(hk0) \qquad (2)$$

$$F_{\text{polymer}}(hk0) = w\sum_j f_j J_0(2\pi R r_j)$$

r_j, radial coordinate of jth atom from the chain axis; w, weight deduced from the mole ratio of host to guest (monomeric unit); $w = 2.28$ (11.01 Å/4.84 Å) when the summation is made for all atoms in one monomeric unit. Both models gave essentially the same reasonable $F(hk0)$ values. The cylindrically averaged intensities of extra layer lines, I_p, were also calculated in a good approximation by using the free-rotating model.

$$I(R, l_p/c_p) = \left|\sum_j f_j J_n(2\pi R r_j)\exp(2\pi i l_p z_j/c_p)\right|^2 \qquad (3)$$

z_j, axial coordinate of jth atom; c_p, identity period of polymer chain, 4.84 Å. The result shown in Figure 2 (bottom)

Table IV
Atomic Coordinates and Thermal Parameters
for the Polymer-Urea Adduct

Atom	x	y	z	B, Å²
O	0.3194	0.6806	0.4167	6.35
C	0.4086	0.5914	0.4167	6.18
N	0.4377	0.5261	0.5227	6.75
H(1)	0.394	0.544	0.598	6.9
H(2)	0.506	0.458	0.519	6.9
C(H)[a]	0.000	0.045	0.051	7.3
C(H$_2$)[a]	0.085	0.044	0.176	7.3
H(CH)[a]	−0.005	0.109	0.052	7.3
H(CH$_2$)[a]	0.146	−0.043	0.173	7.3
H(CH$_2$)[a]	0.206	0.181	0.179	7.3

[a] Since the polymer chain is randomly dispersed about the canal axis, parameters in the table are tentatively given for the T-S-trans-$\bar{S}$ polymer as described in the text. Coordinates of the remaining atoms in the monomeric unit are obtained by a inversion symmetry operation at (0,0,0).

indicates that the second layer line is observable while the first layer line is not detectable as observed experimentally.

The infrared spectrum of the polymer-urea adduct is quite similar to those of the n-paraffin-urea adducts.[9,10] The absorption bands of the polymer (guest component) in the adduct are very weak; only the 966 cm^{-1} [γ(C=C) − γ(CH)], 2350 cm^{-1} [ν_s(CH$_2$)], and 2925 cm^{-1} [ν_a(CH$_2$)] bands were observed. These bands are in accordance with those of the polymer samples. Therefore, no further information about the polymer conformation in the canal could be obtained.

The polymer-urea adduct was found to decompose at 142° from the DSC measurement as shown in Figure 5a. Another endothermic peak at 129° in Figure 5a is ascribable to the fusion of usual urea crystals (tetragonal $P\bar{4}2_1m$, $a = b = 5.661$, and $c = 4.712$ Å).[11] In practice, coexistence of urea crystals in the polymer-urea adduct sample was clearly demonstrated by the X-ray diffraction (Figure 1b). The separated urea crystals orient in two preferable ways; though there is a small amount of polycrystalline urea too, the [001] and [110] axes of urea orient along the canal axis. As is well-known, *trans*-1,4-polybutadiene has a first-order transition from the low-temperature form to the high-temperature form at about 55–76°, depending upon the conditions of preparation of the sample.[12] There is no peak in this region for the polymer-urea adduct. That is, all polymer chains are included in the urea canals, while free urea crystals exist. It is a characteristic in the canal polymerization of butadiene that the monomer-urea adduct is transformed into the polymer-urea adduct with accompanying urea crystals as a by-product. The problem concerning this will be discussed in the following sections.

Polymer. The canal-polymerized polybutadiene is estimated to be almost 100% trans-1,4 polymer from its infrared spectrum: both the 910-cm^{-1} band arising from 1,2 addition and the 740-cm^{-1} band from cis-1,4 addition cannot be seen, while a weak but clear band at 910 cm^{-1} is found for the 98% trans-1,4 polymer. The infrared spectrum of the oriented canal-polymerized polymer gave the same dichroism as a stretched 98% trans-1,4 polymer. The X-ray fiber pattern (Figure 1c) is also essentially the same as the usual one. However, as shown in Figure 6 which presents X-ray diffraction curves for three different polymer samples taken at 25°, the features of the canal-polymerized polymers are scarcely detectable amorphous scatterings and rather broad crystalline diffractions. These features imply that the canal-polymerized polymers have high crys-

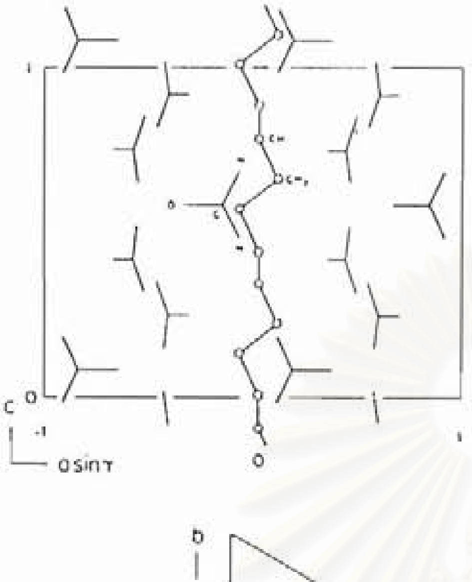

Figure 4. Crystal structure of the polymer–urea adduct. The N–H · · · O hydrogen bonding scheme is essentially the same as that of the monomer–urea adduct.

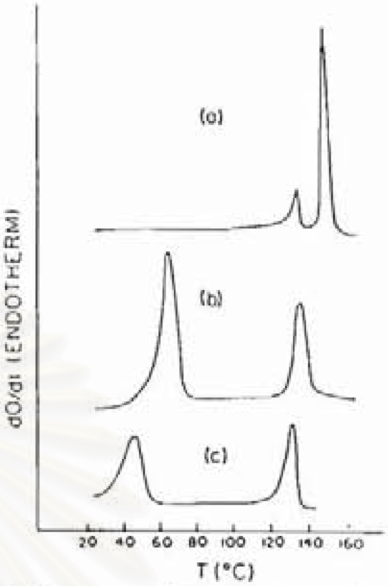

Figure 5. DSC thermograms: (a) the polymer–urea adduct, (b) the canal-polymerized polymer (removal of urea at 100°), (c) the canal-polymerized polymer (removal of urea at 25°).

tallinities, but the crystallites are rather small and/or somewhat paracrystalline.

Table VI shows calorimetric data for the canal-polymerized polymers with the data of Bermudez and Fatou for a predominantly trans-1,4 polymer.[13] In the table the crystallinities of the low-temperature crystalline form (form I) X_I and of the high-temperature form (form II) X_{II} were estimated by using the relationship of the observed heat of transition ΔH_I *vs.* X_I and of the observed heat of fusion ΔH_{II} *vs.* X_{II}, proposed by Bermudez and Fatou (Figure 6 in ref 13). The crystallinities of the canal-polymerized polymers are comparable with those of single crystals grown from *n*-heptane solutions.[14] The X_I of the sample obtained by removal of urea at 25° is exceptionally small, but the increment of X_{II} of this sample may be due to promotion of crystallization during the DSC measurement.

The small-angle X-ray diffraction of an oriented 90% trans-1,4 polymer gave a discrete reflection with a long spacing of 200 Å calculated according to Bragg's law, along the fiber axis, while the canal-polymerized polymer as well as the polymer-urea adduct did not show such a spot (Figure 7). Ng, Stellman, and Woodward[14] reported that solution-grown single crystals have lamellar thicknesses of about 94–110 Å. It is conceivable that the canal-polymerized polymers do not contain any periodic heterogeneous structure in a dimension of 100–200 Å along the fiber axis. From the mechanism of the canal polymerization and of the polymer crystallization, it is likely that the extended polymer chains in the canals aggregate preferably with each other and crystallize in a mode of intermolecular crystallization rather than of intramolecular crystallization.

Figure 8 shows a transmission electron micrograph of the canal-polymerized polymer. The photograph shows a gross lamellar structure of about 2000-Å thickness. The interpretation of this structure is still uncertain, but in the case of the canal polymerization of 2,3-dichlorobutadiene, the obtained polymer was composed of fine needlelike fibrils and had no such lamellar structure.[2] The canal polymerization of 2,3-dichlorobutadiene was performed without breaking-up of the thiourea canals even if large vacancies were produced in the canals due to the polymerization. Therefore, the gross lamellar structure in the canal-polymerized polybutadiene might be interpreted as follows. That is, in the case of urea-canal polymerization of butadiene, owing to the significant shortening of monomer interval upon polymerization and a less stability of urea-canal framework without guest molecules, the urea canals are broken up at regions where some vacancies of neighboring canals are concentrated, say with an interval of observed 2000 Å.

Canal Polymerization. From the present structural studies, the urea-canal polymerization and the polymer crystallization of butadiene can be schematically represented as shown in Figure 9. Ohmori, *et al.*,[15] reported an esr study of preirradiated polycrystalline butadiene-urea adduct. They proposed that the mechanism of canal polymerization is of a radical type, starting from the allyl type radical $CH_3CH{=}CH_2$ produced by proton transfer from a urea molecule to a butadiene anion radical, which may be produced by capture of an ejected electron. Though the details of the structure of such an imperfection site cannot be ac-

Table VI
Calorimetric Data and Estimated Crystallinity

	Transition			Fusion		
Polymer	T_t, deg	ΔH_t, cal/g	X_t, %	T_m, deg	ΔH_m, cal/g	X_m, %
Canal polymerized polymer (removal of urea at 25°)	35.5	14.8	66	123	13.5	86
Canal polymerized polymer (removal of urea at 100°)	55.0	24.3	92	128	12.0	84
Bermudez and Fatou's data*	50 ~52	11.5 ~13.7	57 ~64	100 ~102	4.8 ~7.1	40 ~54

* Lower and upper values in their studies are shown

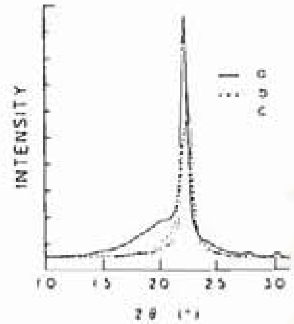

Figure 6. X-Ray diffraction curves of three polymer samples: (a) the 98% trans-1,4 polymer; (b) the canal-polymerized polymer (removal of urea at 25°), (c) the canal-polymerized polymer (removal of urea at 100°).

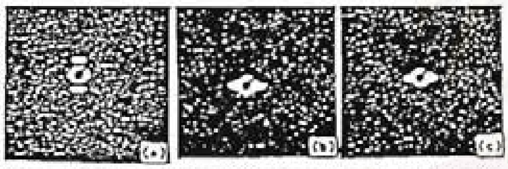

Figure 7. Small-angle X-ray-diffraction photographs: (a) the 98% trans-1,4 polymer; (b) the polymer–urea adduct; (c) the canal-polymerized polymer (removal of urea at 100°). The polymer chain axis is vertical in each photograph.

quired, the polymerization must start by an addition reaction of the nearest neighboring monomer molecule to the radical in a canal. The alignment of monomer molecules in the canal seems to be favorable to trans-1,4 addition. However, the polymerization requires considerable shortening of monomer interval: from 7.27 to 4.84 Å per monomer molecule. From the geometrical viewpoint alone, it appears that the monomer molecules can travel in the canal without any large hindrance. As an approximation, the van der Waals potential energy for one monomer molecule as a function of translational coordinate (z) along the canal axis and rotation angle (ϕ) about the canal axis was estimated

$$V(z,\phi) = \sum_i \sum_j (B_{ij}/r_{ij}^{12} - A_{ij}/r_{ij}^{6}) \qquad (4)$$

using eq 4. The summation was made for atom pairs between one monomer molecule and surrounding urea molecules with interatomic distances r_{ij} less than 7 Å. The constants A_{ij} and B_{ij} were taken from Gō and Scheraga.[16] Figure 10 shows the potential energy map, where the origin (0,0) is chosen as the molecular plane of the guest molecule

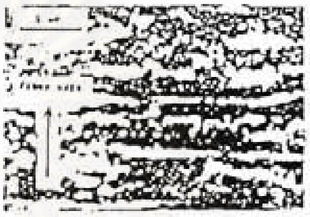

Figure 8. Transmission electron micrograph of the canal-polymerized polymer (removal of urea at 100°).

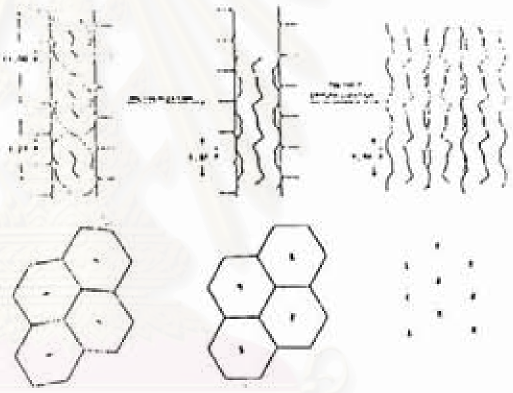

Figure 9. Schematic representation of the urea-canal polymerization and the polymer crystallization for 1,3-butadiene.

and is parallel to the ac plane (at this stage, the C(G1) atom denoted in Table II is at x = 0.561, y = 0.250, and z = 0.0 in the fractional coordinates), and ϕ is taken counterclockwise. Since the canal axis is in accordance with a twofold screw axis

$$V(z,\phi) = V(z + c/2, \phi + 180°) \qquad (5)$$

The potential energy minima are at ϕ = 120 and 300°, which are consistent with the result of crystal structure analysis, and the potential barrier against the translation of a guest molecule along the canal axis at the two angular positions is only 0.5 kcal/mol. Yoshii, *et al.*,[17] studied the temperature dependence of the canal polymerization of butadiene. According to their study, the postpolymerization of preirradiated butadiene–urea adduct at −196° is suppressed at −90° in practice but proceeds significantly at −78° and is promoted gradually with elevating temperature. Since the potential barrier for the translation of monomer molecule along the canal axis is not so high, the temperature dependence of the canal polymerization may be

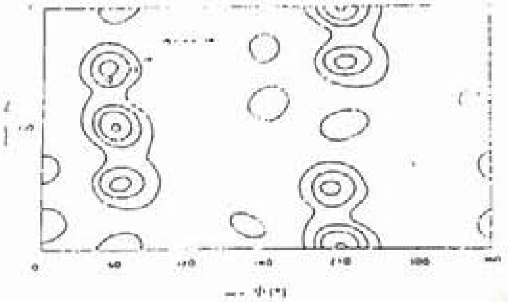

Figure 10. Potential energy contours (kcal/mol) as a function of angular position φ and translational position z of the monomer molecule.

rather related occurrence of some local destruction of the urea canals by which a free space suitable for enchainment of monomer molecules is formed. The local destruction of the canal may occur by the formation of a vacancy upon polymerization. The heat of the canal polymerization, which is still unknown, may also be related to such a local structure change. However, the details of such a local change are still an open question. In any event, from the facts of the appreciable shortening of monomer interval upon polymerization and of the growth of urea crystals, it is likely that some reconstruction of crystal lattices takes place in the vicinity of growing polymer chain end, but finally the polymer–urea adduct can retain the single-crystal features of the original monomer–urea adduct.

The calculated mole ratio of host to guest in the polymer–urea adduct 6:2.26 shown in Table I should be realized for an ideal polymer–urea adduct in which urea canals are filled with endless trans-1,4 polymer chains having the identity period of 4.84 Å. This ideal situation cannot occur in practice, because the original monomer–urea adduct was the mole ratio of 4:1. Accordingly, even if 100% conversion to polymer is achieved, the extent of vacancies (total length of vacancies) in the canals due to the shortening of monomer interval (from 7.27 to 4.84 Å) is calculated to be 33%. The elemental analysis of full postpolymerized single crystals, which were composed of the polymer–urea adduct and the urea crystals as the by-product, showed that the conversion to polymer was almost 100%, because the mole ratio of urea to monomeric unit did not alter from that in the original monomer–urea adduct. On the other hand, from the calorimetric data (measurement of the heat of fusion of urea crystals in Figure 5a) of this sample, we estimated the weight fractions of urea existing as the polymer–urea adduct and as the urea crystals, assuming that the polymer–urea adduct did not decompose prior to the fusion of urea crystals (*cf.* in the case of polyethylene–urea adduct,[18] which was not accompanied by urea crystals, no endothermic peak for the fusion of urea crystals was observed prior to the decomposition of the adduct at 148°). From these data and the mole ratio in the ideal polymer–urea adduct, we estimated the weight fractions of urea existing in the following three states: urea which constructs the ideal polymer–urea adduct, 68%; urea which constructs canals with vacancies, 4%; tetragonal urea crystal, 28%. Therefore, it seems likely that there are no long vacancies in the polymer–urea adduct, and hence some extent of urea (about 18%) which cannot accommodate polymer chains crystallizes into tetragonal crystals. This fact does not conflict with the fact that the calculation of structure factors $F(hk0)$ for the polymer–urea adduct (see eq 2) gave the reasonable result by assuming that the mole ratio was similar to that of the ideal polymer–urea adduct. Therefore, if the monomer–urea adduct is subjected to irradiation for a long time coming into contact with excess monomer, it might be expected that separated urea crystals upon polymerization can form the monomer–urea adduct again with free monomer molecules, and the adduct undergoes polymerization.

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Supplementary Material Available. A comparison between observed and calculated structure factors for the monomer–urea adduct (Table III) and the polymer–urea adduct (Table V) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number *Macro-75-12*.

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SHORT COMMUNICATIONS

Relative Size Effect on the Polymerization with Methyl Cholate Inclusion Compounds

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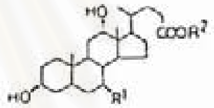
KEY WORDS Inclusion Polymerization / Host Guest / Methyl Cholate / Channels / Relative Size Effect / Microstructure / Propagating Radicals / Molecular Graphics /

Inclusion polymerization can be recognized as a one-dimensional polymerization in an anisotropic molecular-level space, while conventional ones in solution or in bulk are three-dimensional ones in isotropic macroscopic-level spaces. This generalization is based on our following finding; in the former case, the relative size between a monomer molecule and a channel plays a decisive role in the polymerization behavior, while such a relative size effect can be neglected in the latter case.[1]

We so far studied the effect by use of a pair of host, deoxycholic acid (DCA) and apocholic acid (ACA) (Channel size: ACA > DCA). In order to discuss the effect in further detail, we need another hosts which form channels slightly different from those of DCA and ACA in size. Recently, we found that cholic acid (CA) and its derivatives form channel-type inclusion compounds with a variety of organic substances.[2-4] We now find that methyl cholate (MC) among these hosts can serve as the third host suitable for the one-dimensional inclusion polymerization.



Cholic acid (CA): $R^1 = OH$, $R^2 = H$
Methyl cholate (MC): $R^1 = OH$, $R^2 = CH_3$
Deoxycholic acid (DCA): $R^1 = H$, $R^2 = H$
Methyl deoxycholate: $R^1 = H$, $R^2 = CH_3$

Apocholic acid (ACA)

This communication deals with the relative size effect on the polymerization with MC inclusion compounds, as compared with those in DCA and ACA ones. The effect can be understood through a structural viewpoint that MC channels are larger in size than DCA and ACA ones.

EXPERIMENTAL

Methyl cholate was prepared from commer-

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cially available cholic acid (Sigma Co.) by esterification with methanol containing hydrogen chloride.[3] The crude product was purified by recrystallization from methanol. The solvent-free methyl cholate was obtained by heating at 110°C for 20 hours under vacuum. The inclusion compound of a monomer with methyl cholate was prepared as follows; 1.0 g of methyl cholate and an equimolar amount of a monomer were placed in a glass tube of 10 mm diameter, which was sealed under vacuum (10^{-3} Torr) after three freeze thaw cycles. The tube was allowed to stand at 25°C over 20 hours to form inclusion compounds, and then exposed to γ-irradiation from a ^{60}Co source at 0°C for one hour with a total dose of 1.0 Mrad. After the irradiation the tube was allowed to stand at a definite temperature in order to postpolymerize and then cooled again to −78°C. The contents were immediately poured into an excess amount of methanol to separate the polymer from methyl cholate. The methanol-insoluble fraction was filtered, dried under vacuum, and weighed.

The microstructures of the polymers were determined on the basis of IR, ^{1}H, and ^{13}C NMR spectroscopy. ESR measurements were carried out as described earlier.[11]

RESULTS AND DISCUSSION

We carried out the inclusion polymerization of various diene and vinyl monomers by use of MC and its derivatives. The procedure was similar to that employed for DCA and ACA. MC gave a significant amount of the polymers, while CA and methyl deoxycholate did not. In the absence of the host molecules, we obtained only a trace amount of the polymers under the same conditions.

We studied the inclusion polymerization using MC in detail. And we compared the polymerization behavior with ones in cases of DCA and ACA,[1,6] with respect to the polymerizability of the included monomers, the stability of the included propagating radicals, and the microstructure of the resulting polymers, as described below.

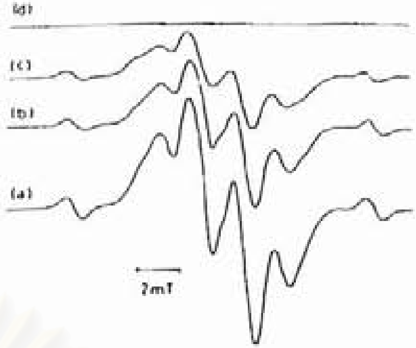

Figure 1. ESR spectra of the propagating radicals derived from methyl 2,4-pentadienoate in methyl cholate inclusion compounds. They were observed at 25°C (a), 50°C (b), 75°C (c), and 100°C (d).

First, conjugated diene monomers, such as 2,3-dimethyl-1,3-butadiene and 1-chloro-1,3-butadiene, polymerized to give rubber-like polymers, while solid polymers in cases of DCA and ACA. The diene monomers with no or one methyl substituent gave the polymers in poor yields, while in significant yields in DCA and ACA channels. In addition, conventional vinyl monomers, such as methyl methacrylate and so on, polymerized to yield atactic polymers, although such vinyl monomers hardly polymerized in channels of DCA and ACA.[7]

Secondly, the propagating radicals were not so stable as those in case of DCA and ACA. We often observed ESR spectra derived from both the propagating radicals and the host radicals at room temperature. Figure 1 shows the ESR spectra of the radicals derived from the inclusion compound of MC with methyl 2,4-pentadienoate. The signals disappeared by increasing temperature up to 100°C, whereas they did not in cases of DCA and ACA.[6]

Thirdly, the stereoregularity of the resulting diene polymers was much lower than those in cases of DCA and ACA. The content of 1,4-*trans* structure was 70 to 90%, while it was almost quantitative in the latter case. For

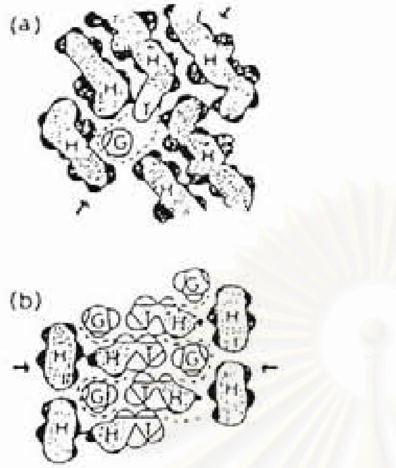

Figure 2. Schematic drawings of cross-sections of the methyl cholate inclusion compounds with 0.2 Å of thickness by means of space-filling models.[9] (a) A horizontal view, two arrows correspond to the cross-section shown in the lower figure (b). (b) A vertical view, two arrows show the position of the section of the upper figure (a). "H", "T", and "G" indicate methyl cholate, its tail part, and methanol, respectively. Dotted lines show the approximate edges of the channel together with side pockets.

example, in case of poly(2,3-dimethyl-1,3-butadiene) obtained by the inclusion polymerization in MC channels, the[3] ^{1}H NMR spectrum showed two large peaks at 1.78 and 2.18 ppm due to 1,4-*trans* structure as well as neighboring small peaks due to 1,4-*cis* structure. The content of 1,4-*trans* structure is higher than that of the polymer obtained in solution, but lower than those obtained quantitatively in DCA and ACA channels.[8]

We observed relative size effects from three viewpoints as mentioned above. All the results are consistent with an idea that the polymerization reaction spaces of MC channels are larger than those of DCA and ACA ones. This is supported by a molecular graphics study[9] of the crystal structure of the inclusion compound of MC with methanol.[3] Figure 2 shows horizontal and vertical views of the assembly. The MC molecules basically form bilayer assembly to leave channels with side pockets, like the cases of DCA, ACA, and CA.[3] The esteric parts of the steroidal tails and the methanol molecules are located in the channels and the side pockets, respectively. In the absence of methanol, however, we may expect that the monomer molecules could be included into the channels and the side pockets instead of the tails and the methanol molecules. Moreover, we clarified that cholic acid inclusion compounds show guest-responsive structural changes through tail parts of the host molecules.[10] Nonpolar character of the esteric part of the MC may lead to an increase of the flexibility of the assembly. Therefore, it seems reasonable to assume that MC channels can serve as polymerization reaction spaces a little larger than DCA and ACA ones.

In conclusion, the present study demonstrates that MC can provide a new channel suitable for the study on the relative size effect on the inclusion polymerization. Further systematic research for the design of channel-type organic inclusion compounds would be useful for finding various molecular-level spaces for polymerization reactions.

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Inclusion Polymerization of 1-Chlorobutadiene in a Deoxycholic Acid Canal*

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Synopsis

Inclusion polymerization of 1-chlorobutadiene was studied using 3α,12α-dihydroxy-5β-cholan-24-oic acid (deoxycholic acid, DCA) as host molecules. It was found that the poly(1-chlorobutadiene) had almost 100% of head to tail, trans-1,4-structure on the basis of ^{13}C-NMR and IR spectroscopies. This was the first example of preparing the highly regulated poly(1-chlorobutadiene) by using the inclusion polymerization technique. The polymers obtained were optically active and the maximum value of specific rotation was $[\alpha]_D$ − 41.9°. Both the rate constants and the value of activation energy of the elementary reactions of inclusion polymerization of 1-chlorobutadiene were determined by graphical evaluation. The activation energy of propagation and termination was 11.7 and 11.1 kcal/mol, respectively.

INTRODUCTION

A convenient method for controlling microstructures of polymers is the inclusion polymerization using various hosts, such as urea, thiourea, and perhydrotriphenylene (PHTP).[1] However polymerizable monomers for this purpose are limited in size of monomer which can be included in their canals and/or instability of monomer–host adducts. Inclusion polymerization using these hosts so far was carried out with monomers of limited sorts.

We have been studying inclusion polymerization using both deoxycholic acid (DCA) and apocholic acid (apoCA) as the host molecules.[2,3] It is well known that various organic compounds are included by DCA and apoCA.[4] The guest molecules are sandwiched between the sheets which are built up with DCA molecules by hydrogen bonding.

In the case of using DCA or apoCA as the hosts, the monomers which have suitable size, shape, polarity, and chirality including vinyl monomer,[5] acyclic[3] or cyclic[6] conjugated diene, and diacetylene,[7,8] were found to be included and polymerized in the canals even at high postpolymerization temperature because of high thermal stability of monomer–host adducts. The monomers applicable for inclusion polymerization were thus extended by using DCA and apoCA as host molecules.

Earlier we reported the inclusion polymerization of 1-chlorobutadiene and characterization of the poly(1-chlorobutadiene).[9] The direct evidence for the

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[*] Functional Monomers and Polymers CLX. Part CLIX of the series: M. J. Moghaddam, S. Hozumi, Y. Inaki, and K. Takemoto, *J. Polym. Sci. Polym. Chem. Ed.*, 26, 3297 (1988).

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occurrence of the polymerization of substituted butadiene monomers in a DCA canal were ascertained by x-ray diffraction of polymer-DCA adducts. We confirmed further asymmetric induction in the resulting polymers.[10]

In this paper we report on the behavior of inclusion polymerization of 1-chlorobutadiene in detail.

EXPERIMENTAL

Monomer

1-Chlorobutadiene was prepared according to the literature[11] as follows: *trans*-1,4-dichloro-2-butene was heated with powdered KOH at 80-90°C. Crude 1-chlorobutadiene was distilled from the reaction mixture, and purified by distillation. Its purity was checked by gas chromatography before use.

Host

Commercially available deoxycholic acid (DCA) was recrystallized from acetone and the resulting crystals were heated under vacuum at 100°C for 1 day to remove acetone.

Polymerization

Two hundred and thirty milligrams of 1-chlorobutadiene (2.5 mmol) and 1.0 g of DCA (2.5 mmol) were added in a glass tube and the tube was sealed under high vacuum. The tube was allowed to stand at 30°C for 1 day to prepare monomer-host adducts. The tube was γ-ray irradiated (dose rate 1 Mrad/h, 1 h, at -78°C) for initiation of polymerization. Postpolymerization was carried out under a definite temperature. After the postpolymerization, the polymer-host adduct was poured into excess methanol (about 100 mL). The polymer separated from host molecule was filtered off, washed with methanol repeatedly, and dried under vacuum. When the time for drying of the polymer was too long, the polymer changed in its color and became insoluble in common organic solvents.

Measurements

Infrared spectra of host, monomer-host adduct, polymer-host adduct, and polymer were measured with a JASCO IR 810 spectrophotometer. Host, monomer-host, and polymer-host adduct were measured on KBr dispersions and polymer was in film state casting from chloroform solution.

^{1}H- and ^{13}C-NMR spectra of the polymers were measured in $CDCl_3$ with a JEOL JNM-PS-100 and a JNM-FX-60S spectrometer, respectively.

Specific rotation of polymers was measured with a JASCO DIP 181 digital polarimeter in chloroform solution.

Molecular weight of polymers was determined by GPC using TSK GEL 4000Hxl column (TOYO SODA Co.) and TOYO SODA CCP & 8000 series system. Poly(styrene) standards with a low polydispersity were used as molecular weight standards.

TG and DTA measurements were made with a SEIKO 580 thermal analysis system, at a heating rate of 10 K/min under nitrogen atmosphere.

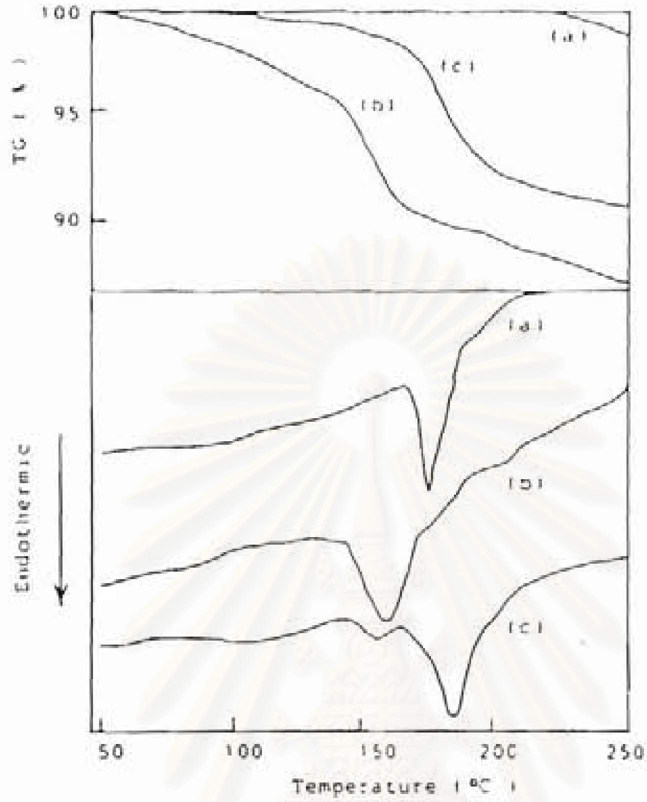

Fig. 1. TG and DTA diagram of (a) DCA, (b) 1-chlorobutadiene-DCA adduct, and (c) poly(1-chlorobutadiene)-DCA adduct at heating rate of 10 K/min under nitrogen atmosphere.

ESR spectra were measured at room temperature with a JEOL JES-FX1X ESR spectrometer. The sample for measurement was prepared in the same way as mentioned above for polymerization, using a quartz tube and the tube was irradiated by γ-ray (1 Mrad/h, 1 h, at −78°C).

RESULTS AND DISCUSSION

Properties of Monomer or Polymer-DCA Adducts

The postpolymerization was carried out in the temperature range from −20 to 50°C. When the postpolymerization was carried out at high temperature, above 50°C, the colorless host crystals in the glass tube changed their color to purple, then to black. At lower temperature, the change in color of the polymers was not noticeble.

The coloration of the polymer-DCA adduct occurred even at room temperature after a few days. Furthermore, the color of the polymer-DCA adduct turned black, and the polymer separated from the host was black and insoluble in common organic solvents.

TG and DTA diagrams of DCA, 1-chlorobutadiene or poly(1-chlorobutadiene)-DCA adduct are shown in Figure 1 (a)-(c).

According to the TG and DTA diagram of monomer-host adduct, release of the monomer occurred remarkably at about 159°C, which is ca. 90°C higher

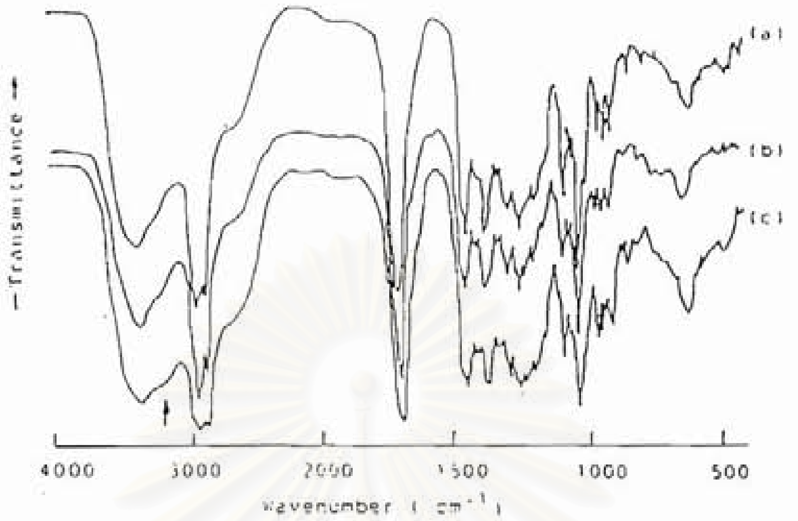

Fig. 2. Infrared spectra of (a) DCA, (b) 1-chlorobutadiene–DCA adduct, and (c) poly(1-chlorobutadiene)–DCA adduct. (Postpolymerization at 0°C, for 48 h.)

than the boiling point of 1-chlorobutadiene (lit.,[11] 65–68.5°C). It suggests that 1-chlorobutadiene is included by host molecules and the adduct is thermally stable.

TG and DTA diagram of poly(1-chlorobutadiene)–DCA adduct is shown in Figure 1(c). Two endothermic peaks were observed along with an accompanying weight loss. The small one is at 152°C and another is at 184°C. The former peak may be due to the release of residual monomer and the elimination of hydrogen chloride from poly(1-chlorobutadiene). The latter peak at 184°C is the melting point of the polymer–DCA adducts. The melting point is higher than that of DCA (176–178°C).

Infrared spectra of DCA, 1-chlorobutadiene–DCA adduct, and poly(1-chlorobutadiene)-DCA adduct are shown in Figure 2 (a)–(c).

Comparing Figure 2(a) with (b), the peaks due to 1-chlorobutadiene are almost overlapped by those of host molecules. In the region between 1600 and 800 cm^{-1} differences are few.

As shown in Figure 2(c), the peaks due to the polymer are also overlapped by host. However at the band 3600–3200 cm^{-1} which is assigned to hydrogen bonded —OH stretching, the difference is shown between Figure 2(a) and (c). Nakamoto et al. reported that the stretching frequencies of hydrogen bonded —OH was a function of the O—H····O distance.[12] Decrease in the distance of O—H····O hydrogen bond caused a shift the wavenumber of —OH stretching. This difference may be attributed to the inclusion of polymer in the DCA canal and its influence on the distance of hydrogen bonds between host molecules.

Microstructure of Poly(1-Chlorobutadiene) Prepared by Inclusion Polymerization

The infrared spectrum of the poly(1-chlorobutadiene) which was prepared by inclusion polymerization is shown in Figure 3.

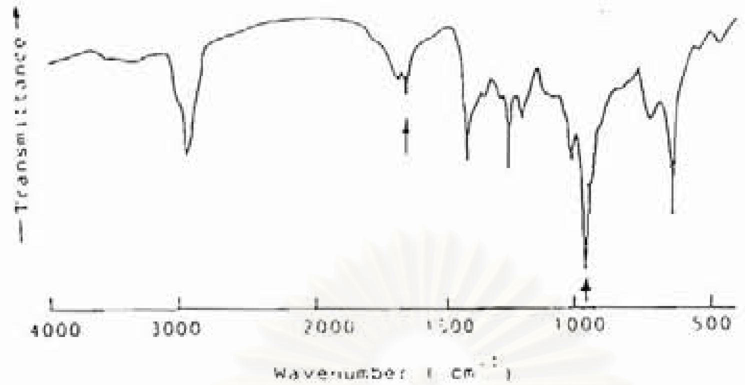

Fig. 3. Infrared spectrum of poly(1-chlorobutadiene) prepared by inclusion polymerization using DCA as host. (Postpolymerization at 0°C, for 24 h.)

The bands at 1660 and 960 cm^{-1} are assigned to C=C stretching and C—H bending vibration of trans double bond, respectively. The bands from 675 to 725 cm^{-1} which are assigned to C—H bending vibration of cis double bond are not observed.

^{13}C-NMR spectrum of poly(1-chlorobutadiene) is shown in Figure 4.

Only four peaks—40.85, 61.16, 128.49, and 133.60 ppm—were observed. The assignment of the peaks is 40.85 C(4), 61.16 C(1), 128.49 C(3), and 133.60 C(2): $-(-C(4)H_2-C(3)H{=}C(2)H-C(1)HCl-)_n-$.

The results indicate that the poly(1-chlorobutadiene) prepared by inclusion polymerization using DCA as host molecule consists almost completely of head to tail, trans-1,4-structure. The polymerization of 1-chlorobutadiene without the host molecules under the same conditions yielded a trace amount of polymer which had 1,4- and 3,4-structure. Kohjiya et al. reported that the poly(1-chlorobutadiene) obtained by using a radical initiator, AIBN, consisted 66% of 1,4-structure and 34% of 3,4-structure.[13] Poly(1-chlorobutadiene) which had almost 100% of head to tail and trans-1,4-structure has been obtained for the first time by inclusion polymerization using DCA as host.

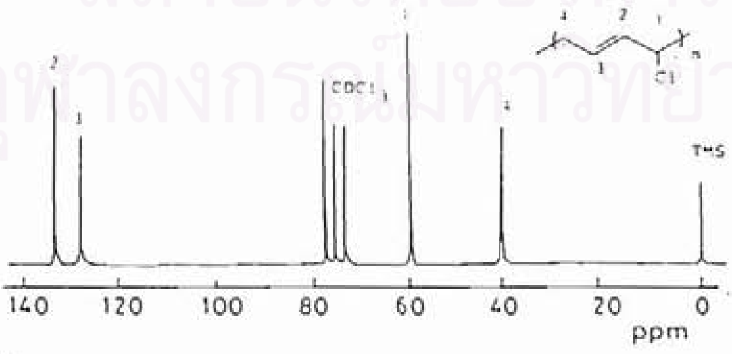

Fig. 4. ^{13}C-NMR spectrum of poly(1-chlorobutadiene) prepared by inclusion polymerization using DCA as host. (Postpolymerization at 0°C, for 24 h.)

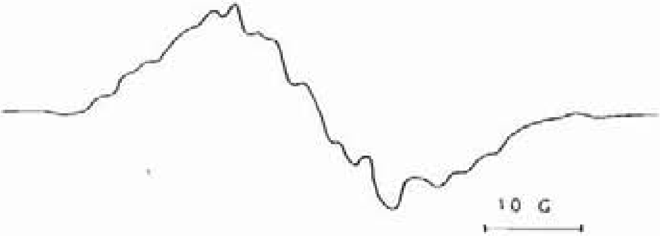

Fig. 5. ESR spectrum of 1-chlorobutadiene–DCA adduct, γ-ray irradiated at −78°C and measured at room temperature.

ESR Spectrum of 1-Chlorobutadiene–DCA System

ESR spectrum of 1-chlorobutadiene–DCA system was measured at room temperature after γ-ray irradiation. The spectrum is shown in Figure 5.

The ESR spectrum is assigned to an allylic radical $(-CH_2-CH-CH-CHCl)$. The complicated line shape is probably due to nuclear spin of chlorine ($I = 3/2$). The ESR spectrum was observed during a few weeks. The radical in question may be the propagating one of the 1-chlorobutadiene, as in the case of 2,3-dimethylbutadiene described in our previous paper.[14] The stability of the propagating radicals can be explained by the fact that the coupling of a propagating radical in a canal with that in another canal is prevented by the canal walls. The result suggests that the inclusion polymerization of 1-chlorobutadiene in a DCA canal proceeds via a free radical mechanism.

Kinetics of Inclusion Polymerization of 1-Chlorobutadiene in a DCA Canal

The rate constants and the activation energy of the elementary reaction of the inclusion polymerization have never been determined. We attempted to determine these values on the system of the inclusion polymerization of 1-chlorobutadiene in a DCA canal.

Kagiya et al. reported on a classification of polymerization from a kinetic point of view[15] and a graphical evaluation of the rate constants of the elementary reactions of various polymerization systems.[16] We used this method to obtain the values.

The relationship between the number average molecular weight and the polymer conversion is shown in Figure 6.

The number average molecular weight of the poly(1-chlorobutadiene) increased with increasing conversion as shown in Figure 6, except for the postpolymerization at 50°C.

Dependence of the conversion on the postpolymerization time is shown in Figure 7.

At the initial stage of postpolymerization, the conversion increased with the postpolymerization time. The polymerization can be classified as a stationary successive polymerization with a rapid initiation from these results. This polymerization system seems to be a "living" radical polymerization at the initial stage. It is known that the methyl methacrylate–orthophosphoric acid system[17] is an example of a "living" radical polymerization system.

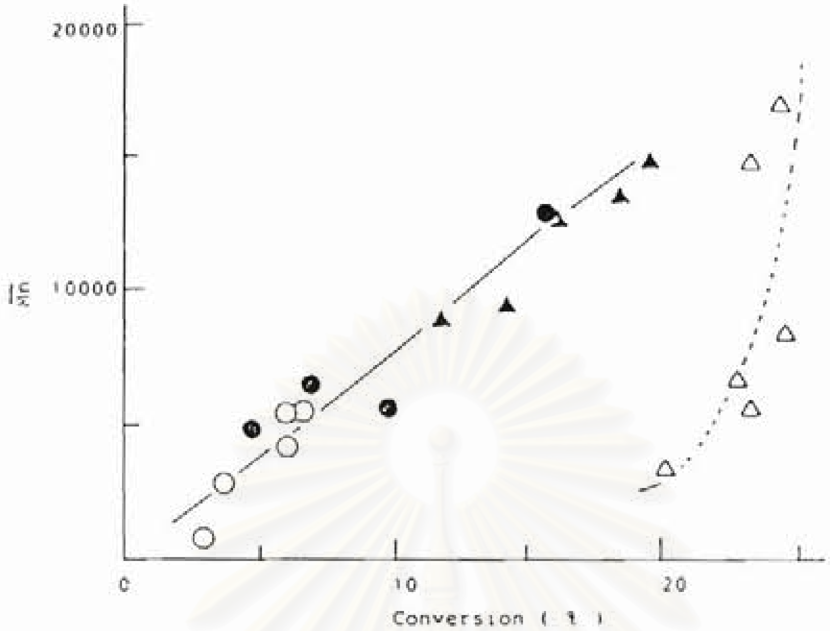

Fig. 6. Relationship between conversion and the number averaged molecular weight of polymer. Postpolymerization at: (○) −20°C, (●) 0°C, (▲) 34°C, (△) 50°C.

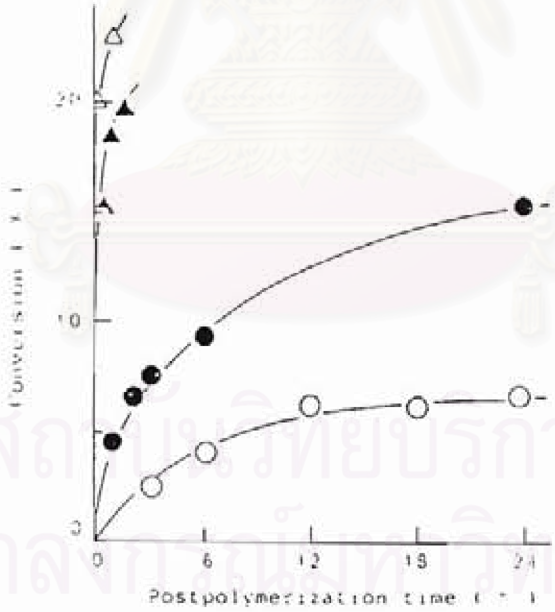

Fig. 7. Relationship between conversion and postpolymerization time under various postpolymerization temperature. Postpolymerization at: (○) −20°C, (●) 0°C, (▲) 34°C, (△) 50°C.

The increasing rate of polymer conversion decreased with the polymerization time. It is suggested that the amount of the propagating species decreases with the progress of polymerization. The polymerization system changes to a nonstationary successive polymerization with increasing postpolymerization time.

The elementary steps of this inclusion polymerization are considered from a kinetic point of view as follows:

Initiation:

$$\mathrm{M} \xrightarrow{\gamma\text{-ray}} \mathrm{M}^{\bullet}$$

$$\begin{aligned}[\mathrm{M}^{\bullet}]_0 &= \text{the initial concentration of propagating species}\\ &\doteq [\mathrm{P}^{\bullet}]_0\\ &= 2.82 \times 10^{-3}\text{-}4.90 \times 10^{-3}(\mathrm{mol/kg})\end{aligned}$$

Propagation:

$$\mathrm{P}^{\bullet} + \mathrm{M} \rightarrow \mathrm{P}^{\bullet} \qquad R_p = k_p[\mathrm{P}^{\bullet}][\mathrm{M}]$$

Transfer:

$$\mathrm{P}^{\bullet} + \mathrm{XY} \rightarrow \mathrm{PX} + \mathrm{Y}^{\bullet} \qquad R_{tr} = k_{tr}[\mathrm{P}^{\bullet}][\mathrm{XY}]$$

Termination:

$$\mathrm{P}^{\bullet} + \mathrm{Z} \rightarrow \mathrm{PZ} \qquad R_t = k_t[\mathrm{P}^{\bullet}][\mathrm{Z}]$$

where M represents monomer; $\mathrm{M}^{\bullet}$, activated monomer; $\mathrm{P}^{\bullet}$, propagating species; XY and Z, host or impurity in the system; R_p, R_{tr}, and R_t, the rate of propagation, transfer, and termination; k_p, k_{tr}, and k_t, the rate constants of these reactions; $[\mathrm{P}^{\bullet}]$ and [M], concentration of propagating species, monomer; [XY], and [Z], concentration of host or impurity in the system; $[\mathrm{P}^{\bullet}]_0$ and $[\mathrm{M}^{\bullet}]_0$, the initial concentration of propagating species. The initial concentration of propagating species was determined by extrapolating the concentration of polymer chains in the system to postpolymerization time 0. The concentration of monomer, polymer, or other species is given as their respective number of moles per kilogram of host (DCA).

By combining these equations with the fundamental relationships of polymerization, the following equations can be derived.

$$\frac{R}{[\mathrm{M}]\int_0^t (R/[\mathrm{M}])\,dt} = \frac{k_p[\mathrm{P}^{\bullet}]_0}{\int_0^t (R/[\mathrm{M}])\,dt} - k_t[\mathrm{Z}] \tag{1}$$

$$\frac{[\mathrm{M}_p]}{P_n\int_0^t (R/[\mathrm{M}])\,dt} = \frac{[\mathrm{P}^{\bullet}]_0}{\int_0^t (R/[\mathrm{M}])\,dt} + \frac{k_{tr}[\mathrm{XY}]}{k_p} \tag{2}$$

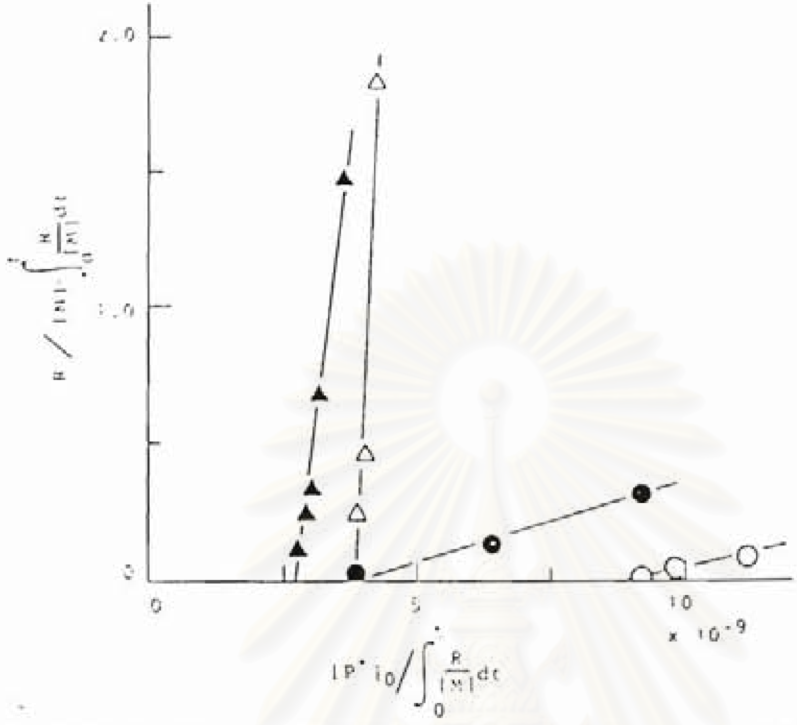

Fig. 8. $R/[M] \int_0^t (R/[M]) dt$ vs. $[P^*]_0/\int_0^t (R/[M]) dt$ in the polymerization of 1-chlorobutadiene in a DCA canal. Postpolymerization at: (○) −20°C, (●) 0°C, (▲) 34°C, (△) 50°C.

where R is the apparent rate of polymerization ($R = R_p$), P_n is the number average degree of polymerization of the polymer formed in a reaction period of from time 0 to time t, and $[M_p]$ is the polymer yield in polymerized monomer moles, $[M]$ is the concentration of monomer.

The plots of $R/[M] \int_0^t (R/[M]) dt$ against $[P^*]_0/\int_0^t (R/[M]) dt$ give straight lines as shown in Figure 8. k_p and $k_t[Z]$ are determined as listed in Table I.

When all species of Z are the DCA molecules, the concentration of Z, [Z], is 2.5 mol/kg. The value of k_t is in the range from 6.8×10^{-10} to 1.4×10^{-8} (mol/kg s). It is substantially smaller than that of k_p. The rate of termination

TABLE I

Rate Constants of Inclusion Polymerization of 1-Chlorobutadiene in a DCA Canal

Postpolymerization temperature (°C)	k_p[a] (kg/mols)	$k_t[Z]$[b] (1/s)
−20	2.0×10^{-1}	1.7×10^{-9}
0	3.8×10^{-1}	1.4×10^{-8}
34	1.2×10^{1}	3.3×10^{-8}
50	2.8×10^{1}	$1.1 \times 10^{-}$[illegible]

[a] Host 1 kg.

[b] [Z] = const.

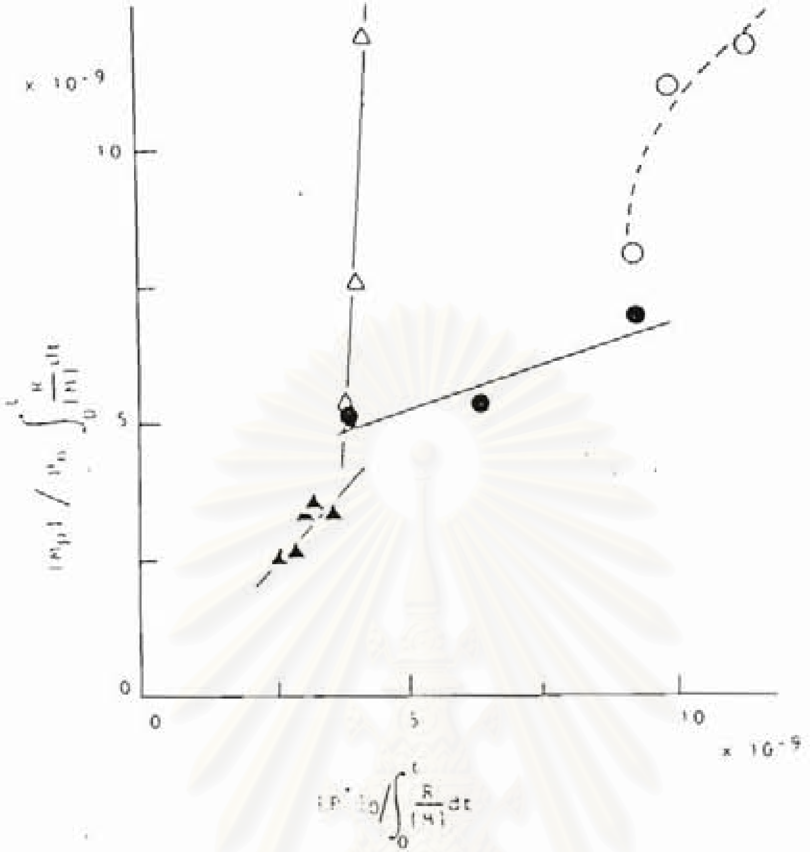

Fig. 9. $[M_p]/P_n \int_0^t (R/[M])\, dt$ v. $[P^{\cdot}]_0/\int_0^t (R/[M])\, dt$ in the polymerization of 1-chlorobutadiene in a DCA canal. Postpolymerization at: (○) −20°C, (●) 0°C, (▲) 34°C, (△) 50°C.

reaction in the polymerization system is slower than that of propagation reaction. Therefore the inclusion polymerization of 1-chlorobutadiene in a DCA canal seems to be a "living" polymerization at initial stage of polymerization.

The Arrhenius plots between $1/T$ vs. $\ln k_p$ or $\ln k_t[Z]$ also gives straight lines and the value of activation energy of propagation and termination, E_p and E_t, are determined as 11.7 and 11.1 kcal/mol, respectively. It is known that the values of activation energy of propagation by free radicals are ca. 9–10 kcal/mol for various butadiene monomers.[16] The values obtained for inclusion polymerization of 1-chlorobutadiene are reasonable.

The plots of $[M_p]/P_n \int_0^t (R/[M])\, dt$ vs. $[P^{\cdot}]_0/\int_0^t (R/[M])\, dt$ are shown in Figure 9.

The plots of postpolymerization at 34°C result in a straight line with a slope of 1.07. The value is very similar to the theoretical value, 1. However the plots at other postpolymerization temperature deviate from a straight line or follow a straight line with a smaller or larger slope than 1. When the postpolymerization temperature is at −20°C, the plots deviate from the straight line. It is probably because the polymers obtained as methanol insoluble part at −20°C contain the low molecular weight substances.