Title	STUDIES ON INCLUSION POLYMERIZATION IN DEOXYCHOLIC ACID CANALS
Author(s)	宮田, 幹二
Citation	大阪大学, 1979, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/995
rights	
Note	

STUDIES ON
INCLUSION POLYMERIZATION IN DEOXYCHOLIC ACID CANALS

MIKIJI MIYATA

PREFACE

The work of this thesis was done under the guidance by Professor Kiichi Takemoto and many other members of Takemoto Laboratory at the Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, for five years since 1973.

The content of this thesis is composed of the following papers:

(1) Radiation-induced Polymerization of 2,3-Disubstituted Butadienes in Deoxycholic Acid Inclusion Compounds.
M.Miyata and K.Takemoto,
J.Polymer Sci.Polymer Lett.Ed., 13, 221 (1975).

(2) Radiation-induced Polymerization of Vinyl and Diene Monomers in Deoxycholic Acid Inclusion Compounds.
M.Miyata and K.Takemoto,
J.Polymer Sci.Polymer Symp., 55, 279 (1976).

(3) Radiation-induced Polymerization of 2,3-Dichlorobutadiene in Deoxycholic Acid Canal Complexes.
M.Miyata and K.Takemoto,
Angew.Makromol.Chem., 55, 191 (1976).

(4) Post-irradiation Polymerization of 2,3-Dimethylbutadiene in Deoxycholic Acid Canal Complexes.
M.Miyata, K.Morioka and K.Takemoto,
J.Polymer Sci.Polymer Chem.Ed., 15, 2987 (1977).

(5) Synthesis of Optically Active Poly(trans-2-methylpentadiene) by Asymmetric Inclusion Polymerization in Deoxycholic Acid.
M.Miyata and K.Takemoto,
Polymer J., 9, 111 (1977).

(6) A Modified Way to Form the Deoxycholic Acid-2,3-Dimethyl-1,3-butadiene Canal Complex and its Polymerization.
M.Miyata and K.Takemoto,
Makromol.Chem., 179, 1167 (1978).

(7) Post-irradiative Polymerization of Butadiene in Deoxycholic Acid Canal Complexes.
M.Miyata and K.Takemoto,
J.Macromol.Sci.-Chem., in press.

(8) Inclusion Polymerization of 2,3-Dimethyl-1,3-butadiene: Competitive Incorporation of Additives with the Monomer in Deoxycholic Acid Canals.
M.Miyata, K.Shinmen and K.Takemoto,
Angew.Makromol.Chem., in press.

CONTENTS

GENERAL INTRODUCTION

"Chemistry of Inclusion Compounds" or "Host-Guest Chemistry" has received enormous attention in recent years, which comes from the fact that host compounds can provide reaction spaces which bring about marvellous controls for chemical reaction.[1] The subject of such reaction spaces fascinates polymer chemists to challenge the synthesis of tailor-made polymers.[2]

A cylindrical space in crystalline state, which is called a canal, was employed by polymer chemists as such a space for polymerization reaction.[3] The polymerization in canal is called "canal polymerization" or "inclusion polymerization". Since monomer molecules in canal may be oriented regularly, and the attack of the monomers to the growing chain may occur only along well-defined direction, canal polymerization enables us to obtain highly stereospecific polymers, particularly optically active polymers. The asymmetric synthesis of polymers represents the logical conclusion of research on stereospecific polymerization.[4]

Urea and thiourea canal have been employed so far by many investigators.[5-14] The first example of canal polymerization was reported by Clasen in 1956.[5] The detailed study was followed by Brown and White, who discovered that high-energy radiations are effective polymerization initiators, and that stereospecific polymers are prepared in good yields.[6] Their work was the starting point for systematic investigations in this field. Afterwards, an accurate structural analysis of the canal polymerization was carried out by Chatani and his co-workers.[7] Furthermore, mechanism of the polymerization has been investigated from various points of view by several groups.[10-14]

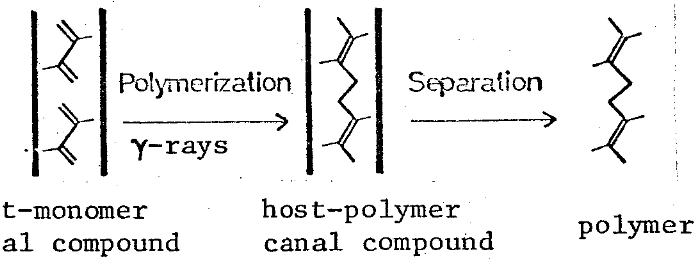


Fig. 1. Schematic representation of canal polymerization.

Alternatively, Farina and his co-workers investigated the inclusion polymerization of diene monomers in perhydrotriphenylene canal extensively.[15, 3(2)] The most important result is that prochiral monomers could be polymerized to give optically active polymers in chiral canal formed from optically active perhydrotriphenylene.[16] However, the investigation of this asymmetric inclusion polymerization gets into trouble because of the difficulty of the resolution of racemic perhydrotriphenylene.[3(2)]

In addition to three kinds of canal described above, the author has found that deoxycholic acid canal can serve as an effective space for polymerization reaction, as exemplified by the synthesis of optically active polymers with high optical rotation.[17,18] Inclusion polymerization in DCA deoxycholic acid canal may be expected to open a further way in the field of asymmetric polymerization.

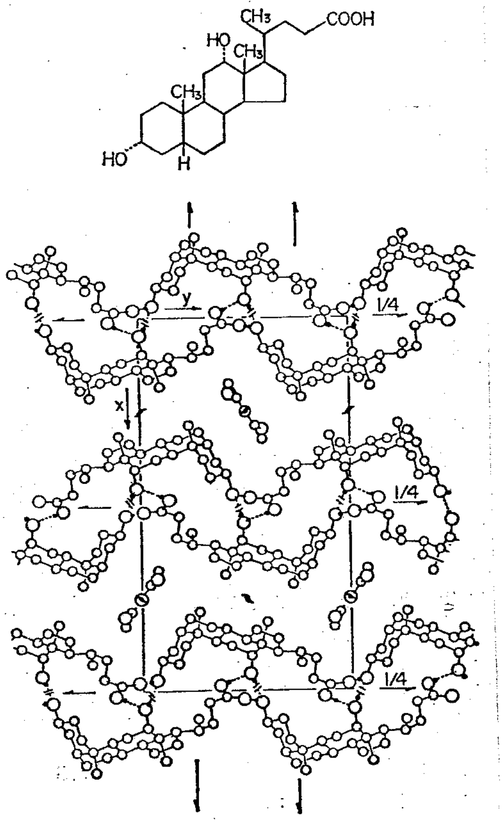


Fig.2. Deoxycholic acid (DCA) and the crystal structure of DCA canal compound with acetic acid.[21]

Deoxycholic acid (3α, 12α-dihydroxy-5β-cholan-24-oic acid; hereafter referred to as DCA; Fig.2) is a naturally occurring steroidal acid. It has been long known that DCA forms crystalline intermolecular compounds, called choleic acids, with a variety of organic substances since early this century.[19,20] However, the crystal structure was hardly determined by Craven and DeTitta in 1972.[21] As shown in Fig.2, the compounds are lattice inclusion compounds of canal type structure, and the canal has a section of approximate rectangular shape with edges of about 7.5 and 4.0 Å. Moreover, it is suggested that DCA canal is different from urea, thiourea, or perhydrotriphenylene canal with respect to the atmosphere, size, shape, and flexibility.[22] In addition, DCA canal is considered to be a chiral space since DCA is a chiral compound. Therefore, it is a fascinating theme how the specificity of DCA canal as mentioned above can be realized for the inclusion polymerization in DCA canal.

The present thesis is concerned with the inclusion polymerization of various monomers in DCA canal, in order to make clear the characteristics of DCA canal as a space for polymerization reaction.

Chapter I deals with the screening for formation and polymerization of DCA canal compounds with various monomers. It is described that DCA canal can serve as an effective space for polymerization of diene monomers.

Chapter II deals with the characteristics of DCA canal for incorporation of guest compounds. Replacement technique to obtain DCA canal compounds, and next competitive incorporation of guest compounds into DCA canal are described on the basis of the inclusion polymerization of a diene monomer in DCA canal.

Chapter III deals with inclusion polymerization of four diene monomers in DCA canal in detail. Space controls for the inclusion polymerization are discussed on the basis of polymerization characteristics, nature of DCA canal compounds, and structures of polymers obtained. Finally, the characteristics of DCA canal are compared with those of urea, thiourea, or perhydrotriphenylene canal.

Chapter I. Screening for Formation and Polymerization of Deoxycholic Acid Canal Compounds with Monomers

I - 1. Introduction

Radiation-induced canal polymerization is a unique method for obtaining stereospecific polymers. Such polymerization have recently been studied by using urea, thiourea, and perhydrotriphenylene as host molecules.

In thiourea canal compounds, poly(2,3-dimethyl-1,3-butadiene) and poly(2,3-dichloro-1,3-butadiene) were found to be highly 1,4-trans tactic[6(1)]; in urea canal compounds, on the other hand, poly(vinyl chloride) was syndiotactic[6(2),8], polyacrylonitrile was isotactic[6(2),24,25] and poly(1,3-butadiene) appeared highly 1,4-trans tactic.[6(2)] Chatani and co-workers have studied the specific feature of the polymerization of some urea- or thiourea-monomer canal compounds from a structural point of view, and indicated that both the structure of urea or thiourea canal compounds with polymerizable monomers and the mode of canal polymerization are by no means the same, but are peculiar to the sort of monomers.[7]

In perhydrotriphenylene canal compounds, different diene monomers were polymerized to afford 1,4-trans tactic polymers.[15] An interesting feature of this canal polymerization is that prochiral *trans*-1,3-pentadiene could be polymerized in the presence of optically active perhydrotriphenylene to give optically active isotactic *trans*-1,4-polypentadiene.[16]

The author has found that a steroidal acid, deoxycholic acid (DCA) , can serve as an effective component for canal polymerization. It has been long known that DCA forms stable intermolecular compounds, called choleic acids, with a variety of organic substances.[20] Recently the crystal structures of the intermolecular compounds of DCA with several guest compounds,[21-23] and it was confirmed that DCA intermolecular compounds have canal type structure.

This chapter concerns with the screening for formation and polymerization of a series of DCA canal compounds with vinyl and diene monomers. It is described that the steric control in DCA canal polymerization was superior in the case of disubstituted butadienes, which gave highly 1,4-trans tactic polymers.

I - 2. Results and Discussion

Formation of DCA Canal Compounds

Reports have recently considered the crystal structures of the DCA canal compounds with acetic acid and so on.[21-23] However, no work seems to have been done on the DCA canal compounds with polymerizable vinyl and diene monomers.[20] The author has succeeded in obtaining various types of DCA canal compounds with such monomers, which were obtained by recrystallization of DCA from liquid vinyl monomers or methanol containing vinyl monomers as shown in Table I-1. Mole ratios of the host to guest molecules were determined from thermogravimetry(TG), NMR spectroscopy, and elemental analysis. It was also found that several sorts of dienes and cyclic monomers can form canal compounds with DCA.

Stability and Property of DCA Canal Compounds

Fig.I-1 shows examples of differential thermal analysis(DTA) and thermogravimetry(TG) diagrams on DCA canal compounds. From DTA on DCA-ethyl acetate canal compound, it was found that ethyl acetate was removed from DCA host molecules at 158-160°C under atmospheric pressure. This releasing temperature of guest component is substantially higher than the boiling point of ethyl acetate itself, which indicates the high stability of DCA-ethyl acetate canal compound. A notable loss of ethyl acetate from the DCA canal compound did not occur even under reduced pressure by heating. The canal compounds of DCA with vinyl and diene monomers such as methyl acrylate, styrene, vinyl acetate, 2,3-dimethyl-1,3-butadiene, *etc.*, showed similar behaviors. TG mearsurements carried out simultaneously indicated that the mole ratios of DCA to monomer molecules in the canal compounds are identical to those found for the DCA canal compounds with hydrogenated, saturated forms of the monomers.

On the other hand, notable loss of acetonitrile from DCA-acetonitrile canal compound occurred at 148-150°C. It was even found that acetonitrile could come out from the canal compounds gradually at room temperature. DCA canal compounds of acrylonitrile, methacrylonitrile, 1,3-butadiene, and isoprene were unstable even at room temperature.

Table I-1. DCA-vinyl monomer canal compounds

monomer	method for formation of DCA canal compound a)	mole ratio b)	c) (°C)
acrylic acid	S	3	158
methacrylic acid	R, S	3	
methyl acrylate	R, S	4	
methyl methacrylate	R, S	4	
vinyl acetate	R, S	4	
styrene	S	2	
acrylonitrile	R		148
methacrylonitrile	R		

a) R: Recrystallization of DCA from vinyl monomer
S: Recrystallization of DCA from methanol containing vinyl monomer

b) Deoxycholic acid/guest molecule

c) Releasing temperature of guest molecule

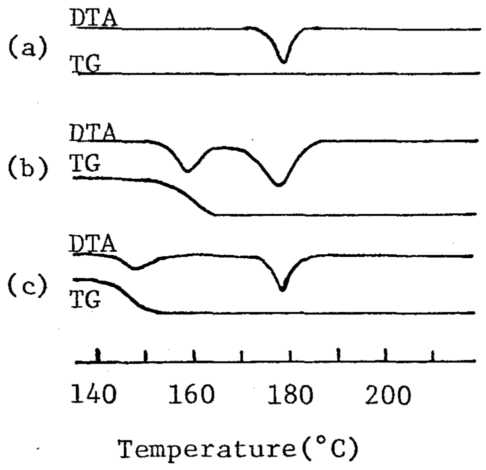


Fig.I-1. DTA and TG diagrams.

(a): DCA without guest molecules
(b): DCA-ethyl acetate canal compound
(c): DCA-acetonitrile canal compound

Polymerization of DCA Canal Compounds

Diene Monomers

The radiation-induced polymerization of DCA-diene monomer canal compounds was carried out with or without mother liquid under various conditions. Several observations indicated that the polymerization proceeded in the solid state, regardless of the presence or absence of the mother liquid: Polymerization inhibitors such as hydroquinone were found to have no effect on the polymerization. The crystals kept their original shapes and appearance even after polymerization. It was also found that the canal compounds after polymerization decomposed at different temperatures from those of compounds before polymerization. After washing the products with methanol in order to remove DCA, the resulting diene polymer particles had fine fibrous structures, observable by microscopic examination. These findings appear to be quite similar to those observed for the polymerization of these monomers in thiourea canal compounds.7(1)

Diene guest monomers could be grouped into three different classes from melting points after polymerization and the structure of polymers obtained, as shown in Table I-2. Fig.I-2 shows DTA diagrams of DCA-diene monomer canal compounds before and after polymerization. As can be seen from Fig.I-2, diene monomers came out from the DCA canal compounds at 158-160°C, and the melting of the host molecules occurred subsequently at 178°C before polymerization. However, after the polymerization, new peaks appeared at a rather high temperature region, which might be attributed to the melting point of the polymer canal compounds.

Table I-2. γ-Ray-induced inclusion polymerization of diene monomers in DCA canal.

diene monomers	mp after polymerization (°C)	structure of polymers
1,3-butadiene 1,3-pentadiene, isoprene	195-198	1,4-trans; 1,2
2,3-dichloro-1,3-butadiene 2,3-dimethyl-1,3-butadiene	213-215	1,4-trans
trans-2-methyl-1,3-pentadiene	165-170	1,4-trans chiral

As shown in Table I-2, in cases of 1,3-butadiene, isoprene and 1,3-pentadiene, new peaks appeared at 195-198°C. Poly(1,3-butadiene) obtained was rubberlike and unstable when allowed to stand in control with the atmosphere. The polymer contained a significant amount of 1,2-unit beside of trans-1,4-unit. Polyisoprene and poly(1,3-pentadiene) obtained were viscous and much more unstable than poly(1,3-butadiene). The latter two polymers could not be characterized because of their instability, although they showed absorptions corresponding to 1,4-trans tactic structures in IR spectra on raw products. Therefore, canal polymerization of isoprene and 1,3-pentadiene were not studied in detail.

A remarkable increase in melting points after polymerization was observed for DCA-2,3-dimethyl- and 2,3-dichloro-1,3-butadiene canal compounds. In these cases, stable solid polymers were obtained in high yield and showed highly 1,4-trans tactic structure.

In the case of *trans*-2-methyl-1,3-pentadiene, the melting point of the canal compound after polymerization was a little lower than that of DCA itself. The polymer which resulted was found to show a high optical rotation. Thus, the author obtained a chiral polymer by a radiation-induced canal polymerization technique, using DCA as the chiral host molecule.

Studies on the polymerization behavior of diene monomers will be described in detail in Chapter III. It is noteworthy that the polymerization of these monomers proceeded predominantly in DCA canal and negligible outside of it under the conditions studied.

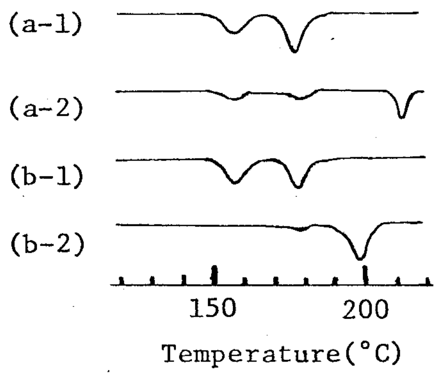


Fig.I-2. DTA diagrams.

DCA-2,3-dimethyl-1,3-butadiene canal compound
(a-1) before polymerization
(a-2) after polymerization

DCA-1,3-butadiene canal compound
(b-1) before polymerization
(b-2) after polymerization

Vinyl Monomers

The radiation-induced polymerization of DCA-vinyl monomer canal compounds was carried out at either 0°C or -78°C, in a similar manner as in the case of DCA-diene monomer canal compounds, and the post-polymerization was done at 50°C. However, no polymerization was observed and their melting points were unchanged.

Polymerization was tried also for DCA-acrylonitrile canal compound prepared by the method described in the Experimental part, by irradiating at -78°C for 18 h with a dose rate of 1.0×10^5 rad/h: DCA-ethyl acetate canal compound was heated at first at different temperatures for 2 h under reduced pressure(10^{-3} Torr), and acrylonitrile monomer was then introduced into the tubes containing DCA-ethyl acetate canal compounds to afford its monomer canal compounds. Fig.I-3 shows the results of the polymerization at -78°C for 18 h, the yield being related with the temperature at which DCA-ethyl acetate canal compounds were treated. Polymerization was found to proceed only in the temperature range 140-180°C, in which ethyl acetate has been thoroughly removed from the DCA canal compound; thus ethyl acetate-free DCA could include acrylonitrile monomer effectively. Above 180°C, the polymerization did not proceed because of melting of the DCA crystals. The fact that ethyl acetate could not easily be removed at 120-130°C but rapidly removed at 140-150°C from their DCA canal compounds, which was shown by IR spectroscopy, supports the results mentioned here. The structure of polyacrylonitrile thus obtained was the same as that obtained by usual free-radical polymerizations. In the cases of polymerization of methacrylonitrile, atactic polymers were obtained by using a similar polymerization technique. At present, the author has not succeeded in preparing stereospecific vinyl polymers by DCA inclusion techniques.

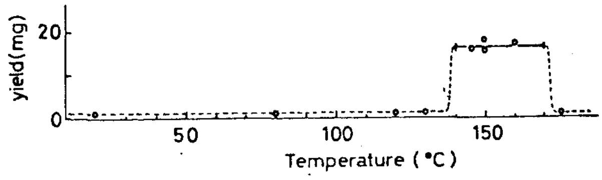


Fig.I-3. In-source polymerization of acrylonitrile in DCA canal; Relationship between polymer yield and the temperature at which DCA-ethyl acetate canal compounds were treated.

DCA-ethyl acetate canal compounds(0.42g)
acrylonitrile($0.20 cm^3$)
irradiation: 1.0×10^5rad/h for 18 h
at -78°C in vacuum

Cyclic Monomers

Although cyclic monomers such as β-propiolactone, diketene, dioxane, *etc.*, form stable DCA canal compounds, polymerization did not proceed by the method here mentioned.

I - 3. Experimental

Materials

Commercially available deoxycholic acid (DCA) was purified by repeated recrystallizations from methanol or acetone. 2,3-Dimethyl-1,3-butadiene was prepared by hydrobromic acid-catalyzed dehydration of pinacol followed by fractionation in a Vigreux column.[26] 2,3-Dichloro-1,3-butadiene, in about 40 % methanol solution, was freed from inhibitors by repeated distillations. Other diene and vinyl monomers were obtained commercially and purified in the usual manner.

Formation of DCA Canal Compounds

The DCA-monomer canal compounds were prepared by adding 0.2 cm^3 of a monomer to 2-4 cm^3 of hot methanol solution containing 1.0 g of DCA-acetone canal compound in a glass tube of 10 mm diameter. In the case of 1,3-butadiene, the tube was sealed under reduced pressure. The solution was then allowed to stand at room temperature for some time and cooled to 0°C. Alternatively, the canal compounds could be prepared by recrystallizing DCA-acetone canal compound with liquid vinyl monomers. Formation of the canal compounds was indicated by the appearance of small needle-like crystals. In the case of acrylonitrile, the canal compound was prepared by a somewhat modified method: by recrystallizing DCA from ethyl acetate or acetone, DCA-ethyl acetate or DCA-acetone canal compound was at first prepared, which was then heated at various temperatures under reduced pressure (10^{-3} Torr) for 2 h. The degassed and purified acrylonitrile was then distilled by vacuum line technique, sealed off and stored for some days at 0°C, and then submitted directly for polymerization.

Polymerization Procedure

Radiation-induced polymerizations were carried out in sealed or open glass vials in a Dewar flask at -196, -78, or 0°C by irradiating with γ-rays from a ^{60}Co source, with a dose rate and total dosage of $1.0\text{-}5.0 \times 10^5$ rad/h and $0.5\text{-}2.0 \times 10^6$ rad, respectively. Post-polymerization of some of the samples was done at 0 or 50°C. After the polymerization, the contents were poured into excess methanol to separate DCA from the canal compounds, and the polymer obtained was dried in vacuo.

Measurements

Differential thermal analysis(DTA) and thermogravimetry(TG) were carried out on the DCA canal compounds by using the analyzer of Rigakudenki Co.(Japan). The scans were taken at a speed of 2.5°C/min under a nitrogen atmosphere. Infrared(IR) spectroscopy was made on KBr dispersions.

I - 4. Summary

A series of deoxycholic acid(DCA) canal compounds with vinyl and diene monomers were prepared, and their radiation-induced polymerization was studied. In the case of 2,3-dichloro-1,3-butadiene and 2,3-dimethyl-1,3-butadiene, highly 1,4-trans tactic polymers were obtained, while in the case of 1,3-butadiene and acrylonitrile, atactic polymers resulted. Optically active poly(*trans*-2-methyl-1,3-pentadiene) was obtained by asymmetric inclusion polymerization in chiral DCA canal.

Chapter II. Characteristics of Deoxycholic Acid Canal for Incorporation of Guest Molecules

II - 1. Introduction

In the preceding chapter, it was described that a naturally occurring steroidal acid, that is, deoxycholic acid (DCA) can serve as an effective host molecule for the canal polymerization of several diene monomers. In these cases, the conventional method was used for obtaining DCA canal compounds, which were prepared by the recrystallization of DCA from methanol containing the guest molecules.

The author has found that a variety of guest molecules can be released from their DCA canal compounds and replaced by new guest molecules which fit into the DCA canal. Such a new, replacement technique may be expected to open a further way for the canal polymerization using DCA as the host molecule. This means that DCA canal may serve as an unique space for the selective incorporation of guest compounds.

This chapter concerns with a study on the polymerization of 2,3-dimethyl-1,3-butadiene(DMB) monomer included into DCA canal, using the replacement technique. At first the author describes the replacement of a variety of guest molecules in DCA canal compounds by DMB monomer, and next discusses the competitive incorporation of non-polymerizable compounds with DMB monomer into DCA canal.

II - 2. Results and Discussion

II - 2 - 1. Replacement of Guest Molecules in DCA Canal

1. Replacement technique to prepare DCA-DMB canal compound

It has been known that DCA forms lattice inclusion compounds of a canal type with a variety of organic substances,[20] and that the canals are formed between hydrogen-bonded pleated sheets of DCA molecules.[21-23] The dynamic properties of the DCA canal compounds, however, seem not yet to be clarified in detail,[20] which prompted us to study the dynamic behavior of guest molecules in DCA canal compounds. The author finds that small guest molecules can be replaced by larger molecules, and that several sorts of diene monomers polymerize in DCA canal. This was confirmed mainly by differential thermal analysis (DTA), thermogravimetry (TG) and IR spectral studies, as an example describes below.

DCA-acetone canal compound

DCA-acetone canal compound was formed by recrystallizing DCA from acetone. The DTA diagram of the DCA-acetone canal compound is shown in Fig. II-1(b), which has two peaks at 148 and 178°C. The former peak corresponds to the temperature at which acetone included is released from DCA canal, which was confirmed by the decrease of weight in a TG measurement carried out at the same time in parallel (peak range; 140-155°C). The TG measurements indicated also that the mole ratio of DCA to acetone in the canal compound amounts nearly unity. Acetone molecules appear to be released from the canal compound if the DCA-acetone canal compound is allowed to stand for a long time at room temperature, which was confirmed also by TG measurements. The second peak in Fig.II-1(b) corresponds to the melting point of DCA itself, which can be readily understood by comparing the curve (b) with that of (a).

Fig.II-2 includes the IR spectra of DCA-acetone canal compound and of DCA after releasing the guest molecules. These spectra differ clearly each other, and from these facts it can be understood how the guest molecules included affect the IR spectrum of DCA.

DCA-DMB canal compound

DCA-DMB canal compound has so far been prepared by the recrystallization of DCA from methanol containing DMB in a sealed tube. The author now finds that it is prepared by the replacement of acetone by DMB as follows.

The DCA-acetone canal compound above mentioned was heated with excess amount of DMB in a sealed tube for 1 h at 60°C. After the treatment, the sample was dried under reduced pressure at room temperature to exclude

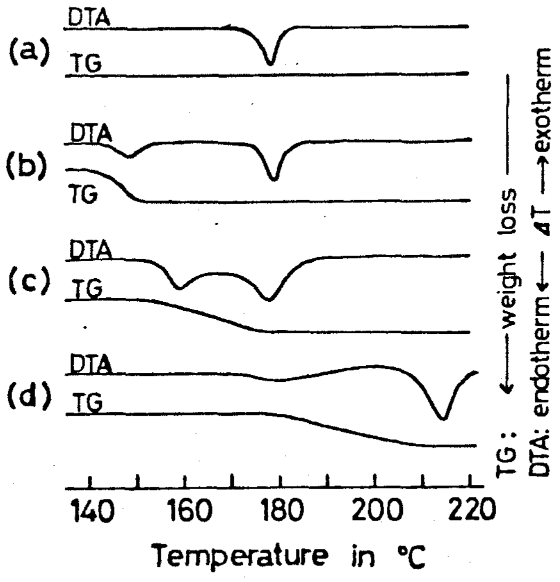


Fig.II-1. DTA and TG diagrams.

(a) DCA without guest molecules
(b) DCA-acetone canal compound
(c) DCA-DMB canal compound
(d) DCA-poly(DMB) canal compound

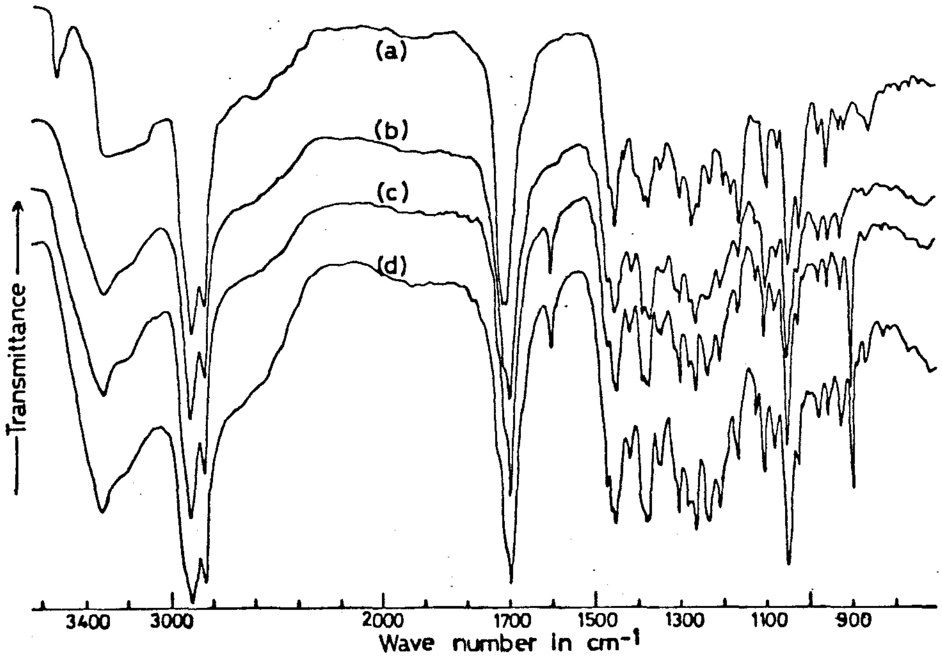


Fig.II-2. IR spectra. (a) DCA without guest molecules. (b) DCA-acetone canal compound. (c) DCA-DMB canal compound. (d) DCA-poly(DMB) canal compound.

components outside of DCA canal. The crystals maintained their original shapes. In Fig.II-1 and II-2, the diagrams of DTA and TG as well as the IR spectrum of the sample thus obtained are included. As can be seen from Fig.II-1(c), the peak at 148°C for DCA-acetone canal compound was replaced by a new peak at 158°C. TG measurement carried out at the same time in parallel showed loss of the guest component at a peak range between 150 to 180°C. The guest component was identified as DMB by gas chromatography and IR spectroscopy. The mole ratio of DCA to DMB in the canal compound amounted nearly equal to 3. The spectrum of the DCA-DMB canal compound was found to be similar to that of DCA-acetone canal compound, with the exception of additional absorption bands at 890 and 1600 cm^{-1} due to DMB itself in the former spectrum. These results suggest that DCA-DMB canal compound here obtained is similar to that prepared by the recrystallization of DCA from methanol containing DMB.

DCA-poly (DMB) canal compound

The DCA-DMB canal compound thus obtained was irradiated with a ^{60}Co source at -196°C, and post-polymerization was done at 0°C for 5 h. As can be seen from Fig.II-1, the peak of the DTA diagram at 158°C observed for DCA-DMB canal compound is no more seen and a new peak appears at 215°C for the DCA-poly(DMB) canal compound [Fig.II-1(d)]. After the polymerization, decreases in the absorbances at 890 and 1600cm^{-1} were observed [Fig. II-2(d)]. It was found that the polymer isolated maintained the original crystal shape and showed the similar IR spectrum as that reported previously, which indicates the formation of highly 1,4-trans tactic polymer. It was confirmed from these results that methanol did not influence the polymerization of DMB in DCA canal compounds.

On the process of the canal polymerization

Fig.II-3 shows a schematic representation of the post-polymerization of DMB included in DCA canal compounds, based upon the results here obtained. The scheme consists of three steps: (1) replacement of the guest component, that is, acetone by DMB monomer in DCA canal, (2) post-polymerization of

DMB included in DCA canal, and (3) separation of poly(DMB) obtained from DCA canal.

In the subsequent section, this research is focussed on the first step, namely, replacement of guest components by DMB.

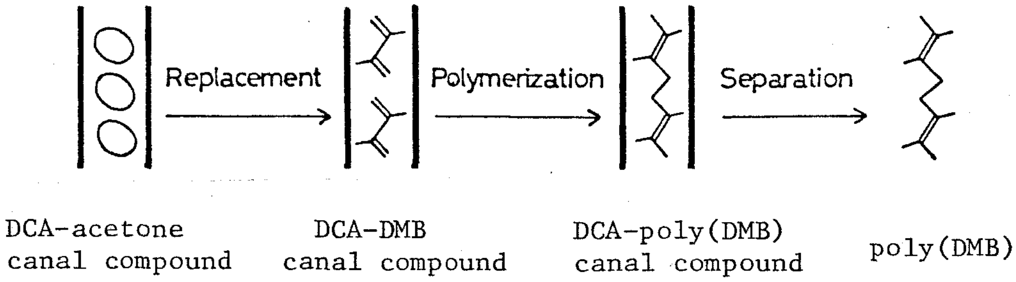
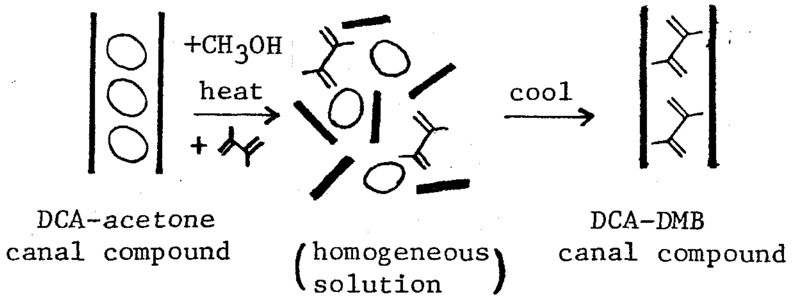


Fig.II-3. Schematic representation of the process of inclusion polymerization of DMB in DCA canal, using replacement technique.

The conventional method to form DCA-DMB canal compound is shown below for comparison; the compound is formed by recrystallization of DCA from methanol containing DMB monomer. DCA canal structure is destroyed because methanol dissolves DCA well, while the canal structure is maintained according to the above replacement technique.



2. Replacement of various guest molecules by DMB

It is well assumed that both the structure of guest molecule and the temperature at which they are replaced play an important role in their replacement by DMB in DCA canal. DCA-DMB canal compound can be formed at different temperatures by replacing acetone, ethyl acetate, and acetic acid from their DCA canal compounds. The DCA-DMB canal compound thus obtained was then post-polymerized after γ-ray irradiation. It is to be noted that the polymerization of DMB proceeds predominantly in the canal and negligible outside of it under the conditions studied.

Fig.II-4 shows how the replacement of acetone by DMB in DCA canal depends on the replacement temperature. The polymerization hardly proceeded at 0°C, but the rate increased with rise in the replacement temperature, and reached saturation in 3 h at 30°C. Under this condition, conversion of the polymerization should be about 50% in DCA canal, assuming that the mole ratio of DCA to DMB in the canal compounds is equal to 3.

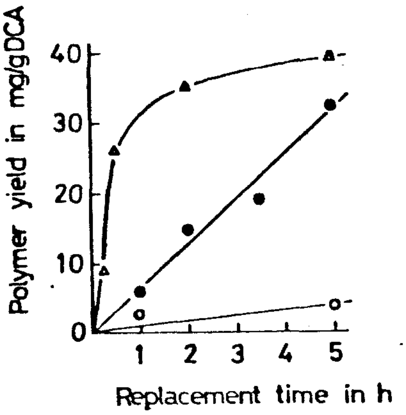


Fig.II-4. Post-polymerization of DMB in DCA canal; Polymer yield in relation to replacement time (DCA-acetone canal compound was used; temperature of replacement, (○): 0°C, (●): 15°C, (△): 30°C). irradiation: 0.3 Mrad at -196°C post-polymerization: 0°C for 5 h

---

Polymer yields were given in mg/g DCA in the case of the canal polymerization of DMB; since the amounts of DMB included in DCA canal have not been determined, the proportion of DMB which polymerized in canal to that present before polymerization is not able to be calculated.

Effect of structure of the guest molecules on the polymerization behavior was compared with each other for the cases of acetone-, ethyl acetate-, and acetic acid-included DCA canal compounds at the same temperature. As can be seen from Fig.II-5 concerning the relationship between the polymerization yield and the time required for replacement, the rate of replacement at 30°C was considerably low in cases of ethyl acetate- and acetic acid-included DCA canal compounds, as compared with that of acetone-included DCA canal compound. Replacement of ethyl acetate by DMB appears to occur gradually at 30°C, and in fact, saturation of the polymer yield was observed after 20 h. On the other hand, no replacement of acetic acid by DMB appears to occur at 30°C. Fig.II-6 shows the results obtained at 60°C, which indicates much easier replacement of ethyl acetate by DMB than the case at 30°C.

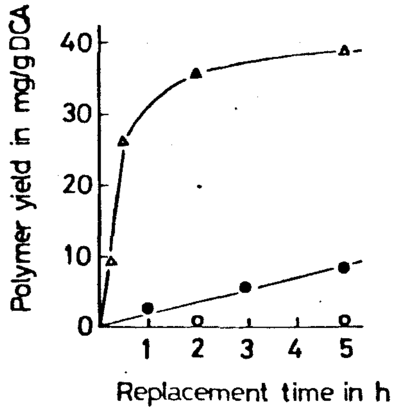


Fig.II-5. Post-polymerization of DMB in DCA canal; Polymer yield in relation to replacement time [(△):DCA-acetone canal compound, (●):DCA-ethyl acetate canal compound, (○):DCA-acetic acid canal compound]

replacement: 30°C
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

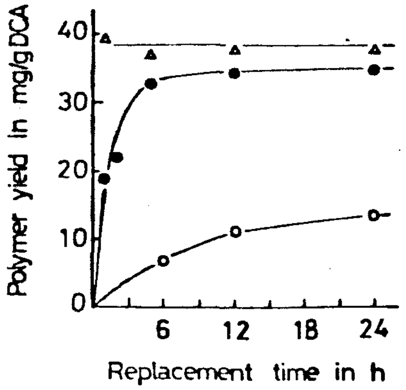


Fig.II-6. Post-polymerization of DMB in DCA canal; Polymer yield in relation to replacement time [(△):DCA-acetone canal compound, (●):DCA-ethyl acetate canal compound, (○):DCA-acetic acid canal compound]

replacement: 60°C
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

The results on the replacement of different guest molecules in DCA canal by DMB are shown in Table II-1. As can be seen from the table, the canal polymerization proceeds in general fairly smoothly, except for the cases of phenanthrene and 2,3-dimethylbutane as the guest components. The results indicate also that DCA-DMB canal compound can be formed, by treating DCA including no guest component with DMB.

From these results it is assumed at least to be sure that the replacement of guest molecules in DCA canal depends on their molecular structure. It may be assumed that linear molecules such as palmitic acid can be replaced easily by DMB in DCA canal, while somewhat bulky, branched molecules such as phenanthrene and 2,3-dimethylbutane can hardly be replaced.

Table II-1. Post-polymerization of DMB in DCA canal in relation to the sort of guest molecules to be replaced[a)]

Guest molecule	Polymer yield in mg
None	39.5
Acetonitrile	38.9
Acetone	39.3
Methyl ethyl ketone	32.2
Ethyl acetate	32.1
Acetic acid	33.4
Palmitic acid	32.1
Phenanthrene	2.7
2,3-Dimethylbutane	1.7

a) DCA: canal compound 1.0 g; DMB: 0.40 cm^3;
replacement: 90°C for 30 min
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

II - 2 - 2. Competitive Incorporation of Guest Molecules into DCA Canal

The polymerization of DMB included in DCA canal can be schematically shown as follows:

$$\text{DCA-acetone canal compound} \xrightarrow[\text{Replacement}]{\text{DMB}} \text{DCA-DMB canal compound}$$

$$\xrightarrow[\text{Polymerization}]{\gamma\text{-rays}} \text{DCA-poly(DMB) canal compound} \xrightarrow[\text{Separation}]{\text{methanol}} \text{poly(DMB)}$$

In this procedure, DCA-DMB canal compound is formed at first by replacing volatile guest compounds such as acetone by DMB in DCA canal at definite temperatures. It can be well assumed that multicomponents are able to be incorporated into DCA canal competitively through the replacement process, which is shown in Fig.II-7. This leads to the following consideration that non-polymerizable compounds might be simultaneously incorporated into DCA canal together with DMB monomer, which causes separation of the included monomer molecules each other, rendering to depress the polymerization within DCA canal. Therefore, the polymer yield is assumed to depend on the amount of additives incorporated into DCA canal. The author carried out the following experiments particularly using DCA-acetone canal compound, since the canal compound can release acetone readily to be replaced by other organic compounds including the monomer.

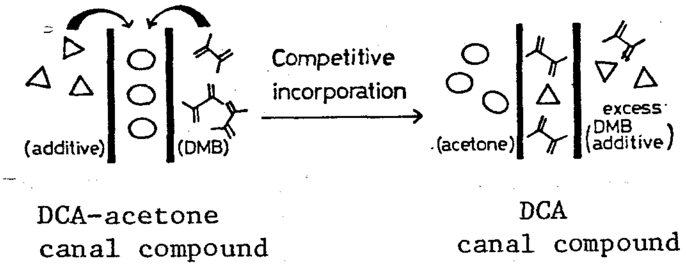


Fig.II-7. Scheme of competitive incorporation in the replacement process for the inclusion polymerization in DCA canal.

1. *Effect of saturated hydrocarbons as additives*

The polymerization of DMB monomer included in DCA canal was at first carried out in the presence of a series of *n*-alkanes. The results are shown in Fig.II-8, in which the polymer yield was plotted against *n*-alkane to DMB mole ratios. The lower curve in the figure was obtained in the presence of *n*-hexane, while the upper curve was obtained in the presence of *n*-decane. As can be seen from the figure, addition of *n*-alkanes led to decrease in polymer yield more or less in all cases, and this tendency was found to be emphasized with increasing amounts of the additives. It is to be noted that the depression of polymer yield was found to depend on the chain length of *n*-alkanes.

In order to see this finding more clearly, Fig.II-9 was shown for the relationship between polymer yield and chain length of *n*-alkanes, in which DMB and *n*-alkane were present in semimolar or equimolar ratio in the reaction systems. The upper broken line indicates the case in which no additives were present. It can be seen from the figure that addition of *n*-hexane led to the most significant decrease in the polymer yield as compared with the cases of *n*-heptane, *n*-octane and *n*-nonane, and only a slight decrease was observed in the cases of *n*-decane, *n*-pentadecane and *n*-pentane. These results suggest that DCA canal in question can incorporate *n*-alkanes having appropriate chain lengths more favorably than those having shorter or longer ones.

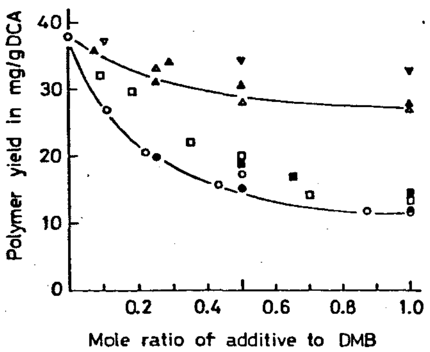


Fig.II-8. Competitive incorporation of *n*-alkanes with DMB into DCA canal: Relationship between polymer yield and the amount of additives.
(△): *n*-pentane, (○): *n*-hexane,
(●): *n*-heptane, (□): *n*-octane,
(■): *n*-nonane, (▲): *n*-decane,
(▽): *n*-pentadecane.

replacement: 60°C for 1 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

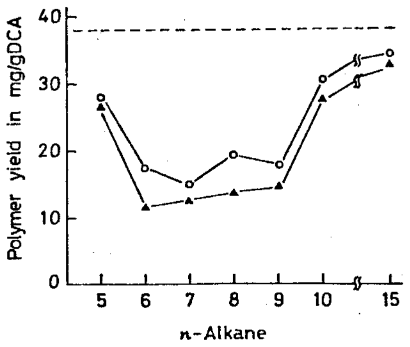


Fig.II-9. Competitive incorporation of *n*-alkanes with DMB into DCA canal: Relationship between polymer yield and chain length of *n*-alkanes.
mole ratio of *n*-alkane to DMB;
(○): 0.5, (▲): 1.0
replacement: 60°C for 1 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

The canal polymerization of DMB in DCA canal was next carried out in the presence of other sort of hexane isomers. As can be seen from Fig.II-10, depression of the polymerization was observed in the following order: 2,3-dimethylbutane > 2-methylpentane ≈ 3-methylpentane > *n*-hexane > 2,2-dimethylbutane. The result would be ascribed to difference in the steric requirements of the hexane isomers. It can be assumed at least that DCA canals incorporate somewhat bulky, branched molecules more favorably than linear ones, with the exception of 2,2-dimethylbutane.

Among five hexane isomers in question, 2,3-dimethylbutane can be regarded as the most suitable saturated model compound for *n*-hexane, which also reflects a sharp decrease in the polymerization when this compound was added in the reaction system. A similar effect of adding 2,3-dimethylbutane will be discussed in Chapter III-2-3 for the polymerization in which methanol was used as the solvent. Comparing the present results with the earlier ones, it is obvious that methanol seems not to affect the polymerization behavior, to which the subsequent section will be refered.

In contrast to the case of adding 2,3-dimethylbutane or methylpentanes, decrease in the polymerization by adding 2,2-dimethylbutane was considerably low. This suggests that both size and shape of 2,3-dimethylbutane fit more suitably in DCA canal than those of 2,2-dimethylbutane. It can be thus well assumed that DCA canals have an ability to select molecules to be included.

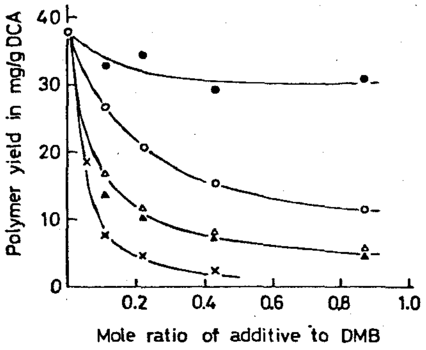


Fig.II-10. Competitive incorporation of hexane isomers with DMB into DCA canal: Relationship between polymer yield and the amount of additives.

(○):*n*-hexane, (△):2-methylpentane,
(▲):3-methylpentane,
(×):2,3-dimethylbutane,
(●):2,2-dimethylbutane.

replacement: 60°C for 1 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

Canal polymerization of DMB in DCA canal was further carried out in the presence of cycloalkanes as additives. Results are shown in Fig.II-11. The result obtained in the presence of cyclopentane (curve A) was in the same order as that in the presence of *n*-hexane. Cyclohexane as well as cyclooctane were found to inhibit the polymerization of DMB effectively similarly to the order as 2,3-dimethylbutane does. These results show that addition of cycloalkanes led to the decrease in the polymer yield more efficiently than that of the cases of adding *n*-alkanes, which seems to indicate that cycloalkanes fit more favorably in DCA canal than *n*-alkanes.

Fig.II-11 includes also the run carried out in the presence of β-pinene, a cyclic monoterpenoid compound, which exhibited very little effect.

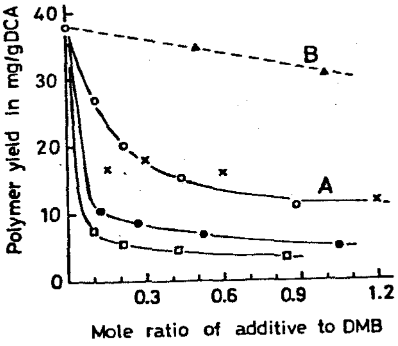


Fig.II-11. Competitive incorporation of cycloalkanes with DMB into DCA canal: Relationship between polymer yield and the amount of additives.

(○):*n*-hexane, (×):cyclopentane,
(●):cyclohexane, (□):cyclooctane,
(▲):β-pinene.

replacement:60°C for 1 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

2. *Effect of polar molecules as additives*

It is well assumed that, not only size and shape of the molecules, but also other factors such as polarity or functionality of the molecules as additives play an important role in their competitive incorporation with DMB monomer into DCA canal. The polymerization was carried out finally in the presence of several polar organic compounds.

Table II-2 shows results of the canal polymerization of DMB in DCA canal, in which excess amounts of polar compounds were present. It is noteworthy that almost all additives examined did not affect the polymerization behavior, except the latter two or three cases in the table. Since the appearance of DCA crystals seems to be left unchanged during the polymerization in all cases because of low solubility of DCA, decrease in polymer yield observed in the cases in which dimethylformamide, dimethyl sulfoxide and acetic acid were present appears to indicate that these compounds were incorporated simultaneously with DMB into DCA canal.

Table II-2. Post-polymerization of DMB in DCA canal in the presence of polar molecules.$^{a)}$

Additive	Polymer yield in mg
None	38.3
Propionitrile	35.9
Acetone	39.8
Ethanol	35.7
Methyl formate	39.5
1,2-Dichloroethane	38.5
Dimethylformamide	28.9
Dimethyl sulfoxide	8.7
Acetic acid	0.8

a) DCA-acetone canal compound:1.0 g; DMB: 0.40 cm^3; additive: 1.0 cm^3; replacement: 60°C for 1 h; irradiation:0.3 Mrad at -196°C; post-polymerization: 0°C for 5 h.

Fig.II-12 shows IR spectra of DCA canal compounds obtained by competitive incorporation under the same conditions as described in Table II-2. The IR spectra of DCA canal compounds formed in the presence of methanol, ethanol, acetone and propionitrile were found to be similar to that of DCA-DMB canal compound formed in the absence of additives[Fig.II-12(a) and (b)]. However, the spectrum of that formed in the presence of acetic acid was quite different and rather similar to that of DCA-acetic acid canal compound obtained by recrystallization of DCA from acetic acid [Fig.II-12(c)]. This fact appears to indicate that an inclusion of acetic acid into DCA canal might occur predominantly, so that the polymerization of DMB could not proceed in the DCA canal in this case.

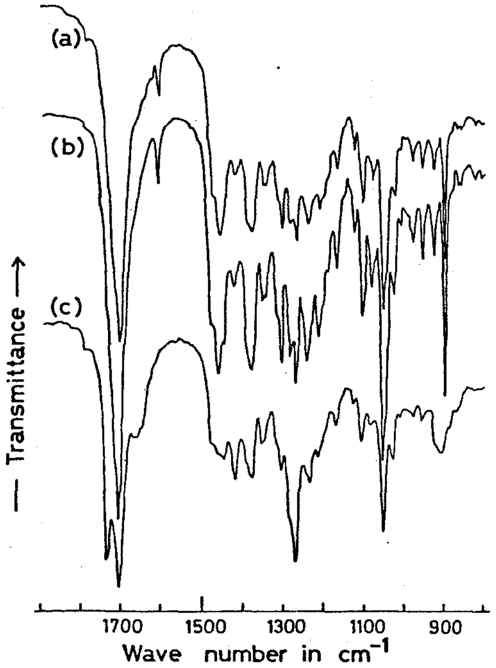


Fig.II-12. Infrared spectra of DCA canal compounds formed in the presence of additives.

(a): none
(b): methanol, ethanol, acetone or propionitrile
(c): acetic acid

Fig.II-13 shows results of polymerization done under the condition in which amount of these additives was varied. It can be seen from the figure that addition of acetic acid caused a sharp decrease in polymer yield as compared with the case of adding *n*-hexane, while methanol and acetone affected it only scarcely. This fact shows that methanol can be effectively used as a solvent for inclusion polymerization of DMB in DCA canal, since such small molecules are assumed not to be closely included into DCA canal so that they seem to have no influence on forming DCA-DMB canal compounds.

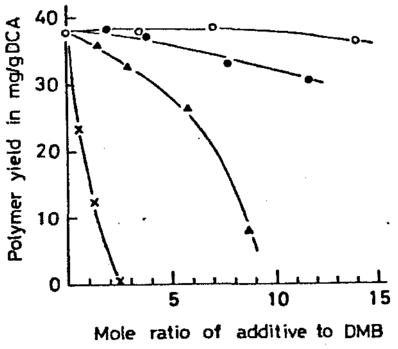


Fig.II-13. Competitive incorporation of polar molecules with DMB into DCA canal: Relationship between polymer yield and the amount of additives.

(O): methanol, (●): acetone,
(▲): ethyl acetate,
(X): acetic acid.

replacement: 60°C for 1 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

II - 3. Experimental

Materials

Commercially available deoxycholic acid (DCA) was purified by repeated crystallization from acetone.

2,3-Dimethyl-1,3-butadiene (DMB) was prepared by hydrobromic acid-catalyzed dehydration of anhydrous pinacol followed by fractional distillation.[26] The fraction was analyzed by gas chromatography and found to be more than 99% pure.

Various guest components used were of analytical grade and used without further purification.

Formation of DCA Canal Compounds

The DCA canal compounds of acetone, ethyl acetate, acetic acid, acetonitrile and methyl ethyl ketone were prepared by recrystallization of DCA from the solvents. DCA canal compounds of palmitic acid and phenanthrene were prepared by recrystallization of DCA from methanol containing the guest molecules.[20-22]

All the volatile guest molecules, with the exception of palmitic acid and phenanthrene, could be effectively removed by heating the canal compounds: for example, DCA-acetone canal compound at 145-150°C under reduced pressure (10^{-3} Torr) for 15 min.

Polymerization Procedure

1.0 g of various DCA canal compounds (2.5 mmol) above mentioned and 0.40 cm^3 (3.5 mmol) of DMB (with additives in the case of runs of II-2-2.) were placed in a glass tube of 10 mm diameter, which was then sealed under vacuum (10^{-3} Torr) after three freeze-thaw cycles. The sealed tube was heated for replacement of the included components by DMB at definite temperatures. Irradiation was provided by γ-rays from a ^{60}Co source at -196°C with a dose of 0.3 Mrad. Post-polymerization was done on the samples at 0°C for 5 h. The tube was then cooled again to -196°C and then opened, and the contents were immediately poured into excess methanol (50 to 100 cm^3) to separate DCA from the canal compounds. Polymers thus obtained were washed thoroughly with hot methanol and dried under reduced pressure.

It is noteworthy that the polymerization of DMB was found to proceed predominantly in the DCA canal and negligible outside of it under the conditions studied.[27]

Measurements

Differential thermal analysis (DTA), thermogravimetry (TG) and infrared (IR) spectral measurements were carried out in the same way as described in Chapter I.

II - 4. Summary

DCA-DMB canal compounds were found to be prepared readily by replacing various sorts of guest molecules in DCA canal by DMB monomer. Post-irradiative polymerization of the monomer included in DCA canal was studied after irradiating with γ-rays from a ^{60}Co source. Both the replacement and the polymerization processes were observed by differential thermal analysis(DTA), thermogravimetry(TG) and IR spectroscopy. The optimum conditions for the replacement of acetone, ethyl acetate, and acetic acid by DMB were established.

Canal polymerization of DMB in DCA canl was studied in the presence of several sorts of non-polymerizable organic compounds including alkanes and polar molecules. These compounds were found to be incorporated competitively with DMB monomer into DCA canal, causing thereby more or less decrease in the rate of polymerization depending on the structure of additives. DCA canal was found to incorporate more favorably branched or cyclic alkanes than linear ones.

Chapter III Space Control for Inclusion Polymerization in Deoxycholic Acid Canal

III - 1. Introduction

It is considered that deoxycholic acid (DCA) canal may play two important roles when it is employed as a reaction space for polymerization. The one is that DCA canal has an ability to select molecules to be included, which was treated in the preceding Chapter II in terms of competitive incorporation of guest components into DCA canal.

The other is that DCA canal can control a polymerization reaction of monomer molecules included in the canal to yield a stereospecific polymer. This might be attributed to the constrained movement of the monomer molecules inside of the canal. In other words, monomer molecules which fit the canal have one dimensional movement, maintaining a definite orientation under the influence of host molecules.

This chapter concerns with the inclusion polymerization of four diene monomers in DCA canal in detail; they are 1,3-butadiene(BD), 2,3-dichloro-1,3-butadiene(DC B), 2,3-dimethyl-1,3-butadiene(DMB), *trans*-2-methyl-1,3-pentadiene, which have different molecular sizes and shapes. It can be suggested from the results of Chapter II that DMB and DC*l*B fit DCA canal preferentially, and BD fits DCA canal less effectively.
Since *trans*-2-methyl-1,3-pentadiene is a prochiral monomer, it is suitable for a study on asymmetric inclusion polymerization in chiral DCA canal.

At first, it is described that these monomers are subject to different space control for inclusion polymerization in DCA canal, in connection with the nature of DCA canal compounds. Finally, peculiarity of DCA canal is described on the basis of comparison of host molecules so far employed for inclusion polymerization in canal.

III - 2. Results and Discussion

III - 2 - 1. 1,3-Butadiene (BD)

1. Process for polymerization of BD in DCA canal

The polymerization of BD included in DCA canal was carried out generally in a similar way as that of 2,3-dimethyl-1,3-butadiene (DMB) described in the preceding Chapter II according to the following Scheme:

$$\text{DCA-acetone canal compound} \xrightarrow[\text{Replacement}]{\text{BD}} \text{DCA-BD canal compound}$$

$$\xrightarrow[\text{Polymerization}]{\gamma\text{-rays}} \text{DCA-poly(BD) canal compound} \xrightarrow[\text{Separation}]{\text{methanol}} \text{poly(BD)}$$

DCA-BD canal compound

DCA-BD canal compound was at first prepared by treating DCA-acetone canal compound with excess amount of BD in a sealed tube for 2 h at 60°C. The sample was then allowed to stand under ordinary pressure at room temperature to exclude BD present outside of the canal compound. It is noteworthy that DCA was scarcely soluble in BD, and that the crystals of the canal compounds kept their original shape and appearance even after the treatment. Fig.III-1 shows DTA diagrams of the samples. The peak at 148°C for DCA-acetone canal compound [Fig.III-1 (a)] was replaced by a new peak at 158°C [Fig.III-1 (b)]. The tendency of the DTA diagram change was similar to that of DCA-DMB canal compound, though the boiling points of these monomers were far different. TG measurement done at the same time in parallel showed a gradual release of the guest component from the canal in a temperature range between 100 to 150°C, and then a marked release to 165°C. It can be recalled, on the other hand, that such a gradual release of monomers from the canal in the temperature range of about 100 to 150°C could not be observed in cases of DCA-DMB and DCA-DClB canal compound (see III-2-2 and III-2-3). From these results, DCA-BD canal compound should be concluded as being more unstable than those DCA canal compounds of 2,3-disubstituted butadienes. Furthermore, BD was found to be released from DCA canal when the DCA-BD canal compound was allowed to stand for a long time at room temperature. The mole ratio of DCA to BD in the canal compound amounted nearly 2.

DCA-poly(BD) canal compound

The DCA-BD canal compound thus prepared was irradiated from a ^{60}Co source at -196°C with a dose of 0.3 Mrad, and the post-polymerization was successively done at 0°C for 5 h. It is noteworthy that the polymerization in question proceeds predominantly in the DCA canal and negligible outside of it. As can be seen from Fig.III-1 (c), peaks at 158 and 178°C observed for DCA-BD canal compound were no more seen for DCA-poly(BD) canal compound, and in the latter case, a new peak appeared at 203°C, which is 15°C lower than that of DCA-poly(DMB) canal compound (see Fig.I-2). This

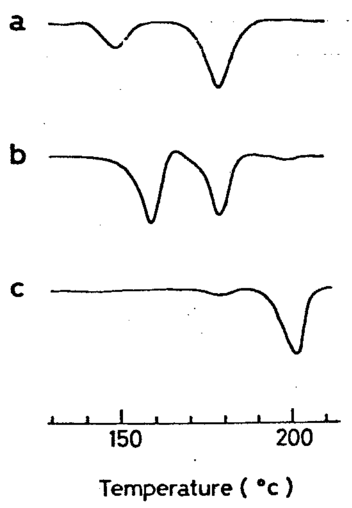


Fig.III-1. DTA diagrams.

(a): DCA-acetone canal compound
(b): DCA-BD canal compound
(c): DCA-poly(BD) canal compound

suggests that DCA forms more stable canal compound with branched molecules such as 2,3-disubstituted polybutadienes than with linear poly(BD) itself. The IR spectrum of the DCA-poly(BD) canal compound showed a very weak absorption band at 970cm^{-1}, which is characteristic for trans-1,4 structure of the polymer.

Poly (BD)

After the polymerization, DCA canal compounds were poured into excess methanol to separate DCA and the polymers resulted. The polymers were a rubbery solid which is soluble in carbon disulfide, toluene, *etc.*, and insoluble in hydrocarbons and alcohols. Its molecular weight amounted to 5×10^4. The microstructure of the polymer consists of trans-1,4 and 1,2-types in a ratio of 73:27, and cis-1,4-structure was not detectable. This fact is in contrast to the highly trans-1,4-structure of poly(DMB).

It might be recalled that the highly trans-1,4 tactic polymers can be obtained by the canal polymerization of BD using urea[3(1),6(2)] and perhydrotriphenylene[15] as the host molecules. These results suggest the importance of a characteristic space control for addition polymerization in DCA canal

2. On the replacement of acetone by BD in DCA canal

The conditions for replacing acetone by BD in DCA canal were further studied. Figs.III-2 and III-3 show how the replacement of acetone by BD in DCA canal depends on the temperature and the time required for the replacement (shown in broken lines). The polymerization was found to proceed very slightly at 0°C for 1 h, however, the polymer yield enhances with rise in both the temperature and the time for replacement. The polymerization yield tends to saturate after 2 h at 60°C.

The runs were further carried out in the presence of ethyl acetate as the additive, the result being shown with full lines. Like the result obtained in the absence of any additive, the polymer yield reached to saturation after 2 h at 60°C. In addition, the presence of ethyl acetate was found to cause a decrease in the polymer yield.

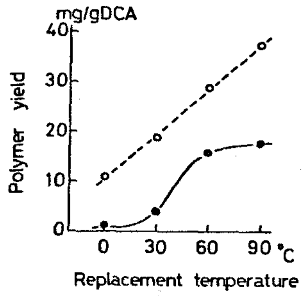


Fig.III-2. Post-polymerization of BD in DCA canal; Polymer yield in relation to replacement temperature.

DCA-acetone canal compound: 1.0g; BD: 1.0cm^3
replacement: 1 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

(○): without additive
(●): in the presence of 1.0cm^3 of ethyl acetate

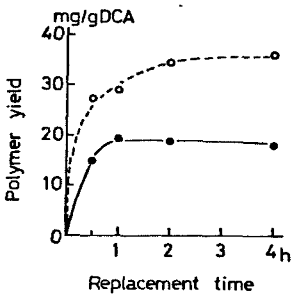


Fig.III-3. Post-polymerization of BD in DCA canal; Polymer yield in relation to replacement time.

DCA-acetone canal compound: 1.0g; BD: 1.0cm^3
replacement: 60°C
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

(○): without additive
(●): in the presence of 1.0cm^3 of ethyl acetate

3. Effect of additives

The inclusion polymerization of BD in DCA canal was then studied in the presence of various sorts of additives.

Effect of additives on the polymerization

The post-polymerization was studied in the presence of 9 sorts of additives. The result is shown in Table III-1. It can be seen that addition of various component affected the polymer yield and the microstructure of the polymers obtained : addition of methanol caused an increase in polymer yield, while it had no effect on the microstructure of the polymer. In contrast to this, addition of acetonitrile, acetone,

Table III-1. Effect of additives on the post-polymerization of BD in DCA canal. a)

Additive	Polymer yield in mg	Microstructure of polymer *trans*-1,4 : 1,2 (%)
None	34	73 : 27
Methanol	42	73 : 27
Ethanol	29	76 : 24
Acetonitrile	18	95 : 5
Acetone	20	98 : 2
Methyl formate	17	98 : 2
Ethyl acetate	20	99 : 1
n-Hexane	14	97 : 3
2,3-Dimethylbutane	10	93 : 7
Benzene	35	72 : 28

a) DCA-acetone canal compound: 1.0 g; BD: 1.0 cm^3; additives: 1.0 cm^3; replacement: 60°C for 2 h; irradiation: 0.3 Mrad at -196°C; post-polymerization: 0°C for 5 h.

methyl formate, and ethyl acetate afforded the polymers composed over 90% of trans-1,4-unit. The table also indicates the decrease in polymer yield in the case of adding *n*-hexane and 2,3-dimethylbutane, respectively, which can be regarded as saturated linear and branched butadiene models. Addition of benzene did not cause any structural change of the polymer. Acetic acid was found to inhibit the polymerization of BD effectively.

Fig.III-4 shows IR spectra of poly(BD)s obtained by the canal polymerization in the presence of additives. The spectrum of poly(BD) obtained in the presence of ethyl acetate [Fig.III-4 (b)] was almost identical

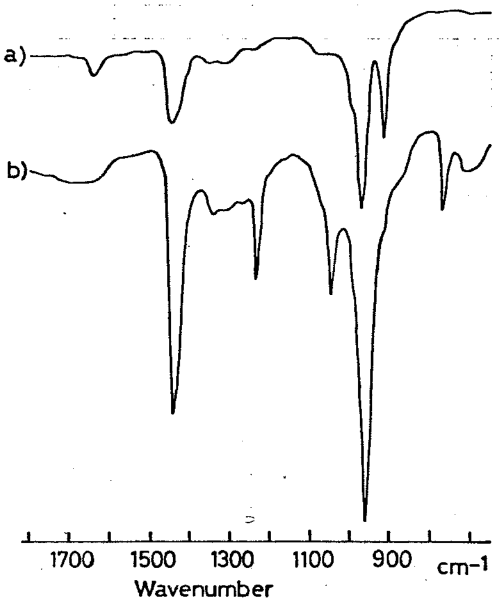


Fig.III-4 . Infrared spectra of poly(BD) obtained by inclusion polymerization in DCA canal in the presence of additives.
(a): methanol
(b): ethyl acetate

to that of the polymer obtained by urea canal polymerization,[3(1)] which afforded a highly trans-1,4 tactic polymer. The crystalline-sensitive bands were observed at 1350, 1250, 1060 and 780cm^{-1}. On the other hand, the spectrum obtained in the presence of methanol indicated a peak at 910cm^{-1} characteristic to 1,2-addition, and no crystalline-sensitive bands seem to appear [Fig.III-4 (a)].

Dependence of the amount of additives on the polymerization

The inclusion polymerization of BD in DCA canal was next carried out, varying the amount of methanol, ethyl acetate and acetic acid as the additives. As shown in Fig.III-5 , addition of small amount of methanol and ethyl acetate caused an increase in polymer yield as compared with that

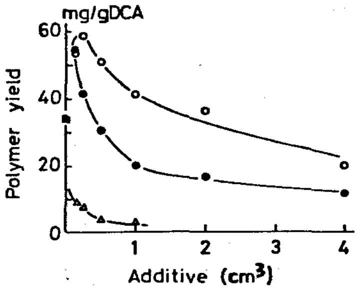


Fig.III-5. Effect of additives on the post-polymerization of BD in DCA canal: Polymer yield in relation to the amount of additives.

DCA-acetone canal compound: 1.0g; BD: 1.0cm^3
replacement: 60°C for 2 h
irradiation: 0.3 Mrad at -196°C
post-polymerization: 0°C for 5 h

(○): methanol, (●): ethyl acetate,
(△): acetic acid

in the absence of any additive, and the polymer yield decreased with rise in an increase of additives. In the case of adding acetic acid, no increase in polymer yield was observed.

Table III-2 shows the microstructure of the polymers obtained. The microstructure of the polymers obtained in the presence of methanol seems to be identical, however, a polymer with high content of trans-1,4 unit (up to 99%) were obtained in the case of adding ethyl acetate.

These results suggest that the polymerization of BD in DCA canal can be controlled by the additives competitively.

Table III-2. Effect of additives on the post-polymerization of BD in DCA canal ; Relationship between the microstructure of polymers and the amount of additives.[a)]

Additive (cm^3)	Microstructure of polymers(*trans*-1,4:1,2)(%)	
	methanol	ethyl acetate
0.12	69 : 31	72 : 28
0.25	71 : 29	85 : 15
0.50	71 : 29	98 : 2
1.00	73 : 27	99 : 1
2.00	71 : 29	99 : 1

a) DCA-acetone canal compound: 1.0 g; BD: 1.0 cm^3;
replacement: 60°C for 2 h; irradiation: 0.3 Mrad at -196°C;
post-polymerization: 0°C for 5 h.

III - 2 - 1. 2,3-Dichloro-1,3-butadiene (DC*l*B)

1. Polymerization Characteristics

On the stability of DCA-DC*l*B canal compound

It is known that the DC*l*B monomer polymerizes readily in methanol solution by γ-ray irradiation. In order to exclude the polymerization outside of the canals, the polymerization was performed only for the crystals of the DCA-DC*l*B canal compounds, which were prepared in methanol solution and filtered off therefrom. The crystal canal compounds thus isolated were stable enough even after allowing to stand for two weeks at room temperature under ordinary pressure; that is, no significant removal of the monomer from the canal compounds was observed, which was ascertained by IR spectral and TG measurements. It is to be recalled for comparison that thiourea-DC*l*B canal compound is rather unstable at room temperature.7(1)(2)

Fig.III-6 shows the relative amount of decrease in the DC*l*B monomer from the canal compounds on standing at different temperatures under ordinary pressure, which was estimated from the decrease in absorption at 890cm^{-1} in IR spectra. It can be seen that the monomer was removed rapidly at 150°C, but very slowly at room temperature. As shown in Fig.III-7, for both cases of polymerization in air and in vacuum, the conversion after 3 h was constant, independently of the time of standing at room temperature under reduced pressure.

Influence of air on polymerization

As can be seen from Fig.III-7 and III-8, conversion* was considerably lower in air than in vacuum. The result suggests that oxygen atoms may interact the canal compounds and inhibit the polymerization within DCA canal.

---

* Polymer yields were given in % conversion in the polymerization of DC*l*B in DCA canal; since only isolated crystalline canal compounds were used, all the monomer existed in DCA canal.

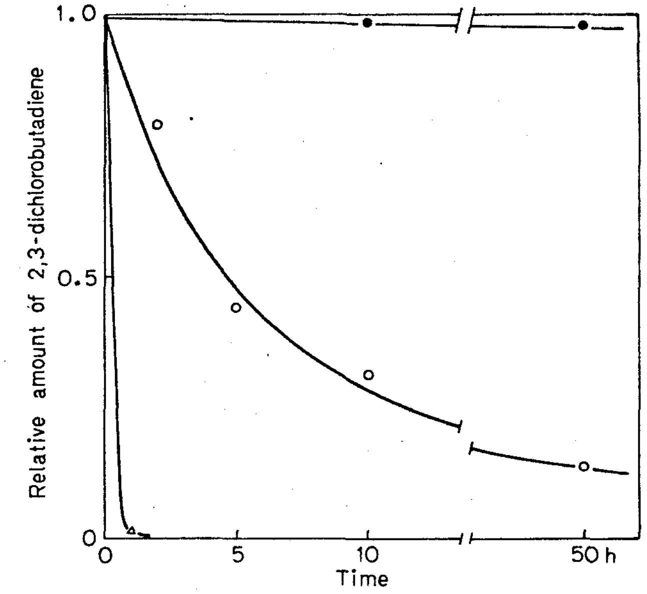


Fig.III-6. Decrease in the amount of DCℓB from its DCA canal compounds when standing under 1 Torr pressure at different temperatures. (●): 15°C, (○): 100°C, (△): 150°C.

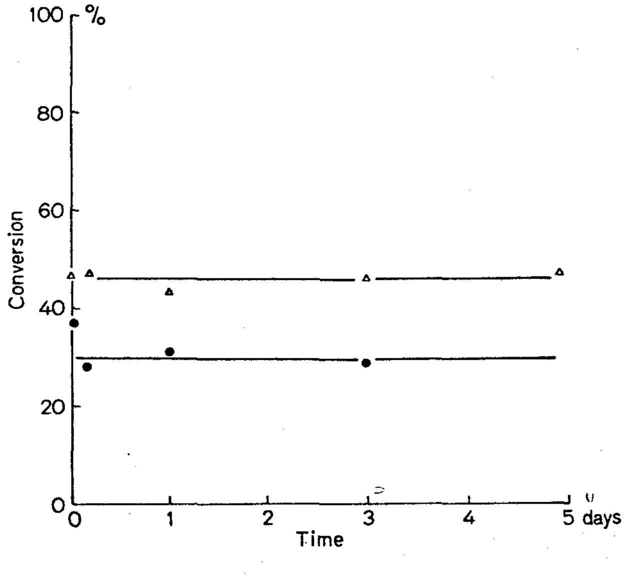


Fig.III-7. In-source polymerization of DCℓB in DCA canal; Relationship of conversion with time of pretreatment of the compounds under 1 Torr pressure at 15°C [dose rate, 1.7×10^5 rad/h; irradiation time, 3 h at 0°C; (△):in vacuum, (●):in air].

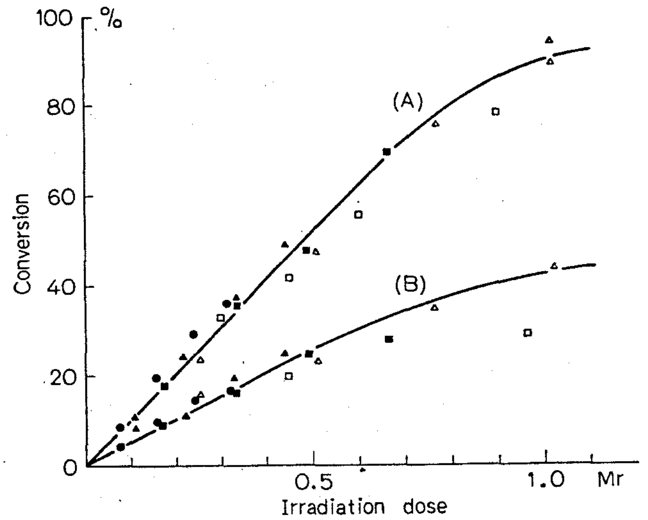


Fig.III-8. Effect of irradiation on conversion for the in-source polymerization of DClB in DCA canal at 0°C ; (A) in vacuum, and (B) in air [dose rate (rad/h): (□):3.0×10^5, (△):1.7×10^5, (■):1.1×10^5, (▲):7.4×10^4, (●):5.3×10^4].

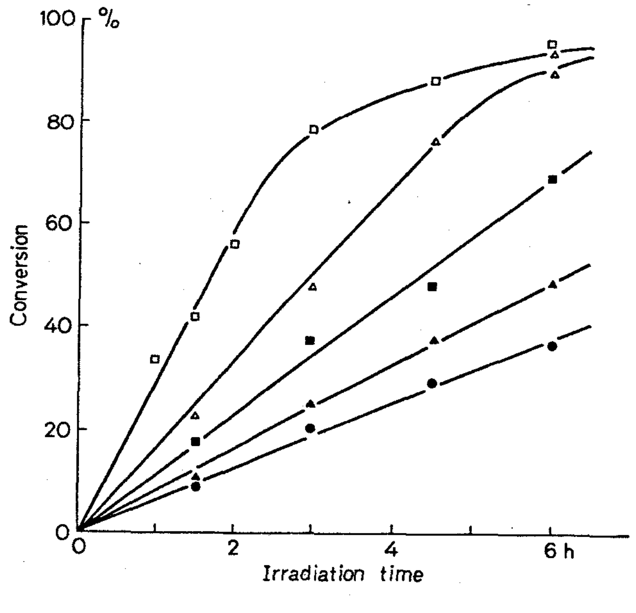


Fig.III-9. Effect of dose rate on conversion for the in-source polymerization of DClB in DCA canal at 0°C ; Time-conversion relationships. [dose rate (rad/h): (□):3.0×10^5, (△):1.7×10^5, (■):1.1×10^5, (▲):7.4×10^4, (●):5.3×10^4].

Effect of dose rate on polymerization

Fig.III-8 and III-9 show relationships of conversion with irradiation dose and irradiation time, respectively. Conversions were found to be proportional to the reaction time and to the total irradiation doses up to about 60%, and then the polymerization proceeded quantitatively. As can be seen also from Fig.III-10, the initial rate of polymerization was proportional to the 0.9th order of the dose rate, in the dose rate range examined. The fact that the rate of polymerization shows nearly the first-order relationship to the dose rate suggests that contribution of the bimolecular termination is fairly small, and at least, unimolecular or otherwise, no termination reaction predominates in the canal polymerization in question. In other words, the propagating free radicals in DCA canal should be considered to have longer life times. This can be also supported by the occurrence of post-polymerization as well as the result on the trapped free radicals by ESR measurements.

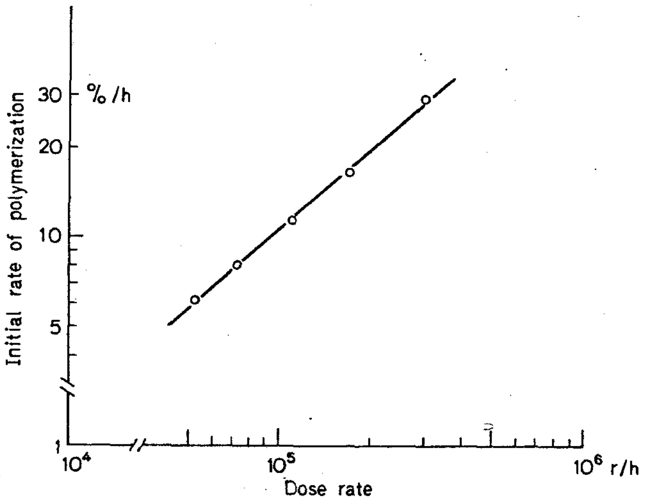


Fig.III-10. Dependence of the dose rate on the initial rate of in-source polymerization of DClB in DCA canal at 0°C.

Effect of temperature on polymerization

The temperature dependence of the conversion was examined in the range between -78 and 50°C. The result is shown in Fig.III-11. Arrhenius plots of the initial rate of polymerization showed a folded line, which gave an apparent activation energy of 3.4 kcal/mol(14.3 kJ/mol) for the canal polymerization in the temperature range between -23 and 50°C, and 0.9 kcal/mol (3.8 kJ/mol) for that below -23°C (Fig.III-12). These values are much lower than that obtained by Kiss and Polgar,[12] who reported an apparent activation energy of 22 kcal/mol (92.4 kJ/mol) for the thermal and photo-initiated polymerization of DC*l*B monomer in thiourea canal compounds.

From the results on the polymerization behavor here obtained, together with those of ESR as well as post-polymerization studies, it can be concluded that the polymerization of DC*l*B in DCA canal proceeds by a free radical mechanism, in which the propagating free radicals have long lifetimes. They are quite analogous to those reported for the radiation-induced polymerizations of acrylonitrile in urea canal compounds[10,12,14], as well as of 1,3-pentadiene in perhydrotriphenylene canal compounds.[15](6)(7)

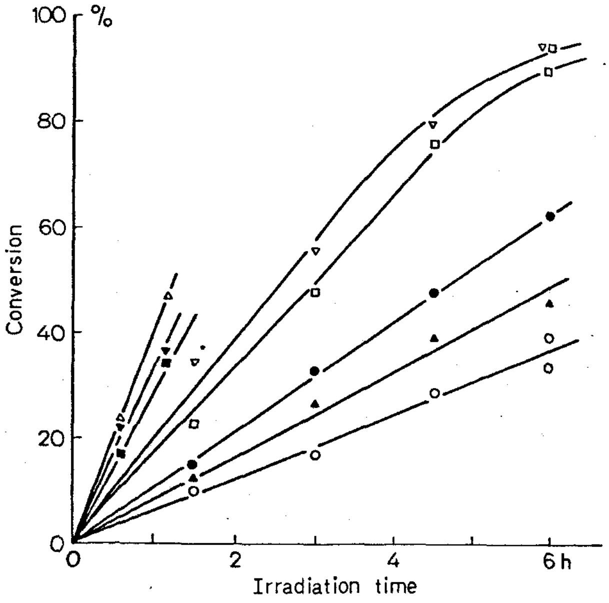


Fig.III-11. Temperature dependence of the in-source polymerization of DC*l*B in DCA canal ; dose rate, 1.7x10^5 rad/h, for 3 h.
(△):50°C, (▼):30°C, (■):18°C, (▽):10°C, (□): 0°C, (●):-23°C, (▲):-45°C, (○):-78°C.

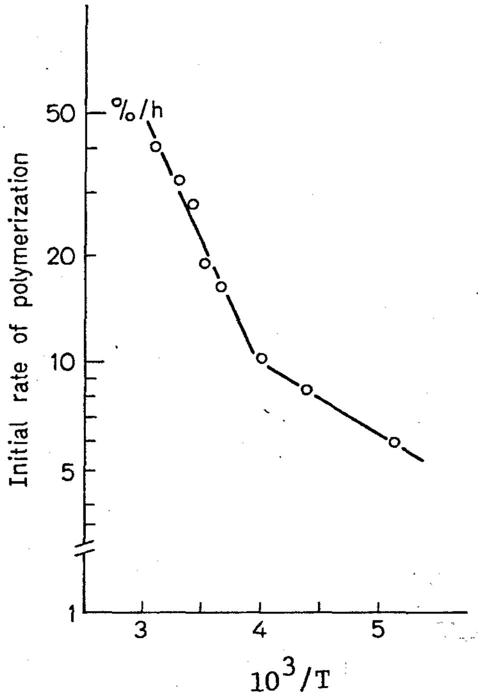


Fig.III-12. Arrhenius plots of the initial rate of in-source polymerization of DC*l*B in DCA canal ; dose rate, 1.7x10^5 rad/h, for 3 h.

2. *Nature of the DCA-DClB Canal Compounds*

DTA and TG of the canal Compounds

Fig.III-13 shows DTA diagrams of DCA-DC*l*B canal compounds before and after irradiation. The diagram before irradiation has two peaks, at about 158°C and 178°C, respectively. The former peak corresponds to the temperature at which the monomer included is released from DCA canal, which was confirmed by TG measurements carried out at the same time in parallel. The TG measurements indicated also that the mole ratio of DCA to DC*l*B monomer in the canal compounds amounts nearly 3. This value is identical to those obtained for the cases of DCA-2,3-dimethylbutane and DCA-2,2-dimethylbutane canal compounds,[20,28] the guest molecules of which being assumed to be the saturated model compounds of the corresponding disubstituted butadienes. The latter peak corresponds to the melting point of DCA itself.

After the irradiation, DTA diagrams of the canal compounds show a new peak at 215°C, which was ascribed to the melting of the polymer canal compounds produced. The absorption at 215°C tended to increase with increasing conversion, accompanying the decrease in the absorption at 158 and 178°C. This feature appears to explain well a gradual change of DC*l*B monomer into its polymer within canal compounds.

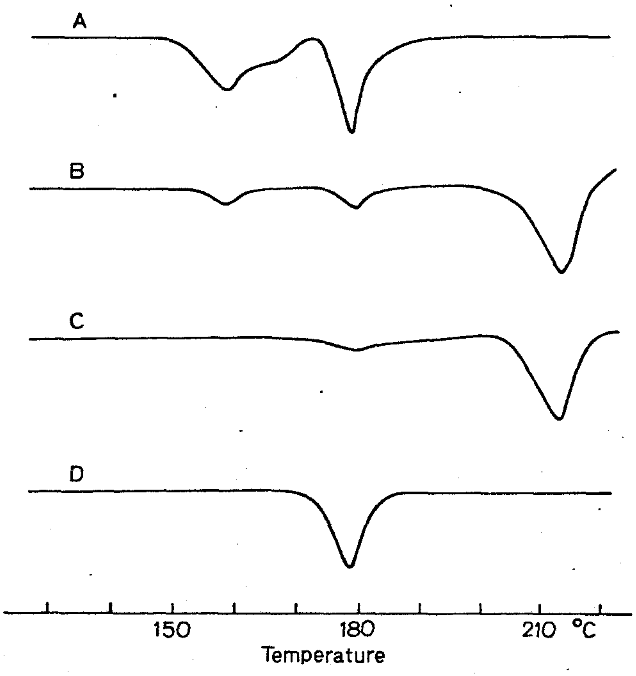


Fig.III-13. DTA diagrams of DCA-DC*l*B canal compounds before and after irradiation.
A: before irradiation
B: after irradiation(conv.14%)
C: after irradiation(conv.90%)
D: DCA without guest molecules

IR spectra of the canal compounds

Fig.III-14(A) shows the IR spectrum of DCA-DC*l*B canal compound. The monomer in the canal compound shows absorption bands at 710, 890 and $1580\mathrm{cm}^{-1}$, which are quite similar to those observed for the monomer in a liquid form, that is, in the absence of host DCA molecules. After the canal compound was allowed to stand at 150°C under reduced pressure, the spectrum changed its form to Fig.III-14(B), indicating some change in the crystal structure of DCA molecules. The spectrum seems, however, not to have changed if the canal compound has been treated at 100°C even for 50 h, except for decreases in absorbances at 710, 890 and $1580\mathrm{cm}^{-1}$. Since it is assumed that the crystal structure of DCA itself did not change after 50 h treatment at 100°C, the decrease in their absorbances may be caused by the release of the monomer from DCA canal during heat treatment.

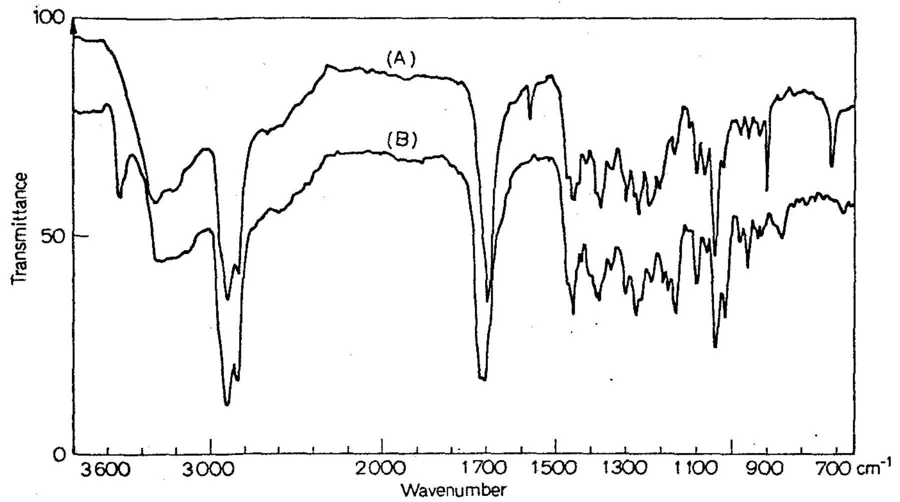


Fig.III-14. Infrared spectra of DCA-DC*l*B canal compound (A) and of the canal compound after standing at 150°C for 1 h under reduced pressure (B).

Fig.III-15 shows IR spectra of DCA-DClB canal compounds before and after radiation-induced polymerization. As can be seen from the figure, the absorptions at 710 and 890cm^{-1} decreased with increasing the conversion, and a small peak appeared at 830cm^{-1}, without changing in the spectrum of DCA itself. The new peak at 830cm^{-1} appears to belong to the polymer canal compounds. From these facts it is suggested that the polymerization of DClB monomer in DCA canal compounds proceeds without damaging the canal structure.

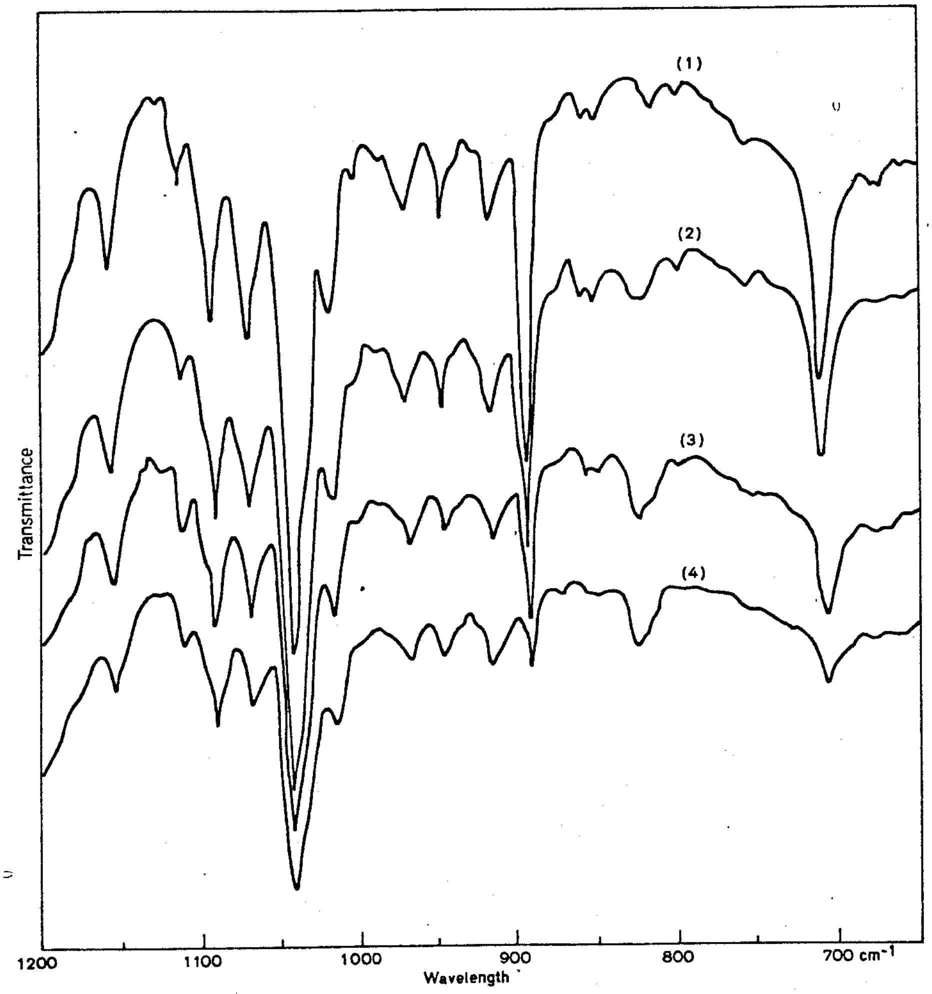


Fig.III-15. Infrared spectra of DCA-DClB canal compounds before and after irradiation. (1) before irradiation, (2) after irradiation(conv.14%), (3) after irradiation(conv.45%), and (4) after irradiation(conv.90%).

3. Properties of polymers

The polymers obtained and freed from the host molecules were insoluble in usual organic solvents such as chlorobenzene, dichlorobenzene, dimethylformamide, dimethyl sulfoxide, and only slightly soluble in hot tetralin. It was difficult to find a better solvent for the polymer to enable the measurement of the intrinsic viscosities. The poly(DC*l*B) did not melt below 300°C. In the X-ray diffraction pattern, strong maxima were observed at the d-values of 4.8, 3.7 and 2.9 Å.

Poly(DC*l*B) thus obtained were highly 1,4-trans tactic, as can be seen from the IR spectra (Fig.III-16), which showed no 910 and 1650cm^{-1} bands that are characteristic of 1,2-addition. The structure of this polymer was found to be identical to that of thiourea canal polymerization as described in previous papers.7(1)(2)

The IR spectra of poly(DC*l*B) obtained are almost the same, independently of the conversion, which suggests that the polymerization in question is controlled effectively in DCA canal over all conversion ranges.

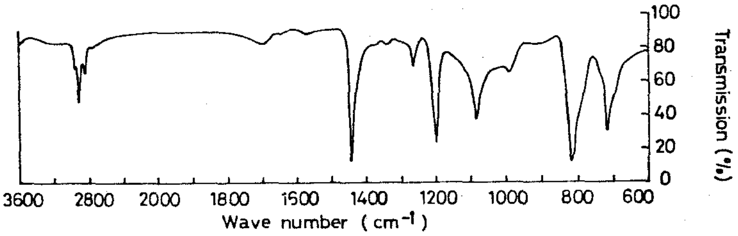


Fig.III-16. Infrared spectrum of poly(DC*l*B) obtained by inclusion polymerization in DCA canal.

III - 2 - 3, 2,3-Dimethyl-1,3-butadiene (DMB)

1. Polymerization Characteristics

General features of the polymerization

It has been reported that in the case of the bulk polymerization of DMB, conversion did not exceed 13% if the monomer was irradiated with a dose of 65 Mrad.[27] On the other hand, radiation-induced polymerization of DMB in thiourea canal compounds was found to proceed readily to about 80% conversion even with a dose of 1 Mrad.[27,6(1)] Such a marked increase in reactivity of DMB in the canal compounds might be attributed to the preferential orientation of the monomer molecules inside of the thiourea canal. Our present work shows also that the polymerization proceeds predominantly in the canals and negligible outside of them, under the conditions studied.

Table III-3 shows the influence of the atmosphere on the post-polymerization of DMB included in DCA canal. The polymerization was found to be extremely slow in the absence of DCA (run 1). Run 2 in an open tube gave also substantially low yield, which was ascribed to insufficient formation of the canal compounds. Sealing in air at ordinary pressure raised the yield considerably (run 3). The highest yield was attained when the canal compound formed in a degassed, sealed tube (run 4).

Fig.III-17 shows the relationship between the post-polymerization time and conversion for cases carried out in open and sealed tubes. As can be seen, the polymer yield was considerably lower in the case of open tubes than in case of sealed tubes. These experiments show clearly that oxygen has some effect on the post-polymerization of DMB included in DCA canal. A similar influence of the atmosphere has been pointed out for the radiation-induced in-source polymerization of 2,3-dichloro-1,3-butadiene (DC*l*B) in DCA canal compounds. Based on these results, the successive experiments were done in degassed sealed tubes.

Table III-3. Influence of atmosphere on the post-polymerization of DMB in DCA canal in the presence of methanol[a)]

Run	Formation of the canal compound	Irradiation	Polymer yield in mg
1	Without DCA	Air or vacuum	1 >
2	Open to air	Open to air	5.1
3	Sealed in air	Sealed in air	21.1
4	Sealed *in vacuo*	Sealed *in vacuo*	45.7

a) DCA: 1.0 g; DMB: 0.3 cm^3; methanol: 4.0 cm^3
irradiation: 1.6 Mrad at -78°C
post-polymerization: 0°C for 20 h

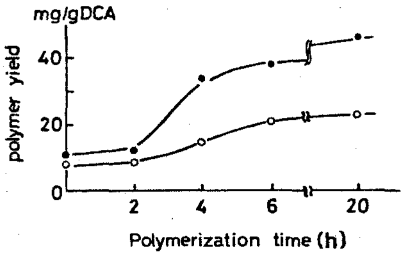


Fig.III-17. Influence of air on the post-polymerization of DMB in DCA canal in the presence of methanol.
(○): in air, (●): in vacuum

DCA: 1.0 g; DMB: 0.3 cm^3; methanol: 4.0cm^3
irradiation: 1.6 Mrad at -78°C
post-polymerization: 0°C

Dependence of the amount of monomer, methanol and other additives

The polymerization of DMB monomer included in DCA canal was carried out at first with constant amounts of DCA and methanol, with varying amounts of DMB monomer. As shown in Fig.III-18, an increase in the amount of DMB resulted in an increase in polymer yield, and then the polymer yield attained a constant value for the case in which 0.2 cm^3 of DMB was used. Assuming that the mole ratio of DCA to DMB in the canal compound is nearly 3 (from the results of thermogravimetry(TG) as will be mentioned later), 1.0 g of DCA-acetone canal compound (2.5 mmol) present in a sealed tube should include 0.10 cm^3 of DMB (0.8 mmol). The present result shows that an excess of DMB was necessary to obtain the maximal polymer yield under these polymerization conditions.

Fig.III-19 shows the results of the polymerization in which the amounts of DCA and DMB were kept constant and that of methanol varied. As can be seen, the polymer yield was independent of the amount of methanol present, which may indicate sufficient formation of the canal compound under these experimental conditions.

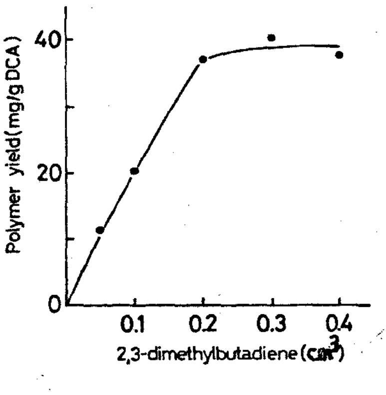


Fig.III-18. Post-polymerization of DMB in DCA canal in the presence of methanol; Polymer yield in relation to the amount of DMB.

DCA: 1.0 g; DMB: varied; methanol: 4.0 cm^3
irradiation: 1.0 Mrad at -196°C
post-polymerization: 0°C for 20 h

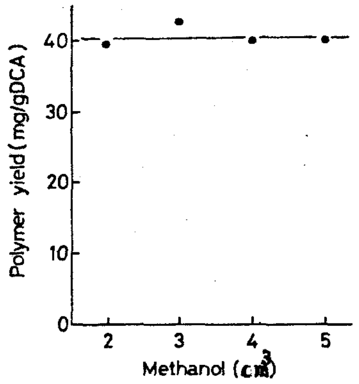


Fig.III-19. Post-polymerization of DMB in DCA canal in the presence of methanol; Polymer yield in relation to the amount of methanol.

DCA: 1.0 g; DMB: 0.3 cm^3; methanol: 4.0cm^3
irradiation: 1.0 Mrad at -196°C
post-polymerization: 0°C for 20 h

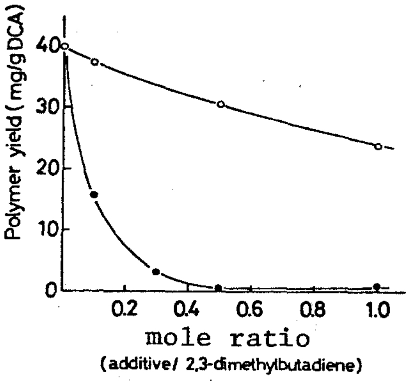


Fig.III-20. Influence of additives on the post-polymerization of DMB in DCA canal;
(○): hydroquinone, (●):2,3-dimethylbutane

DCA: 1.0 g; DMB: 0.3cm^3; methanol: 4.0cm^3
irradiation: 1.0 Mrad at -196°C
post-polymerization: 0°C for 20 h

In order to obtain more information about the canal polymerization, the reaction was next carried out in the presence of 2,3-dimethylbutane, which was regarded as a saturated model compound of DMB monomer. As can be seen from Fig.III-20, addition of 2,3-dimethylbutane led to a sharp decrease in polymer yield. This fact may be explained by the competitive inclusion of both DMB monomer and 2,3-dimethylbutane at the same time, causing incomplete orientation of DMB diluted with the additives in the canal.

In contrast to this case, the decrease in the polymer yield afforded by adding hydroquinone to the polymerization system was slight. This fact suggests that the extent of inclusion of hydroquinone into DCA canal is much less than that with DMB, while the polymerization outside of the canal can be effectively inhibited by hydroquinone.

Dependence on temperature

The post-polymerization of DMB included in DCA canal was further studied at different temperatures after irradiation to a definite dose. Fig.III-21 shows the resulting time-conversion relationships. The rate of polymerization was found to be negligible at -45°C. However, the rate increased with increasing temperature. Polymer yield could readily be controlled at 0°C, causing saturation after 20 h. Such a saturation of the polymer yield was observed even within 30 min at 30°C.

The prolonged post-polymerization at low temperature increased the polymer yield remarkably: while post-polymerization at -23°C for 6 h, for example, yielded only 2.5 mg polymer, the yield increased to 9.6 mg for 20 h and 15.4 mg for 44 h, starting from 1.0 g DCA-DMB canal compounds irradiated with a dose of 1.0 Mrad at -196°C. The post-polymerization at higher temperature seems not to be influenced even after long periods of time: for example, the post-polymerization performed at 0°C for 24 h, after standing for 20 h at -45°C, afforded 39.5 mg polymer, which was nearly the same result as the case in which the post-polymerization was done immediately after irradiation. These results suggest long lifetimes of the free radicals generated in DCA canal, and the occurrence of a living-like

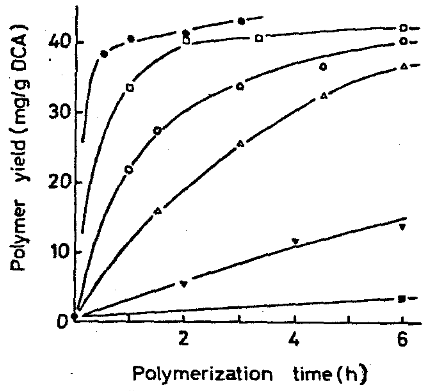


Fig.III-21. Temperature dependence of the post-polymerization of DMB in DCA canal in the presence of methanol.

DCA: 1.0g; DMB: 0.3cm^3; methanol: 4.0cm^3
irradiation: 1.0 Mrad at -196°C
post-polymerization: (■):-23°C, (▼):-14°C, (△):0°C, (○): 10°C, (□): 20°C, (●): 30°C

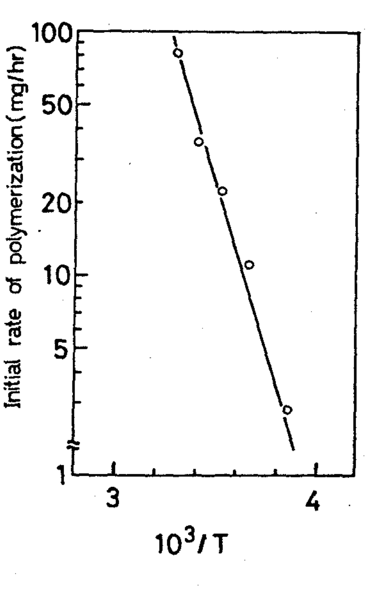


Fig.III-22. Arrhenius plot of the initial rate of post-polymerization of DMB in DCA canal in the presence of methanol.

polymerization of the free-radical type.

Fig.III-22 shows Arrhenius plots of the initial rate of polymerization, which gave an apparent activation energy of 13.7 kcal/mol (57.5 kJ/mol) for the canal polymerization in question in the temperature range of -14 to 30°C.

Effect of irradiation dose

The DMB monomer included in DCA canal was then irradiated with a variety of doses. Results of the post-polymerization at 0°C are shown in Fig.III-23. The rate of polymerization was found to increase with increasing irradiation dose.

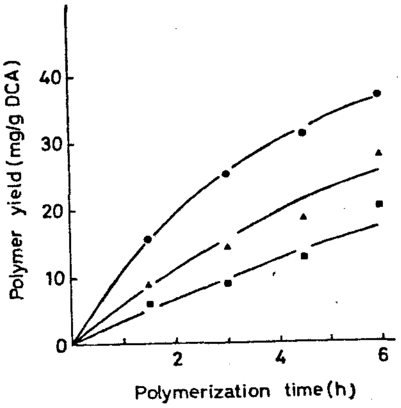


Fig.III-23. Effect of irradiation dose on the post-polymerization of DMB in DCA canal in the presence of methanol.

DCA: 1.0g; DMB: 0.3cm^3; methanol: 4.0cm^3
irradiation: (■): 0.2 Mrad, (▲): 0.5 Mrad
(●): 1.0 Mrad at -196°C
post-polymerization: 0°C

2. Nature of the DCA-DMB canal compounds

DTA and TG of the canal compounds

In a previous section, the author described the stability of the DCA-2,3-dichloro-1,3-butadiene (DC*l*B) canal compound on the basis of IR spectra and TG measurements. The stability of DCA-DMB canal compounds was found to be in the same order: no significant removal of DMB monomer from the canal compound was observed even after being allowed to stand for 2 weeks at room temperature at ordinary pressure: however, DMB was removed rapidly from the canal compounds at 150°C.

Fig.III-24 shows DTA diagrams of DCA-DMB canal compounds before and after irradiation. The diagram before irradiation has two peaks at about 158 and 178°C. The former peak corresponds to the temperature at which DMB monomer included is released from the DCA canal, as confirmed by simultaneous TG measurements. The TG measurement indicated also that the mole ratio of DCA to DMB monomer in the canal compounds was nearly 3. The peak at 178°C corresponds to the melting point of DCA itself.

After the irradiation, DTA diagrams of the canal compounds show, in addition, a peak at 215°C, which was ascribed to the melting point of the polymer canal compounds produced. The absorption at 215°C tended to increase with an increase in polymer yield and was accompanied by a decrease

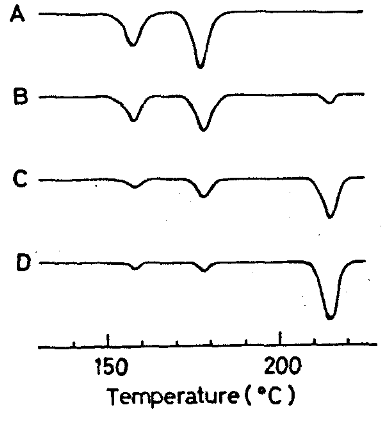


Fig.III-24. DTA diagrams of DCA-DMB canal compounds before and after irradiation.

A: before irradiation
B: after irradiation(polymer yield, 5.1 mg)
C: after irradiation(polymer yield, 36.9 mg)
D: after irradiation(polymer yield, 45.7 mg)

in the absorptions at 158 and 178°C. These observations seem to explain well a gradual change of DMB monomer into its polymer within the canal compounds.

IR spectra of the canal compounds

Fig.III-25 shows the IR spectrum of the DCA-DMB canal compound obtained by recrystallization of DCA from methanol containing DMB. DMB included in DCA canal shows absorptions at 890 and 1600cm^{-1}. These absorptions decreased with a rise in polymer yield without changes in other spectral regions; however, they did not disappear completely even in the case of the canal compounds after polymerizing to the highest yield. This fact suggests that the polymerization of DMB monomer in DCA canal proceeds without damaging the canal structure, which leads to the polymer canal compounds containing unpolymerized monomer.

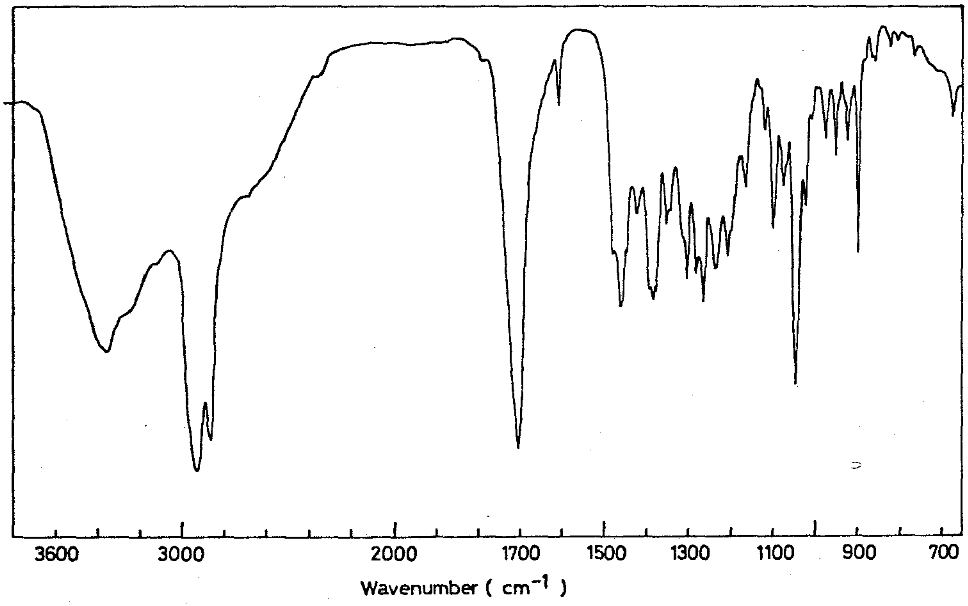


Fig.III-25. Infrared spectrum of DCA-DMB canal compound.

3. Properties of polymers

The poly(DMB) thus obtained melted at 240 - 250°C in a sealed capillary, and were insoluble in boiling benzene and chlorobenzene and slightly soluble in hot dichlorobenzene and tetralin. In the X-ray diffraction pattern, strong maxima were observed at the d-values of 5.2 and 4.3 Å.

The intrinsic viscosities of the polymers prepared by the post-polymerization at 0°C were measured at 30°C with an Ubbelohde viscometer. The results are shown in Fig.III-26. The values of η_{sp}/c increased with an increase in post-polymerization time. This suggests that the lifetime of the active free-radical species produced in the canal is long enough to propagate the polymer chain length as the polymerization proceeds.

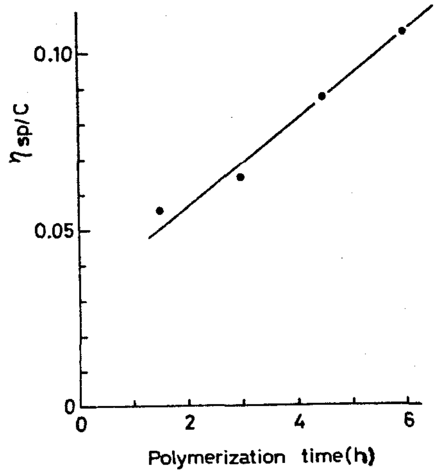


Fig.III-26. Effect of post-polymerization time on η_{sp}/c of polymers.
DCA: 1.0g; DMB: 0.3cm^3; methanol: 4.0cm^3
irradiation: 1.0 Mrad at -196°C
post-polymerization: 0°C

Fig.III-27 shows IR spectrum of poly(DMB) obtained. This spectrum was found to be almost identical to that of the same polymer obtained by thiourea canal polymerization[7(2)] as well as by the usual polymerization with a Ziegler-type catalyst,[29] which afford highly 1,4-trans tactic polymers.

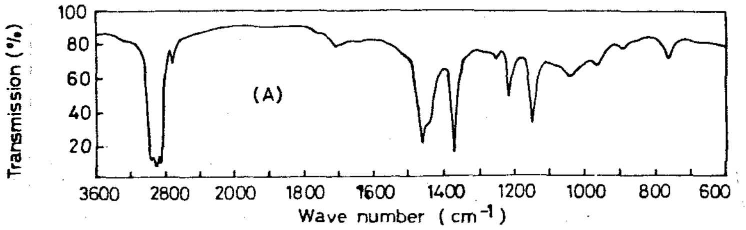


Fig.III-27. Infrared spectrum of poly(DMB) obtained by inclusion polymerization in DCA canal.

The 100-MHz NMR spectrum of the poly(DMB) is shown in Fig.III-28. Methyl and methylene resonances appear at 1.78 and 2.18 ppm, respectively. However, no signal for 1,2-structure was obtained. Though the 100-MHz NMR is insufficient to distinguish methyl and methylene protons, whether in 1,4-trans or 1,4-cis type,[29] the production of all 1,4-trans tactic polymers is suggested on considering both IR and NMR spectral results.

It was further found that the IR and NMR spectra of a series of the polymers are almost identical, independently of the conversion, which suggests that the post-polymerization in question is effectively controlled in the DCA canal over a wide conversion range.

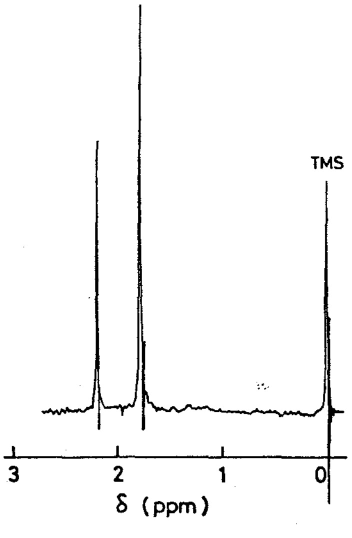


Fig.III-28. 100-MHz NMR spectrum of poly(DMB) obtained by inclusion polymerization in DCA canal.

III - 2 - 4. *trans*-2-Methyl-1,3-pentadiene

Canal polymerization is one of the unique polymerization techniques used in the solid state to prepare stereoregular polymers, particularly optically active diene polymers. In 1967, Farina, *et al.*,[16] reported on the first asymmetric canal polymerization of *trans*-1,3-pentadiene using chiral perhydrotriphenylene as the host molecule. Very recently, Audisio, *et al.*,[18] studied the asymmetric inclusion polymerization of 1,3-pentadiene in deoxycholic acid(DCA) canal.

In this section, the author wish to describe the first synthesis of the optically active polymer, poly(*trans*-2-methyl-1,3-pentadiene), from its prochiral monomer, *trans*-2-methyl-1,3-pentadiene, by asymmetric canal polymerization using DCA as the host molecule. It is worth noting that the polymer thus prepared showed a substantially higher optical rotation than the rotations of other usual synthetic vinyl and diene polymers hitherto known.

The polymer which resulted melted at 159-164°C and was soluble in *o*-dichlorobenzene and tetralin. Its viscosity number (η_{sp}/c) in *o*-dichlorobenzene and tetralin at 70°C was 0.26 d*l*/g (c=0.20 g/d*l*). IR and H^1-NMR spectra were found to be almost identical with those of poly(*trans*-2-methyl-1,3-pentadiene) obtained by canal polymerization using racemic perhydrotriphenylene as the host molecule.[15(8)]

The polymer was found to show a high optical rotation of the same sign as that of DCA itself ($[\alpha]_D$= +55° in ethanol) : $[\alpha]_D$= +250° ; $[\alpha]_{577}$ = +290° ; $[\alpha]_{546}$ = +350° ; $[\alpha]_{435}$ = +560° ; $[\alpha]_{365}$ = +940° (measured at 26°C in 0.11 x 10^{-3} g/cm^3 in *o*-dichlorobenzene solution). It is noteworthy that these specific rotation values are much higher than those of polypentadienes obtained either by inclusion or by coordination polymerization. That is, cis-1,4-polypentadiene obtained by inclusion polymerization in DCA canal[18] showed a specific rotation of -21° ($[\alpha]_D$ in toluene) and trans-1,4-polypentadiene obtained by the inclusion polymerization in chiral perhydrotriphenylene canal showed one of +7.5° ($[\alpha]_D$).[16,3(2)]

It should also be recalled that the coordination polymerization of these monomers gave polymers having specific rotation values of +10° to -10°[30] and -7.95°.[31]

In the above experiments, the conventional method was used for obtaining DCA canal compounds, which were prepared by the recrystallization of DCA from methanol or ethanol containing the monomer molecules. Next the replacement technique, which was described in Chapter II-2-1 in terms of replacement of guest molecules in DCA canal, was applied to the inclusion polymerization of *trans*-2-methyl-1,3-pentadiene in DCA canal.

DCA-monomer canal compounds were prepared as follows; 1.0 g of DCA-acetone canal compound and 0.4 cm^3 of *trans*-2-methyl-1,3-pentadiene were placed in a glass tube and then sealed under reduced pressure. The tube was heated at 90°C to replace acetone by the monomer, and irradiated at -196°C with a total dose of 1.0 Mrad. Post-polymerization was done at different temperatures as shown in Table III-4.

It can be seen that temperature dependence of canal polymerization of the monomer, *trans*-2-methyl-1,3-pentadiene, was quite different from those of monomers, BD, DC*l*B, DMB. The latter monomers polymerized at 0°C, while the former monomer at above 50°C for long hours to give a saturation of the polymer yield. This result suggests that the mobility of these monomers in DCA canal may be different from each other.

Table III-4. Temperature dependence of the post-polymerization of *trans*-2-methyl-1,3-pentadiene in DCA canal; Relationship of polymer yield with the time and temperature of the post-polymerization.

temperature(°C)	time(h) 5	10	20
40	4		11
60	16	31	45
80	41		50

DCA-acetone canal compound: 1.0g; *trans*-2-methyl-1,3-pentadiene: 0.4cm^3; replacement: 90°C for 1 h; irradiation: 1.0 Mrad at -196°C; polymer yield: mg in g DCA.

III - 2 -5. Comparison of Space Control for Inclusion Polymerization in Canal

The comparison of space control for inclusion polymerization in DCA canal with those in other canals so far studied may be considered to provide a good way to make clear the characteristics of DCA canal employed as a space for polymerization reaction. This is summarized in Table III-5.

Scope of monomers included in canal

Scope of monomers included in canal may depend on the shape, size and versatility of canal. Perhydrotriphenylene canal can accommodate various diene monomers because of the versatility of the canal, while urea or thiourea canal can not. Since DCA canal exists between pleated sheets which posses a translational degree of freedom, it is expected that DCA canal can include various kinds of monomer. Actually this work indicates that DCA provides versatile canal to include various kinds of monomer.

Space control for inclusion polymerization of vinyl monomers

It was reported that syndiotactic poly(vinyl chloride) or isotactic polyacrylonitrile was obtained by inclusion polymerization in urea canal, and that the canal structure of urea-vinyl chloride or urea-acrylonitrile canal compound was destroyed during polymerization.

In the case of DCA canal, acrylonitrile and methacrylonitrile polymerized to give no stereospecific polymers, and other monomers did not polymerize. We requires further examination from various points of view to prepare stereospecific vinyl polymers by inclusion techniques.

Space control for inclusion polymerization of diene monomers

In contrast to the limited adaptability of urea or thiourea canal, both DCA and perhydrotriphenylene canal can include many monomers, such as 1,3-butadiene, mono or disubstituted butadienes. Stereospecific 1,4-trans tactic polymers were prepared in these canals except for the polymerization of 1,3-butadiene in DCA canal. In this case, poly(1,3-butadiene) obtained contained 1,2-unit in addition to trans 1,4-unit, and moreover microstructures of the polymers were influenced by additives. Thus, DCA canal can provide a good space control for inclusion polymerization of diene monomers.

Asymmetric inclusion polymerization

The first asymmetric inclusion polymerization was reported by Farina and his co-workers in 1967, using chiral perhydrotriphenylene obtained by the resolution of racemic one. This work demonstrated the effectiveness of inclusion polymerization in canal. But the investigation of the asymmetric inclusion polymerization gets into trouble because of the difficulty of the resolution of racemic perhydrotriphenylene.

In contrast to the above case, DCA is a naturally occurring chiral compound and commercially available. Thus, DCA is a favorable compound for the research on asymmetric inclusion polymerization.

Actually, DCA canal is found to serve as a space for asymmetric inclusion polymerization. Optically active polymers of cis or trans-1,3-pentadiene were at first prepared by Audisio and Silvani. The author succeeded in preparing optically active poly(*trans*-2-methyl-1,3-pentadiene) with high optical rotation, although such polymer can not be prepared by other usual polymerization method. This work suggests that DCA canal provides an extremely efficient space control for the polymerization reaction.

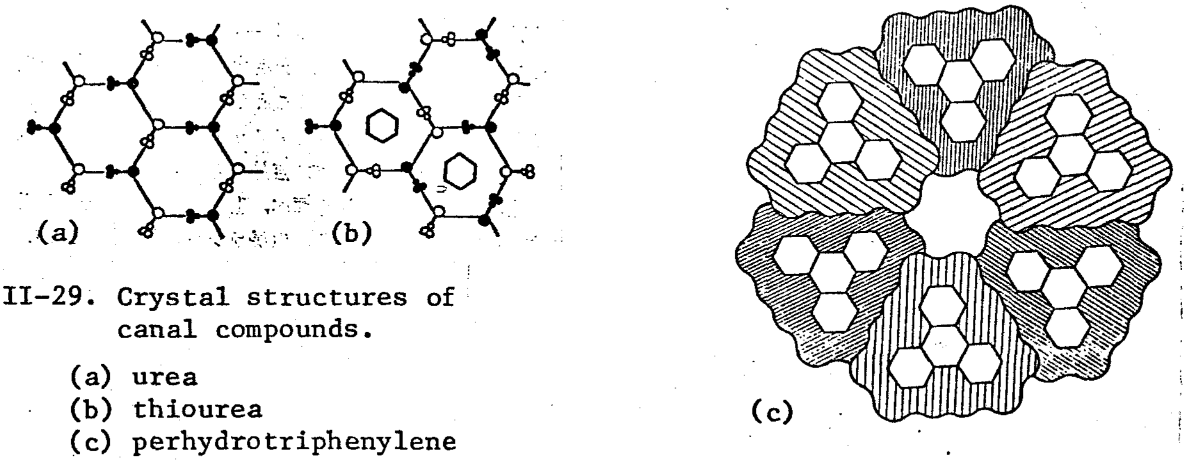


Fig.III-29. Crystal structures of canal compounds.

(a) urea
(b) thiourea
(c) perhydrotriphenylene

Table III-5. Comparison of space control for inclusion polymerization in canal.

host compound	shape and size of canal	polymerizable monomer(polymer structure)		
		vinyl	diene	prochiral
urea	hexagon 5Å	acrylonitrile (isotactic) vinyl chloride (syndiotactic)	1,3-butadiene 1,3-pentadiene	*
thiourea	hexagon 7Å	*	2,3-dimethyl-1,3-butadiene 2,3-dichloro-1,3-butadiene	*
perhydrotriphenylene	hexagon 5-7 Å versatile	*	1,3-butadiene 1,3-pentadiene 2,3-dimethyl-1,3-butadiene 2-methyl-1,3-pentadiene 2,4-hexadiene	*trans*-1,3-pentadiene ($[\alpha]_D=+7.5^\circ$)
deoxycholic acid	rectangle 4Å x 7Å versatile	acrylonitrile (random)	1,3-butadiene 1,3-pentadiene 2,3-dimethyl-1,3-butadiene 2,3-dichloro-1,3-butadiene 2-methyl-1,3-pentadiene 2,4-hexadiene	*cis*-1,3-pentadiene ($[\alpha]_D=-21^\circ$) *trans*-2-methyl-1,3-pentadiene ($[\alpha]_D=+250^\circ$)

* ; unreported

III - 3. Experimental

Materials

Deoxycholic acid (DCA) was purified by recrystallization from methanol or acetone. 2,3-Dichloro-1,3-butadiene (DC*l*B), in about 40% methanol solution, was freed from inhibitors by distillation before use. 2,3-Dimethyl-1,3-butadiene (DMB) was prepared by hydrobromic acid-catalyzed dehydration of anhydrous pinacol followed by fractional distillation.[26] 1,3-Butadiene (BD), *trans*-2-methyl-1,3-pentadiene and various guest components were of pure grade, and used without further purification.

Formation of DCA Canal Compounds and Polymerization Procedure

DCA-BD canal compound

The replacement technique described in Chapter II-2-1 was employed to prepare DCA-BD canal compound ; 1.0 g of DCA-acetone canal compound (with additives when necessary) were placed in a glass tube of 10 mm diameter, and then the tube was evacuated. Liquefied butadiene monomer was purified by the freeze-thaw technique and distilled into the tube in vacuo. The tube was then sealed under vacuum (10^{-3} Torr) after three freeze-thaw cycles, and heated for replacement of the included components by BD at 60°C for 2 h. Irradiation was provided by γ-rays from a ^{60}Co source at -196°C with a dose of 0.3 Mrad. Post-polymerization was done on the samples at 0°C for 5 h. Then the contents were treated with methanol in a similar manner as above.

DCA-DC*l*B canal compound

DCA-DC*l*B canal compounds were prepared as follows: 14 cm^3 of about 40% methanol solution of the monomer was added to 90 cm^3 of hot methanol solution containing 40 g of DCA. The solution resulted was then allowed to stand at room temperature for 1 h and cooled to 0°C in dark. Formation of canal compounds was indicated by the appearance of small needle-like crystals, which were separated by filtration and then dried in vacuo for 3 h.

0.5 g of DCA-DC*l*B canal compound was placed in a glass tube of 10 mm diameter, which was then sealed under vacuum (10^{-3} Torr). Irradiation was provided by γ-rays from a ^{60}Co source; the temperature of the samples was kept usually at 0°C, in some cases, however, the irradiation was made at -78 to 50°C. After irradiation, the tubes were cooled again to -196°C and opened. The samples were poured into excess methanol (50 to 100 cm^3) to separate DCA from the canal compounds. Polymers obtained were washed with hot methanol thoroughly and then dried under reduced pressure. Conversions were estimated, assuming that the mole ratio of DCA to the monomer in the canal compound is equal to 3, which means that the DCA-DC*l*B canal compound contains about 47 mg of DC*l*B monomers per 0.5 g of the canal compound.

DCA-DMB canal compound

DCA, DMB, and methanol were placed in glass tubes of 12 or 18 mm diameter, which were then sealed under vacuum (10^{-3} Torr) after three freeze-thaw cycles. Some of the samples were sealed in air at atmospheric pressure. The sealed tubes were warmed to 70-80°C to give homogeneous solutions. The tubes were then allowed to stand for several hours at room temperature and cooled to 0°C. Formation of the canal compounds was indicated by the appearance of small needle-like crystals.

The tubes were exposed to γ-irradiation from a ^{60}Co source at -196 or -78°C. Post-polymerization was done on the samples at different temperatures. Then the contents were treated with methanol as mentioned in the case of DCA-DC*l*B canal compound.

DCA-*trans*-2-methyl-1,3-pentadiene canal compound

1.0 g of DCA, 0.4 cm^3 of *trans*-2-methyl-1,3-pentadiene, and 2.5 cm^3 of ethanol were placed in a glass tube of 10 mm diameter, which was then sealed under vacuum (10^{-3} Torr) after three freeze-thaw cycles. The sealed tubes was warmed to 70-80°C to give a homogeneous solution and then cooled gradually. Formation of the canal compounds was indicated by the appearance of small needle-like crystals. The tube was exposed to γ-irradiation from a ^{60}Co source at -196°C for 2 h with a dose rate of 3.0×10^5 rad/h. After the irradiation, the tube was warmed overnight at 50°C in order to allow the content to polymerize, and then cooled to -196°C and cut off. The content of the tube was immediately poured into excess methanol to separate DCA from the polymer formed. The polymers thus obtained were washed with hot methanol thoroughly and dried under reduced pressure (18 mg yield).

Measurements

Differential thermal analysis(DTA), thermogravimetry(TG) and infrared (IR) spectral measurements were carried out in the same way as described in Chapter I. Content of the microstructural units of poly(BD) was determined by IR spectral measurements carried out in a KRS solution cell of 1.0 mm thickness used for poly(BD).[32] NMR spectra were measured at 150°C with *o*-dichlorobenzene as solvent and tetramethylsilane as internal standard. Viscosity numbers, η_{sp}/c, of poly(DMB) were measured on 0.5 g/d*l* supercooled solution in *o*-dichlorobenzene at 30°C. The specific rotation of poly(*trans*-2-methyl-1,3-pentadiene) was measured at room temperature in *o*-dichlorobenzene.

III - 4. Summary

Inclusion polymerization of four diene monomers (BD, DC*l*B, DMB, *trans*-2-methyl-1,3-pentadiene) in DCA canal was studied in detail. Different space control for polymerization was found to occur under the influence of DCA canal. In the case of DC*l*B and DMB, highly 1,4-trans tactic polymers were obtained over all conversion ranges of inclusion polymerization in DCA canal, while in the case of BD, polymer obtained was found to contain a significant amount of 1,2-unit in addition to trans-1,4-unit. Furthermore, various additives had a marked effect on the microstructure of the poly(BD), which suggests that the inclusion polymerization of BD in DCA canal can be controlled by additives included in the canal competitively.

Optically active poly(*trans*-2-methyl-1,3-pentadiene) was prepared by inclusion polymerization in chiral DCA canal, starting from a prochiral monomer. This indicates that the polymerization reaction is controlled effectively in DCA canal.

In addition to the effective space control in DCA canal, the existence of living-like free radicals having long lifetimes, the gradual change of the monomer into the polymer within the canal were discussed on the basis of the post-polymerization behavior, the nature of the DCA canal compounds.

CONCLUSION

The results obtained from the present study may be summarized as follows;

[1] Deoxycholic acid (DCA) canal has been found to serve as an effective space for polymerization reaction of four diene monomers; 1,3-butadiene (BD), 2,3-dichloro-1,3-butadiene (DC*l*B), 2,3-dimethyl-1,3-butadiene(DMB), *trans*-2-methyl-1,3-pentadiene.

[2] DCA canal has been found to the following characteristics for incorporation of guest molecules into the canal;

i) Guest molecules in DCA canal can be replaced easily by other guest molecules which fit into DCA canal more favorably by heat treatment.

ii) DCA canal incorporates more favorably branched or cyclic molecules than linear ones.

[3] DCA canal has been found to provide the following efficient space controls for inclusion polymerization of diene monomers in the canal;

i) 2,3-Dichloro-1,3-butadiene(DC*l*B) and 2,3-dimethyl-1,3-butadiene(DMB) polymerize in DCA canal under the effective control to yield highly 1,4-trans tactic polymers over all conversion ranges.

ii) 1,3-Butadiene(BD) receives insufficient space control from DCA canal to yield polymers containing significant amounts of 1,2-unit in addition to trans-1,4-unit. However, various additives have a marked effect on the microstructure of the polymers to yield highly 1,4-trans tactic polymers, which suggests that the inclusion polymerization of BD in DCA canal can be controlled by additives included in the canal competitively.

iii) Optically active poly(*trans*-2-methyl-1,3-pentadiene) with high optical rotation was prepared by inclusion polymerization in DCA canal starting from a prochiral monomer, although such polymer can not be prepared by other usual polymerization method. The preparation of polymers with high optical rotation suggests that DCA canal provides an extremely efficient space control for the polymerization reaction.

REFERENCES

[1] 1)F.Cramer, *Einschlussverbindungen*, Springer-Verlag (1954).
2)M.M.Hagan, *Clathrate Inclusion Compounds*, Reinhold Publishing Co.(1962).
3)K.Takemoto, *Chemistry of Inclusion Compounds*, Tokyo Kagaku Dojin (1969).
4)D.J.Cram, J.M.Cram, *Accounts Chem.Res.*, 11,8 (1978).

[2] 1)T.Kawai *et al.*, *Molecular Design of Polymer*, Baihukan (1972).
2)K.Takemoto, *Functional Polymer*, Asakura Shoten (1974).

[3] 1)Y.Chatani, *Progress in Polymer Science, Japan*, 7,189 (1974).
2)M.Farina, *Proceedings of the International Symposium on Macromolecules*, Rio de Janeiro,1974,ed. E.B.Mano, Elsevier, Amsterdam (1975), p.21.
3)K.Takemoto, M.Miyata, *Kagaku*, 32,779 (1977).
4)S.Nozakura, M.Furue, *Kobunshi*,26,716 (1977).
5)J.E.D.Davies, *J.Chem.Educ.*, 54,536 (1977).

[4] 1)G.Natta, *Science*, 147,261 (1965).
2)M.Farina, G.Bressan, *Optically Active Stereoregular Polymers* in *The Stereochemistry of Macromolecules*, Ketley ed., M.Dekker, New York, 1968, vol.III,chapter 4, p.181-211.

[5] H.Clasen, *Z.Elektrochem.*, 60,982 (1956).

[6] 1)J.F.Brown,Jr., D.M.White, *J.Amer.Chem.Soc.*, 82,5671 (1960).
2)D.M.White, *J.Amer.Chem.Soc.*, 82,5678 (1960).

[7] 1)Y.Chatani, S.Nakatani, H.Tadokoro, *Macromolecules*, 3,481 (1970).
2)Y.Chatani, S.Nakatani, *Macromolecules*, 5,597 (1972).
3)Y.Chatani, S.Kuwata, *Macromolecules*,8,12 (1975).
4)For a review see [3] 1).

[8] I.Sakurada, K.Nanbu, *Nippon Kagaku Zasshi*, 80,307 (1959).

[9] V.S.Ivanov, T.A.Sukhikh, Yu.D.Medvedev, A.Kh.Breger, V.B.Osipov, V.A.Gol'din, *Vysokomolekul.Soedin.*, 6,782 (1964).

[10] 1)M.Kawasaki, T.Maekawa, K.Hayashi, S.Okamura, *J.Macromol.Chem.*,1,489 (1966).
2)T.Maekawa, M.Kawasaki, K.Hayashi, S.Okamura, *J.Macromol.Chem.*,1,507 (1966).
3)T.Maekawa, S.Okamura, *J.Macromol.Sci.-Chem.*, A9,257 (1975).

[11] K.Hayashi, K.Hayashi, *JAERI* 5028, p.96 (1973).

[12] 1)L.Kiss, S.Polgar, *Kinet.Mech.Polyreactions, Intern.Symp.Macromol.Chem.,* Prepr. 1969, 49.
2)P.Hedvig, S.Kulcocir, L.Kiss, *Eur.Polym.J.,* 4,601 (1968).
3)L.Kiss, S.Polgar, *Third Int.Symp.on Rad.Chem.* (Tihany, Hungary, May 1971)

[13] T.Ohmori, T.Ichikawa, M.Iwasaki, *Bull.Chem.Soc.Japan,* 46,1383 (1973).

[14] 1)F.Yoshii, T.Abe, O.Yoda, *Kobunshi Ronbunshu,* 32,399 (1975).
2)F.Yoshii, T.Abe, K.Kobayashi, *ibid.,* 32,477 (1975).
3)F.Yoshii, T.Abe, N.Hayakawa, N.Tamura, *ibid.,*32,406 (1975).
4)F.Yoshii, T.Abe, N.Hayakawa, *ibid.,* 32,429 (1975).
5)F.Yoshii, N.Hayakawa, T.Abe, *ibid.,* 32,717 (1975).

[15] 1)M.Farina, G.Allegra, G.Natta, *J.Amer.Chem.Soc.,* 86,516 (1964).
2)G.Allegra, M.Farina, A.Immirzi, A.Colombo, U.Rossi, R.Broggi, G.Natta, *J.Chem.Soc.* B, 1967, 1020.
3)G.Allegra, M.Farina, A.Colombo, G.Casagrande-Tettamanti, U.Rossi, G.Natta, *J.Chem.Soc.* B, 1967, 1028.
4)M.Farina, G.Natta, G.Allegra, M.Löffelholz, *J.Polym.Sci.* C, 16,2517 (1967).
5)M.Löffelholz, M.Farina, U.Rossi, *Makromol.Chem.,* 113,230 (1968).
6)M.Farina, U.Pedretti, M.T.Gramegna, G.Audisio, *Macromolecules,* 3, 475 (1970).
7)M.Farina, G.Audisio, M.T.Gramegna, *Macromolecules,* 4,265 (1971).
8)M.Farina, G.Audisio, M.T.Gramegna, *Macromolecules,* 5,617 (1972).
9)A.Colombo, G.Allegra, *Macromolecules,* 4,579 (1971).
10)M.Farina, G.Di Silvestro, *J.Chem.Soc.Chem.Commun.,* 1976, 842.
11)For a review see [3] 2).

[16] M.Farina, G.Audisio, G.Natta, *J.Amer.Chem.Soc.,* 89,5071 (1967).

[17] 1)M.Miyata, K.Takemoto, *Polym.J.,* 9,111 (1977).
2)M.Miyata, H.Sanda, K.Takemoto, unpublished.

[18] G.Audisio, A.Silvani, *J.Chem.Soc.Chem.Commun.,* 1976, 481.

[19] H.Wieland, H.Sorge, *Z.physiol.,* 97, 1 (1916).

[20] W.C.Herndon, *J.Chem.Educ.,* 44,724 (1967); references cited therein.

[21] B.M.Craven, G.T.DeTitta, *J.Chem.Soc.Chem.Commun.*, 1972, 530.

[22] S.C.DeSanctis, E.Giglio, V.Pavel, C.Quagliata, *Acta Cryst.*, B28, 3656 (1972).

[23] 1)N.Friedman, M.Lahav, L.Leiserowitz, R.Popovitz-Biro, C.P.Tang, Z.Zaretzkii, *J.Chem.Soc.Chem.Commun.*, 1975, 864.

2)M.Lahav, L.Leiserowitz, R.Popovitz-Biro, C.P.Tang, *J.Amer.Chem.Soc.*, 100,2542 (1978).

[24] K.Matsuzaki, T.Uryu, M.Okada, H.Shiroki, *J.Polym.Sci.* A-1, 6,1475 (1968).

[25] Y.Inoue, A.Nishioka, *Polym.J.*, 3,149 (1972).

[26] C.F.Allen, A.Bell, *Organic Synthesis*, Coll.Vol.3, New York, John Wiley & Sons, 1955, p.312.

[27] V.Stepan, J.Vodehnal, I.Kösler, *J.Polym.Sci.* A-1, 5,503 (1967).

[28] E.H.Huntress, R.F.Phillips, *J.Amer.Chem.Soc.*, 71,458 (1949).

[29] D.Blondin, J.Regis, J.Prud'homme, *Macromolecules*, 7,187 (1974).

[30] G.Costa, P.Locatelli, A.Zambelli, *Macromolecules*, 6,653 (1973).

[31] G.Natta, M.Farina, M.Donnati, *Makromol.Chem.*, 43,251 (1961).

[32] J.Brandrup, E.H.Immergut, *Polymer Handbook*, 2nd Ed. V-1, Wiley-Interscience (1975).

SUPPLEMENTARY TREATISES

The Supplementary Treaties are as follows;

(1) Synthesis of Carboxylic Acid Derivatives of Adenine and Theophylline.
K.Kondo, M.Miyata and K.Takemoto,
Bull.Chem.Soc.Japan, 44, 2554 (1971).

(2) On the Synthesis of Tetrahydrofolic Acid Analogs.
K.Kondo, M.Miyata and K.Takemoto,
Makromol.Chem., 160, 339 (1972).

(3) Zur Synthese von DL-β-(7-Theophyllinylmethyl)alanin.
M.Miyata, K.Kondo und K.Takemoto,
Techn.Repts.Osaka Univ., 23, 339 (1973).

(4) Synthesis and Polymerization of Vinyl Cholate and Vinyl Dehydrocholate.
M.Miyata, M.Sato, T.Ishikawa and K.Takemoto,
Makromol.Chem., 176, 2139 (1975).

ACKNOWLEDGEMENT

The work of this thesis was carried out at Osaka University under the guidance of Professor Kiichi Takemoto.

I would like to express my grateful acknowledgement to Professor Kiichi Takemoto for his invaluable guidance and continuous encouragement throughout this investigation.

I am very much obliged to Dr. Koichi Kondo and Dr. Yoshiaki Inaki for their encouragement and helpful advices.

I am also deeply grateful to Professor Koichiro Hayashi, Dr. Yozo Chatani, Dr. Masahiro Irie and Dr. Noritake Yasuoka for their helpful discussions and suggestions.

I wish to acknowledge the hospitality of the Radiation Laboratory, the Institute of Scientific and Industrial Research for the use of ^{60}Co facilities.

I owe it to my colleagues that this work has been accomplished, and express my thanks to Dr. Keiichi Kimura, Dr. Mitsuru Akashi, Mr. Masaaki Sato, Mr. Tomohiro Ishikawa, Mr. Kiyoshi Morioka, Mr. Hisanari Sanda and Mr. Katsutoshi Shinmen.

I further wish to thank all the members of the Takemoto Laboratory and all my friends for their friendships.

Finally, I would like to thank my father Nanakazu Miyata and my mother Kimiko Miyata for their heartful encouragement.

September, 1978

Mikiji Miyata