INCLUSION POLYMERIZATION OF DIENE AND DIACETYLENE MONOMERS
IN DEOXYCHOLIC ACID AND APOCHOLIC ACID CANALS [†]

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Inclusion polymerization is a unique one-dimensional polymerization
which proceeds in a canal (channel) of inclusion compounds, and an
excellent way for giving stereoregular polymers as well as composite
materials at molecular level [1,2]. Such materials have a potential
possibility to show some characteristic electrical, optical and magne-
tic properties in the inclusion state due to their one-dimensional
structure.

   We found earlier that deoxycholic acid (3α, 12α-dihydroxy-5β-cho-
lan-24-oic acid ; DCA) and apocholic acid (3α, 12α-dihydroxy-5β-chol-
8(14)-en-24-oic acid ; apoCA) can provide tunnel-like spaces, called
canals or channels, which are suitable for one-dimensional polymeriza-
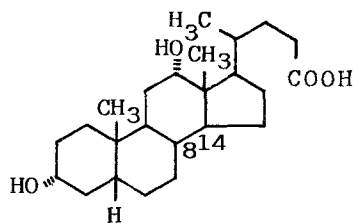tion [3-8].

   In this paper we summarize our recent study on inclusion polymeri-
zation of various kinds of diene and diacetylene monomers in DCA and
apoCA canals.

1. Characteristics of DCA and apoCA hosts

Both hosts form hydrogen-bonded bilayers
stacked in an array which leaves hydro-
phobic canals between them [9]. Since
the bilayer structure is thermally stable,
we can study inclusion polymerization in
a wide range of temperatures in DCA and
apoCA canals as compared with other hosts
such as urea and thiourea.

Deoxycholic acid(DCA)
[Apocholic acid(apoCA)]
[8(14)en]

   The hosts have slightly different
canals in the sizes and shapes, but form inclusion compounds with the
same monomers. So we can get significant information regarding effects
of canal sizes and shapes on the inclusion polymerization.

   The hosts form inclusion compounds with a great variety of organic
substances with polar, nonpolar as well as bulky groups. Therefore we
can try to polymerize more comprehensive monomers than before. That
involves cyano, carbomethoxy or propyl group.

[†]Functional Monomers and Polymers 146

2. ESR observation of propagating radicals in the canals

Conventional free-radical initiators such as di-*t*-butyl peroxide can serve as the effective initiators for the inclusion polymerization of diene monomers in DCA and apoCA canals [10]. During the course of the polymerization we succeeded in observing ESR spectra of living-like propagating radicals of allylic type in the canals. This result confirms the existence of the polymerization reaction via free-radical mechanism.

3. Stereoregular polymerization

In case of a pair of DCA and apoCA hosts, we can study the inclusion polymerization of the same monomers in slightly different canals in size and shape at various temperatures ranging from -20 °C to 140 °C. This study enables us to find a dependence of the microstructures of the resulting polymers on polymerization temperatures and canal sizes. In case of butadiene derivatives, the following microstructures of the polymers should be evaluated : (1) 1,4-trans, 1,4-cis, 1,2; (2) head-to-tail, head-to-head(tail-to-tail); (3) erythro, threo; (4) asymmetry.

<u>1,4-trans</u> : In case of butadiene derivatives, the resulting polymers usually prefer 1,4-trans unit to 1,4-cis and 1,2 units. Inclusion polymerization of 2,3-dimethyl-1,3-butadiene in a DCA canal yielded almost completely 1,4-trans unit in a wide range of temperature from -20 °C to 140 °C. The microstructure, however, decreased remarkably over 80 °C in an apoCA canal. In case of 1,3-butadiene the resulting polymer was composed of a mixture of those units even at low temperatures. These results are considered to reflect the difference of canal sizes of the hosts [11].

<u>head-to-tail</u> : In case of nonsymmetric monomers such as 1- or 2-alkyl-1,3-butadiene, the microstructure of head-to-tail or head-to-head (tail-to-tail) can be estimated. While the poly(1,3-pentadiene)s obtained always had completely head-to-tail structure, the polymers obtained from isoprene showed a dependence of the microstructure on polymerization temperatures and canal sizes. The fraction of head-to-head (tail-to-tail) unit of the latter polymer increased as decreasing the polymerization temperature from 50 °C to -20 °C in a DCA canal, while it was constant in an apoCA canal [11].

<u>erythro, threo</u> : In case of 1,4-disubstituted butadienes such as 2,4-hexadiene we can distinguish between erythro and threo structure. 2,4-Hexadiene was found to polymerize in DCA and apoCA canals on heating over 100 °C for 10 to 20 days after γ-ray irradiation. Particullary trans, trans-2,4-hexadiene polymerized in an inclusion state via radical mechanism for the first time. The polymers from the monomer prefer erythro structure to threo structure in a DCA canal, while they do slightly threo to erythro in an apoCA canal. It is considered that the polymerization proceeded preferentially in the canals through trans opening to yield erythro diisotactic structure in a DCA canal [11].

Similarly many other monomers with bulky groups polymerized in DCA and apoCA canals on heating over 100 °C for a long time on the basis of propagating radicals with very long life-times.

4. Asymmetric polymerization

DCA and apoCA can serve as effective host components for

$$\underset{CH_2=\overset{R_1}{\overset{|}{C}}-CH=\overset{R_2}{\overset{|}{C}}H}{} \longrightarrow \underset{(CH_2\overset{R_1}{\overset{|}{C}}=CH\overset{R_2}{\overset{|}{C}}H)}{*}$$

asymmetric inclusion polymerization of prochiral monomers such as 1-substituted butadienes. We reported previously the preparation of optically active polymers with extremely high specific optical rotation of arbitrary sign from (E)- or (Z)-2-methyl-1,3-pentadiene by inclusion polymerization in the canals [7,12-14]. Moreover we have found that butadiene derivatives with polar groups such as cyano or carbomethoxy group can be polymerized to yield optically active polymers. The $[\alpha]_D$ values of the resulting polymers were much higher than those of polymers obtained by other known polymerization method.
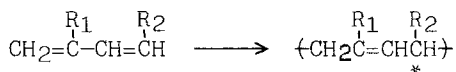
5. Inclusion of highly conjugated polymers

Electrically conductive polymers such as polyacetylene have recently received much attention as representative low-dimensional materials. This highly oriented assembly of the polymers is very attractive, because such chain alignment should improve their physical and chemical properties. It is expected that the incorporation of such polymers into canals will yield a novel type of functional composite materials at molecular level with unique electrical and optoelectronic properties.

$\underline{HC\equiv C-C\equiv CH}$: It was found that the simplest diacetylene, butadiyne, can be polymerized spontaneously and mildly in DCA and apoCA canals at temperatures ranging from -20°C to 30°C. The polymerization was accompanied by a sequence of colour change from colorless through violet and brown to finally yield a black material with a metallic luster. The resulting polymers are characterized by infrared and Raman spectroscopies as having a polyconjugated main chain by 1,4-addition. The electric conductivity of the polymers in the inclusion state and of the separated polymers were about 10^{-7} to 10^{-9} S/cm under doping with iodine at room temperature [15].

$\underline{H_2C=CH-CH=CH-X}$ (X : Cl, Br) : 1-Chloro- or 1-bromo-1,3-butadiene can be polymerized in DCA and apoCA canals to yield polymers with 1,4-trans structure. Since the separated polymers from the hosts are soluble in chloroform, they serve as precursors for polyacetylene. The dehydrohalogenation from the precursor polymer occurred slowly at room temperature and rapidly over 150°C in an atmosphere of dry nitrogen, accompanying a colour change from light yellow through brown to finally yield a black material with a metallic luster. The electric conductivity was about 10^{-3} S/cm under doping with iodine [16].

$\underline{H_2C=CX(CN)}$ (X : Cl, Br) : The polymerization of 2-chloroacrylonitrile in DCA and apoCA canals was carried out in a way similar to that in case of butadiene derivatives. The dehydrochlorination of the polymer in the canals occurred gradually on heating at 140°C without adding an acceptor. The conversion in a DCA canal amounted to 70 % after one day. The electric conductivity of the polymer in the inclusion state was about 10^{-6} S/cm under doping with iodine at room temperature [17].

Ferrocene : We have recently found that DCA forms inclusion compounds with ferrocene and its derivatives. Particularly DCA-ferrocene inclusion compound is very easy to get a large crystal enough to analyze the crystal structure by X-ray diffraction method. It was found from the analysis of a single crystal that ferrocene molecules are tightly accommodated into a DCA canal in an array different from those of crystals of ferrocene itself [18]. It was also ascertained that DCA-ferrocene inclusion compounds are doped with iodine. On the other hand, apoCA does not form an inclusion compound with ferrocene itself, but with its derivatives.

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