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Solubility of Liquid Crystalline Hydroxypropyl Chitin in Organic Solvent

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액정성 히드록시프로필키틴의 유기용매에 대한 용해성

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Abstract: Hydroxypropyl chitin(HPCH) was prepared from chitin by reacting it with propylene oxide. The formation of liquid crystalline character of HPCH was investigated using halogenated organic solvents. Solid state ^{13}C NMR spectra for chitin and HPCH confirmed the incorporation of hydroxypropyl moiety. The degree of substitution of HPCH was around 0.8 as detected by elemental analysis. WAXD patterns of chitin and HPCH showed that an incorporation of hydroxypropyl unit in chitin contributed to reducing the crystallinity and enhancing the solubility in organic solvents. Polarized light microscopic pictures of concentrated HPCH solution showed that HPCH formed cholesteric liquid crystalline character at about 25w/v% solution in dichloroacetic acid and 1, 2-dichloroethane. Inherent viscosity of HPCH solution in a mixed solvent showed a transient decrease.

요 약: 키틴과 프로필렌 옥시드를 반응시켜 히드록시프로필 키틴(HPCH)을 얻었고 할로겐화 유기용매내에서 HPCH의 액정형성능을 관찰하였다. 키틴과 HPCH의 고체 ^{13}C NMR 스펙트럼 분석 결과 히드록시프로필기의 도입을 확인하였다. 원소분석결과 히드록시프로필기의 치환도는 0.8정도였다. WAXD패턴 측정결과 키틴에 히드록시프로필기가 도입됨에 따라 결정성은 감소하였고 유기용매에 대한 용해도는 증가하였다. HPCH를 디클로로아세트산과 1, 2-디클로로에탄 혼합용매에 녹여 편광현미경으로 관찰한 결과 25% 이상의 용액농도에서 콜레스테릭 액정상에서 전형적으로 관측되는 지문영역이 나타남을 알 수 있었다. 용액의 점도는 시간변화에 따라 감소함을 알 수 있었다.

1. Introduction

In the preceeding paper we reported on the cholesteric liquid crystalline(LC) hydroxypropyl chitin(HPCH) in formic acid detected by differential scanning calorimetry(DSC) and polarized light microscopy[1]. HPCH exhibits a lyotropic LC at 30 wt% formic acid solution. It also showed an enhanced solubility and decreased crystallinity compared with chitin.

There has been many reports on the preparation of chitin derivatives. Poor solubility of chitin in organic solvent prevents chitin from the widespread application[2-8]. Chitosan, however, found many applications since it can dissolve in many organic solvents. Chitin is similar in its structure to cellulose. There has been reports on the cellulose and cellulose derivatives that form liquid crystalline phase [9-15]. Because of the structural similarity between cellulose and chitin, there has been attempts to prepare LC chitin and chitosan derivatives.

In the present study we investigated on the enhancement of solubility in dichloroacetic acid(DCA) and halogenated organic solvent. The aim of this study is to show the formation of liquid crystallinity of HPCH in dichloroacetic acid and organic solvents other than formic acid.

2. Experimental

2. 1. Materials

Chitin was purchased from Tokyo Kasei Co. It was dried at 60℃ under reduced pressure and kept in a dessicator over calcium chloride until used. Propylene oxide(Janssen Chimica) was stored at 4℃ before use. Formic acid(extra pure grade) was purchased from Junsei Chemical Co., Ltd. Methylene chloride, chloroform, carbon tetrachloride, 1, 2-dichlorethane were purchased from Shinyo Pure Chemical Industries, LTD. Dichloroacetic acid (Fluka Chemical) were used without further purification.

2. 2. Synthesis of HPCH[1]

HPCH was synthesized as reported previously (see Fig. 1). 5g of chitin(45-60mesh), which was crushed by roll-mill and 77mℓ of propylene oxide were stirred in an ice bath under reflux for two hours. Then 3mℓ of 40 wt% aqueous NaOH solution was added dropwisely. Reaction vessel was heated up to 34℃ with continuous stirring. The reactant was precipitated in a water at 85-95℃ and kept at pH = 7. It was filtered and washed with distilled water and acetone several times and dried at 60℃ in vacuo for 48 hours.

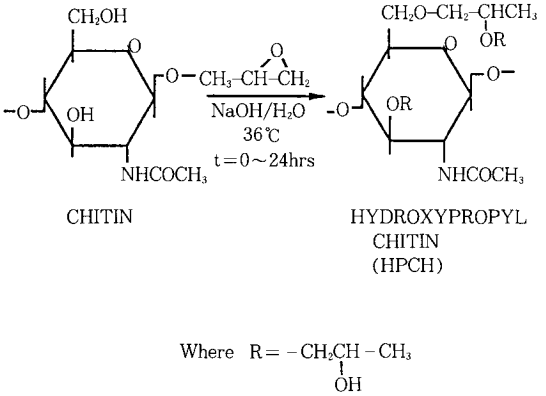

Fig. 1. Schematics of the systhesis of hydroxypropyl chitin.

2. 3. Manufacture of Highly Concentrated HPCH Solution

Because of the limited solubility of HPCH at room temperature, solvent was carefully evaporated to prepare highly concentrated HPCH solution. DCA and DCA/1, 2-dichloroethane(5/5(v/v)) were used as solvents. Dried HPCH powder was first added to the solvent to prepare 5(wt/v)% of HPCH solution at room temperature. Then, 5(wt/v)% solution was heated to 65-70℃ and let the solvent evaporate to concentrate up to 35(wt/v)% HPCH solution.

2. 4. Characterization

Solid state CP/MAS ^{13}C-NMR spectra was obtained from Bruker ARX-300 NMR spectrometer operating at room temperature and at 4kHz MAS spin rate with 512 scanning number and 0.043 seconds of aquisition time. Elemental analysis was carried out at a combustion temperature of 1000℃ and with a He flow rate of 100cc/min. Degree of substitution(DS) was estimated in proportion to the relative contents of C, H, N in chitin and HPCH. Fourier transform infrared(FTIR) spectrometer (Nicolet, Model 5DX) was employed to confirm the structure of HPCH. To compare the crystalline

character of chitin with that of HPCH, wide angle X-ray diffraction(WAXD) patterns were measured by the reflection method with Nickel-filtered CuKα radiation using Rigaku Denki X-ray diffractometer operated at 50 Kv, 180mA in the 2θ scanning mode between 5° and 35°. A crossed polarized light microscope equipped with a hot stage was used to observe the formation of liquid crystalline phase of chitin derivative. Differential scanning calorimetric (DSC) analysis was performed with a Du Pont Instruments 910 DSC under 50cc/min nitrogen flow. DSC thermograms of samples were taken from the second run.

3. Results and Discussion

Fig. 2 shows the solid state ^{13}C NMR spectra for chitin (a) and HPCH (b), respectively. From the comparison of spectra (a) and (b), a peak at 19.1ppm in Fig. 1(b) is assigned to be a CH_3 peak in hydroxypropyl unit in HPCH. A broad peak detected at around 66.2 ppm is caused by the CH_2 and CH unit in hydroxypropyl unit.

FT-IR spectra of chitin and HPCH[1] showed that the bands appeared at around 1660, 1560 and 1420cm^{-1} for chitin have been assigned to amide I, II, and III, repectively. For HPCH we observed characteristic peaks due to amide I, II and III at 1664, 1561 and 1423 cm^{-1}, respectively. In the previous studies[16], there appear two peaks in amide I band in α-chitin while there is only one band for β-chitin. Two peaks resulted from amide I band were observed at 1660cm^{-1} and 1633cm^{-1} in chitin and at 1664cm^{-1}, 1632cm^{-1} in the case of HPCH, respectively. Accordingly, chitin and HPCH considered in this study are known to possess α-structure with antiparallel chains.

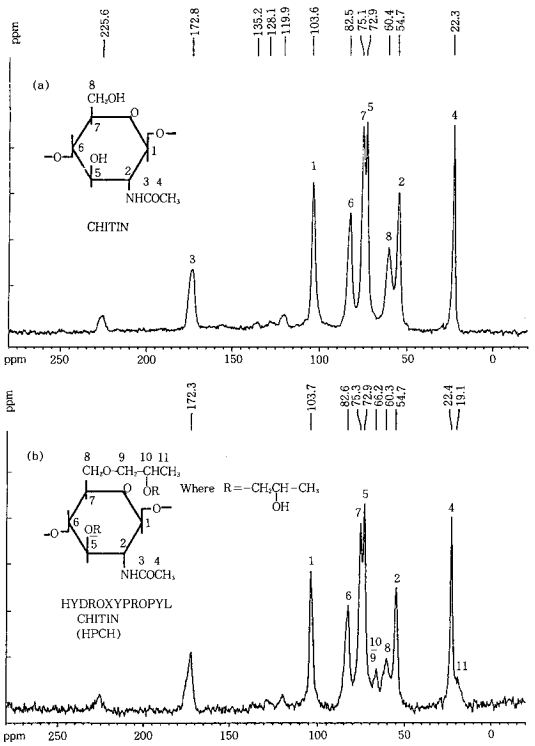

Fig. 2. Solid state CP/MAS ^{13}C-NMR spectra of (a) chitin and (b) hydroxypropyl chitin.

Table 1. Solubility of Hydroxypropyl Chitin

Solvent	Ratio of DCA : Chlorinated hydrocarbon(vol %)			
	7:3	6:4	5:5	4:6
DCA/CH_2Cl_2	S	PS	PS	SW
$DCA/CHCl_3$	S	PS	PS	SW
DCA/CCl_4	S	PS	SW	SW
$DCA/ClCH_2CH_2Cl$	S	S	S	PS

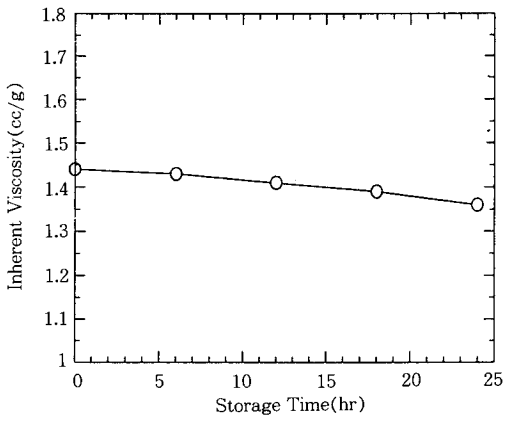

Fig. 3. Dependence of storage time on inherent viscosity of hydroxypropyl chitin in DCA/DCE (5/5 vol%).

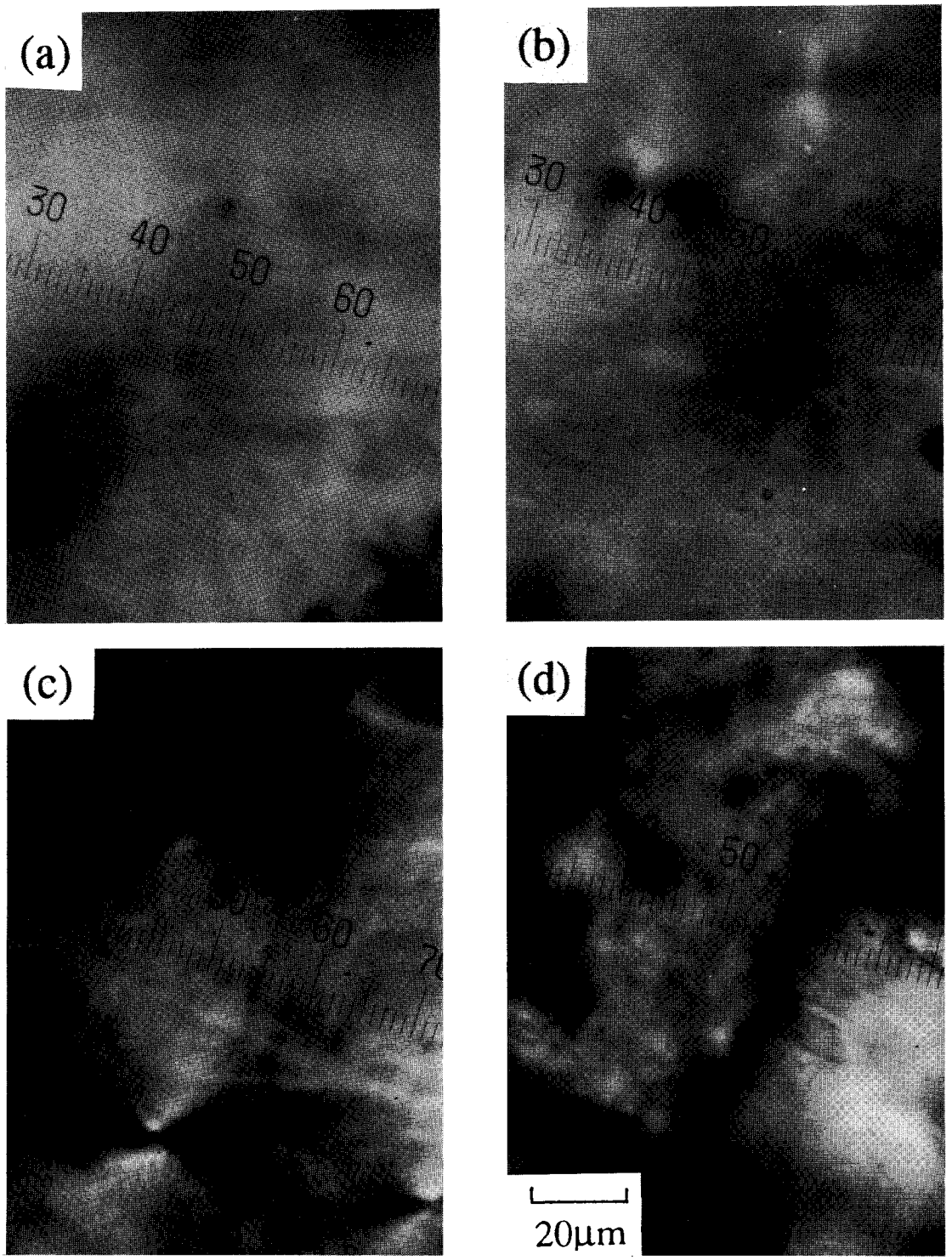

Fig. 4. Polarized light microscopes of HPCH in (a) 10% (wt/v), (b) 25%, (c) 30% and (d) 35% DCA solution measured at room temperature.

Peak intensity due to C–O stretching vibration of primary alcohol at around 1025cm^{-1} became much smaller in HPCH than in chitin. Only a slight decrease in peak absorption at 1113cm^{-1} for a secodary alcohol was observed. New peak appeared at 2970cm^{-1} for HPCH indicated an incoporation of hydroxypropyl moiety. Since the primary alcohol is more reactive than the secondary alcohol, it seemed that the hydroxypropylation is occurred primarily on the C_6 position in chitin backbone. Studies on the alkylation of chitin showed the similar results as analysed by ^{13}C NMR spectrum[17].

HPCH was synthesized by varying reaction time from 6 hr to 24 hr. Its DS was examined by elemental analysis. DS values reached about 0.8 after 6 hrs of reaction time and no further increase of DS is seen after 6 hrs[1].

X-ray diffraction patterns of chitin and HPCH showed that the relative intensity of crystalline peak became smaller for HPCH. It can be said that a decrease in hydrogen bonding force resulting from substituted bulky hydroxypropyl moiety apparently affects the decrease of the degree of crystallinity. As the degree of crystallinity decrease for HPCH, it is expected that HPCH may be dissolved in many organic solvents.

Solubilities of HPCH in DCA and mixed solvent containing DCA were investigated and listed in Table 1. We employed a cosolvent system consisting of dichloroacetic acid(DCA) and chlorinated hydrocarbon, varying the ratio of the composition of the solvent mixture. As the relative amounts of DCA to chlorinated hydrocarbon increases, the solubility of HPCH is enhanced. The best solubility was observed in DCA/1, 2-dichloroethane(DCE).

Inherent viscosity was investigated from the relative viscosity measured by Ubbelohde viscometer to examine the storage stability. Fig. 3 exhibited the dependence of storage time on inherent viscosity of HPCH in DCA/DCE(5/5 v/v%). A transient decrease in viscosity is observed in the solvent mixture.

Many polymers with a rigid backbone have been reported to show liquid crystalline phases[18–22]. Most polymeric liquid crystals form either a lyotropic or a thermotropic mesophases, but not both. Cellulose-based polymers and derivatives[23–26] have shown an ability to form both lyotropic and thermotropic mesophases.

Fig. 4 showed polarized light photomicrographs of HPCH solution prepared in different concentration. As shown in Figures, liquid crystalline phases were not observed below 25(wt/v)% of concentration. When the concentration of HPCH solution reached 25(wt/v)%, HPCH began to show mesophases. At this concentration transition behavior of polymer was changed from isotropic state to anisotropic phase. The wholly anisotropic solution at above 30 (wt/v)% displayed fingerprint patterns that are typical for cholesteric liquid crystals. It was thought that chiral center in mesogenic group of HPCH contributed to give cholesteric characteristics.

DSC thermogram of HPCH demonstrated that there is no noticeable peaks detected in HPCH, meaning that it is not a thermotropic liquid crystalline polymer.

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