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Dilute solution properties of hexanoyl chitosan in chloroform, dichloromethane, and tetrahydrofuran

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Abstract

Hexanoyl chitosan (H-chitosan), a chitosan derivative, was synthesized using a new method to obtain an organically soluble chitosan derivative. H-chitosan with the degree of substitution of 3.92 was dissolved in selected three organic solvents namely chloroform, dichloromethane, or tetrahydrofuran in order to study the effect of solvent type on H-chitosan solution properties. The solution properties of H-chitosan were determined by dilute solution viscometry, dynamic light scattering, and surface tension techniques. The solubility parameter of H-chitosan was estimated to be about 9.31 (cal cm^{-3})$^{0.5}$, which is closer to that of chloroform than those of dichloromethane and tetrahydrofuran. Intrinsic viscosity values of H-chitosan dissolved in chloroform, dichloromethane, or tetrahydrofuran were determined by the Huggins–Kramer extrapolation and found to be ∼1.427, 1.442, and 1.385 dl g^{-1}, respectively. The k_H values for H-chitosan indicate that the three H-chitosan solutions possess nearly the same degree of polymer–solvent interactions. The hydrodynamic radius, R_H, in chloroform appears to be larger than those in dichloromethane and tetrahydrofuran, suggesting a more free chain expansion occurring in chloroform. Surface tension values of the H-chitosan dissolved in chloroform and tetrahydrofuran decrease with increasing concentration, whereas the surface tension value of H-chitosan dissolved in dichloromethane increases with increasing concentration.

Keywords: Hexanoyl chitosan; Solution properties; Viscosity; Dynamic light scattering; Surface tension; Solvent

1. Introduction

Ability to dissolve chitosan in organic solvents is important in many applications. It is well known that chitosan is generally insoluble in many common solvents, e.g. water, alkali, and organic solvents, but it is soluble in solutions of organic acids when the pH of the solutions is less than about six (Muzzaerelli, 1977). Aqueous solutions of acetic and formic acids are generally used in dissolving chitosan. However, these solvents offer only limited practicality for the chemical derivatization of chitosan, in particular large-scale modifications. Poor solubility of chitosan in some common organic solvents can be traced to its rigid crystalline structure through both intra- and inter-molecular hydrogen bondings (Roberts, 1992) and is the main reason for its limited usefulness. In order to overcome this problem, chemical modification of chitosan is thus required.

Solubility of chitosan derivatives in organic solvents is an essential requirement in designing novel molecular structures as functional materials. Several modification techniques for imparting hydrophobicity to the chitosan structure, such as phthaloylation (Nishimura, Kohgo & Kurita, 1991), alkylation (Yalpani & Hall, 1984), and acylation (Hirano, Ohe & Ono, 1976; Moore & Roberts, 1981; Zong, Kimura, Takahashi &Yamane, 2000) reactions, have been available in the open literature. Organically-soluble derivatives of chitosan can be used to formulate by-designed materials for biomedical applications, such as polymeric drugs and artificial organs with high specificity and wide applicability. Acylated chitosans are soluble in various organic solvents, such as chloroform, benzene, pyridine, and tetrahydrofuran. *N*-acylated chitosan has been fabricated as membranes (Seo, Ohtake, Unishi & lijima, 1995), fibers (Hirano, Usutani, Yoshikawa & Midorikawa, 1998), and films (Xu, McCarthy, Gross & Kaplan, 1996). *N*-hexanoyl chitosan was found to exhibit the best blood compatibility in comparison with *N*-propionyl, *N*-butyryl, and *N*-pentanoyl chitosans (Lee, Ha & Park, 1995). Furthermore, *N*-hexanoyl and *N*-octanoyl chitosans were found to be antithrombogenic and resistant to the hydrolysis by lysozyme (Hirano & Noishiki, 1985). Thus, acylated chitosan is an

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interesting chitosan derivative suitable for biomedical applications.

Zong et al. (2000) reported successful syntheses of hexanoyl, decanoyl, and lauroyl chitosans (H-, D-, and L-chitosans, respectively). Chemical characterizations suggested that the degree of substitution of these polymers was four per monosaccharide ring. These acylated chitosans exhibited an excellent solubility in organic solvents such as chloroform, benzene, pyridine, and tetrahydrofuran (THF). Dynamic mechanical analyses (DMA) showed that all acylated chitosans exhibited two phase transitions in the solid state. The first transition at 210, 242, and 240 °C can be attributed to the glass transition (T_g) of H-, D-, and L-chitosans, respectively. The second transition, occurring at about 88 °C, could be due to the secondary or the β transition related to the side chain structure. WAXS analyses indicated that these polymers formed a layered structure in the solid state and the layer spacing d increased linearly with increasing side chain length.

Despite an indepth study by Zong et al. (2000), dilute solution properties of those acylated chitosans, especially those of H-chitosan, have not been available in the open literature. The present contribution then focusses on examining the dilute solution properties of H-chitosan in chloroform, dichloromethane, and tetrahydrofuran through dilute solution viscometry and dynamic light scattering techniques. Our results demonstrate the importance of solvent and polymer–solvent interactions on chain corformation and provide an explanation for some poorly-understood experimental observations for this particular organic soluble chitosan derivatives. The surface tension values of H-chitosan in these solvents will also be reported.

2. Experimental

2.1. Materials

Shells of Penaeus merguiensis shrimps were donated from Surapon Foods Public Co., Ltd. (Thailand). Hydrochloric acid aqueous solution (37% w/w) was purchased from Carlo Erba (Italy). Sodium hydroxide aqueous solution (50% w/w) was kindly supplied by KPT Corporation (Thailand). Hexanoyl chloride was purchased from Fluka Co., Ltd. (Switzerland). Pyridine, chloroform, and methanol were purchased from Labscan (Asia) (Thailand). Pyridine and chloroform were distilled and dried over a molecular sieve prior to use, while other chemicals were of analytical grade and used without further purification. The organic solvents used in this study were chloroform, dichloromethane, and tetrahydrofuran (THF) [Labscan (Asia) (Thailand)]. Some properties of these solvents are summarized in Table 1.

Table 1
Properties of the solvents used

Properties	Chloroform	Dichloromethane	Tetrahydrofuran
Viscosity@30 °C (cP)	0.539	0.440	0.460
Refractive index	1.443	1.424	1.407
Surface tension (mN/m)	27.50	28.60	26.40
Density (g/cm^3)	1.483	1.327	0.889
Solubility parameter (Cal/cm^3)$^{1/2}$	9.34	9.70	9.10

2.2. Preparation of hexanoyl chitosan

The viscosity-average molecular weights of chitin and chitosan obtained from this particular batch of shrimp shells were determined by the viscometric method based on the Mark–Houwink equation (Painter & Colerman, 1997) to be about 8.2×10^5 and 3.7×10^5 g mol^{-1}, respectively. The as-prepared chitosan was first pulverized into powder (71–75 μm in size) and the powder was soaked in pyridine for a period of 1 week, after which the chitosan powder was filtered off and further soaked in a mixture of pyridine and chloroform for another 24 h. The mixture was later cooled to −10 °C in an ice–salt bath, in which hexanoyl chloride dissolved in chloroform was added dropwise into the mixture during a 2-h period under gentle stirring. The mixture was stirred for 2 more hours at room temperature and later refluxed for 6 h at 98 °C. At this point, aggregates of the product were clearly observed within the mixture. The resulting mixture was then poured into methanol, while the precipitated product was filtered off. The product was dissolved again in chloroform and then reprecipitated in methanol, filtered off, extracted in a soxhlet extractor with methanol for 8 h, and later dried at 40 °C in vacuo for 24 h. Finally, a sticky yellowish H-chitosan product was obtained. In order to obtain the H-chitosan with a high degree of substitution (DS) of hexanoyl groups on the chitosan chain (i.e. DS of perfectly substituted H-chitosan = 4 per monosaccharide ring), the above procedure was repeated several times until the yellowish H-chitosan product was obtained (Zong et al., 2000).

2.3. Characterization of hexanoyl chitosan

Fourier-transformed infrared spectroscopic (FT-IR) analysis was conducted on a Bruker EQUINOX55 spectrometer using a resolution of 4 cm^{-1}. Proton-nuclear magnetic resonance (^{1}H NMR) spectrum was recorded on a JOEL JNM-A500 FT-NMR 500 MHz spectrometer. Hexanoyl chitosan was dissolved in deuterated chloroform ($CDCl_3$), and tetramethylsilane (TMS) was used as the reference for the chemical shift measurement. Elemental analysis data were obtained from a Perkin–Elmer PE2400 Series II CHNS/O analyzer with CHN option at the combustion temperature set of 950 °C. The sample (about 1–2 mg) was filled in a tin foil and analyzed in air using oxygen as the combustion gas (flow rate of 20 ml min^{-1}) and helium as the carrier gas (flow rate of 200 ml min^{-1}).

2.4. Solution properties

2.4.1. Calculation of solubility parameter of hexanoyl chitosan

The solubility parameter (δ) of H-chitosan was calculated based on the so-called group contribution method (Teraoka, 2002; Berne & Pecora, 1976). The essence of this approach is to assume that a polymeric molecule can be 'broken down' into a set of functional groups. To calculate the δ parameter of a polymer, one uses the relationship:

$$\delta = \frac{\sum_i F_i}{\sum_i V_i} (\mathrm{cal\ cm}^{-3})^{0.5}, \tag{1}$$

where F_i is the molar attraction constant of the i^{th} group, and V_i is the corresponding molar volume constant of this group (Teraoka, 2002; Berne & Pecora, 1976).

2.4.2. Intrinsic viscosity measurement

Intrinsic viscosity $[\eta]$ is a measure for a chain size of a polymer in the infinitely dilute. In this regime, the solution viscosity can be represented by a power series of the polymer concentration (c_p):

$$\eta = \eta_\mathrm{s}\left(1 + [\eta]c_\mathrm{p} + k_\mathrm{H}[\eta]^2 c_\mathrm{p}^2 + \ldots\right), \tag{2}$$

where η_s is the solvent viscosity, and k_H is the Huggins coefficient. The intrinsic viscosity can be determined by measuring the viscosity value of solutions at low concentrations and extrapolating the values in the limit of infinite dilution, according to the Huggins or Kraemer relationship, respectively (Zimm, 1948):

$$\frac{\eta_\mathrm{sp}}{c_\mathrm{p}} = [\eta] + k_\mathrm{H}[\eta]^2 c_\mathrm{p}, \tag{3}$$

$$\frac{\ln(\eta_\mathrm{r})}{c_\mathrm{p}} = [\eta] + k_\mathrm{K}[\eta]^2 c_\mathrm{p}, \tag{4}$$

where η_r is the relative viscosity which is defined as the ratio between the solution and the solvent viscosities (i.e. $\eta_\mathrm{r} = \eta/\eta_\mathrm{s}$), and η_sp is the specific viscosity which equals $\eta_\mathrm{r} - 1$.

H-chitosan solutions of various concentrations ranging between 0.1 and 0.5 g dl^{-1} in chloroform, tetrahydrofuran and dichloromethane were prepared. Each solution was passed through a polytetrafluoroethylene membrane (average pore size = 0.45 μm) to remove insoluble materials. A Cannon-Fenske 50 capillary viscometer was filled with 5 ml of the solution and thermally equilibrated in a water bath (30 ± 0.1 °C). The solution sample was passed through the capillary viscometer once before the running time was measured. For each solution sample, its viscosity was measured 3 times and the average value was calculated and reported.

2.4.3. Light scattering measurement

Dynamic light scattering (DLS) measurement was carried out using a Malvern photon correlation spectrometer (PCS) equipped with a PCS7 step-motor controller, a PCS8 temperature controller, and a photomultiplier. The measurement was carried out at a fixed temperature of 30 ± 0.1 °C.

In DLS experiments, a normalized time autocorrelation function $[g_2(\tau,q)]$ of the scattered intensity was measured (Zimm, 1948):

$$g_2(\tau, q) = \frac{\langle I^*(0,q)I(\tau,q)\rangle}{\langle I(0,q)^2\rangle}, \tag{5}$$

where $I(\tau,q)$ is the scattering intensity of a delay time τ. In dilute solutions, $g_2(\tau,q)$ can be expressed in terms of the normalized field correlation function $g_1(\tau,q)$ based on the Siegert relationship:

$$g_2(\tau, q) = 1 + \beta|g_1(\tau, q)|^2, \tag{6}$$

where the coefficient $\beta < 1$ is the optical coherence factor. Over short delay times, $g_1(\tau,q)$ is well approximated by a single-exponential decay:

$$g_1(\tau, q) \approx \exp[-\Gamma(q)\tau] \text{when } \Gamma(q)\tau < 1, \tag{7}$$

This decay rate $[\Gamma(q)]$ is related to an apparent mutual diffusion coefficient as (Zimm, 1948; Zhang, Da, Butler & Hogen-Esch , 1992):

$$\Gamma(q) = q^2 D_\mathrm{app}(q, c), \tag{8}$$

where

$$D_\mathrm{app}(q, c) = D_\mathrm{cm}\left(1 + CR_\mathrm{g}^2 q^2 - \ldots\right), \tag{9}$$

where D_cm is the diffusion coefficient of the center of mass of the scattering moiety and $q = (4\pi/\lambda)n_0\sin(\theta/2)$ (with n_0 the refractive index, θ the scattering angle, and λ the wavelength of incident light) is the wave vector. D_cm depends on concentration and is well represented by a linear relation:

$$D_\mathrm{cm} = D'_\mathrm{cm}(1 + k_\mathrm{D}c_\mathrm{p}), \tag{10}$$

where k_D is the first-order concentration coefficient which depends on the second virial coefficient (A_2) and the hydrodynamic friction coefficient (ζ_1), which is given by (Zimm, 1948)

$$k_\mathrm{D} = 2A_2M - \zeta_1 - \upsilon_\mathrm{sp}, \tag{11}$$

where M is the molecular weight of polymer and ν_sp is the specific volume of the polymer.

The ratio $\Gamma(q)/q^2$ is angle dependent, for small value of $R_\mathrm{g}^2 q^2 < 2$ this ratio is equivalent to the apparent diffusion coefficient $D_\mathrm{app}(q,c)$. This angular dependence stems mainly from segmental motions and polydispersity.

The double extrapolation of $D_\mathrm{app}(q,c)$ in the limits of $c \to 0$ and $q \to 0$ can be alternatively carried out in a dynamic Zimm plot, giving the diffusion coefficient at infinite dilution (D_0) from which the hydrodynamic radius (R_H) can be obtained from the Stokes–Einstein relationship:

$$R_\mathrm{H} = \frac{k_\mathrm{B}T}{6\pi\eta D_0}, \tag{12}$$

where η is the solvent viscosity and $k_\mathrm{B}T$ is the Boltzmann constant multiplied by the absolute temperature.

2.4.4. Surface tension measurement

Surface tension of polymer solutions was measured on a KRÜSS DSA10-Mk2 drop shape analyzer at a fixed temperature of 30 ± 0.1 °C.

3. Results and discussion

3.1. Characterization of hexanoyl chitosan

Hexanoyl chitosan (H-chitosan) was synthesized and its chemical structure was characterized by FT-IR, ^{1}H NMR and elemental analysis prior to other characterizations.

The FT-IR spectra of chitosan and H-chitosan, prepared by repeated hexanoylation of chitosan for up to four times, are shown in Fig. 1. Apparently, the characteristic absorption band at 3000–4000 cm^{-1} (OH, NH_2) in the spectrum of chitosan was not observed in the spectrum of our synthesized H-chitosan. In addition, the spectrum of the H-chitosan showed new characteristic absorption peaks at 1717 cm^{-1} (C=O of $N(COR)_2$), 1749 cm^{-1} (C=O of OCOR), 2958 and 2932 cm^{-1} (ν_{as} CH_2), 2873 cm^{-1} (ν_s CH_2), 1458 cm^{-1} (δ CH_2), and 1171 cm^{-1} (twisting vibration of CH_2), respectively. It should be noted that these characteristic peaks are more pronounced with the number of repeated hexanoylations of chitosan. The absence of the absorption band at 3000–4000 cm^{-1} for our H-chitosan indicates that the hexanoyl groups are apparently substituted at the hydroxyl and amino groups on the monosaccharide units of the chitosan chains (Scheme 1).

^{1}H NMR was used to confirm the chemical structure of the obtained H-chitosan. ^{1}H NMR spectrum of the H-chitosan in $CDCl_3$ (Fig. 2) exhibits signals at 5.6 (H1), 5.2 (H3), 4.2 (H4), 3.4–3.6 (H6, H5), and 2.6 (H2) ppm due to the protons of the polysaccharide ring and signals at 2.4 (–CO–CH_2), 1.3–1.6 (–CH_2–) and 0.9 (–CH_3) ppm due to the contributions from the hexanoyl chains (Zong, 2000). Both FT-IR and ^{1}H NMR results thus confirm a successful synthesis of the H-chitosan. The EA result for the H-chitosan synthesized after four times of hexanoylation reaction of the chitosan reveals the molar percentages of C, H, and N atoms as 66.48, 10.01, and 2.68%, respectively. In comparison, the calculated values are 65.10, 9.22, and 2.53% for the H-chitosan with a perfect degree of substitution (Scheme 1). The degree of substitution of the hexanoyl group along chitosan chains for the H-chitosan synthesized was 3.92, which is very close to the theoretical value of 4.00.

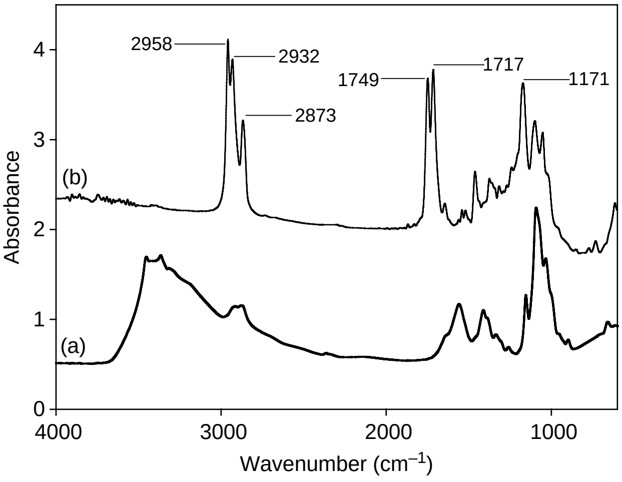
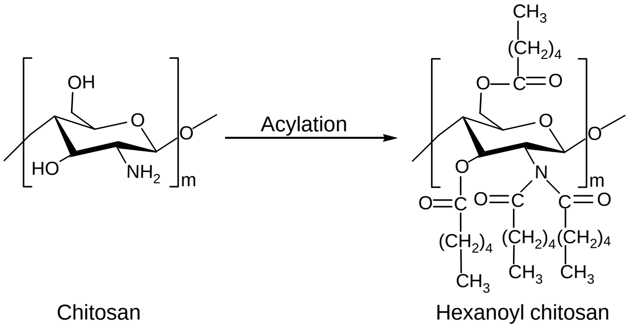


Fig. 1. FT-IR spectra of (a) chitosan, and (b) H-chitosan,



Scheme 1. A synthesis route for H-chitosan.

3.2. Solubility parameter of hexanoyl chitosan

The group contribution method (Teraoka, 2002; Berne & Pecora, 1976) for the calculation of the solubility parameter (δ) of a polymer is based on the contributions from individual groups, atom and bonds constituting the molecules. H-chitosan consists of –N<, –CH, –CH_2, –CH_3, –O–C=O, –C=O, and –O– groups (Scheme 1). Table 2 gives the molar volume and the molar attraction constants of various groups of H-chitosan. Accordingly to these values, the calculated δ parameter of H-chitosan was estimated to be about 9.3 cal$^{0.5}$ cm$^{-1.5}$. This can be compared with the estimated δ values of the solvents used in this work (i.e. 9.2 cal$^{0.5}$ cm$^{-1.5}$ for chloroform, 9.6 cal$^{0.5}$ cm$^{-1.5}$ for dichloromethane, and 9.1 cal$^{0.5}$ cm$^{-1.5}$ for tetrahydrofuran (Berne & Pecora, 1976)). The data clearly suggest that chloroform should be the best solvent for the H-chitosan.

3.3. Dilute solution properties of hexanoyl chitosan

3.3.1. Intrinsic viscosity

For our dilute solutions, we used the Huggins equation in determining the intrinsic viscosity and the Huggins constant. These parameters are qualitative measures of the hydrodynamic volume of the polymer chain and the interaction between different polymer chains and/or between the polymer chains and the solvent molecules, respectively (Utraki & Simha, 1963).

Table 3 lists the intrinsic viscosity and the Huggins coefficient of our H-chitosan solutions. Intrinsic viscosity values of the H-chitosan dissolved in chloroform, dichloromethane and tetrahydrofuran were determined by the Huggins–Kramer extrapolation and found to be ~1.427 ± 0.008, 1.402 ± 0.003, and 1.385 ± 0.003 dl/g (Fig. 3), respectively. These data suggest that the polymer–solvent interaction between the H-chitosan and each solvent is comparable in magnitude.

The Huggins coefficient, k_H, is a measure of polymer–polymer interactions in solution. Experimentally, the Huggins coefficient is independent of molecular weight for long chains, with values of roughly 0.30–0.40 for good solvents and

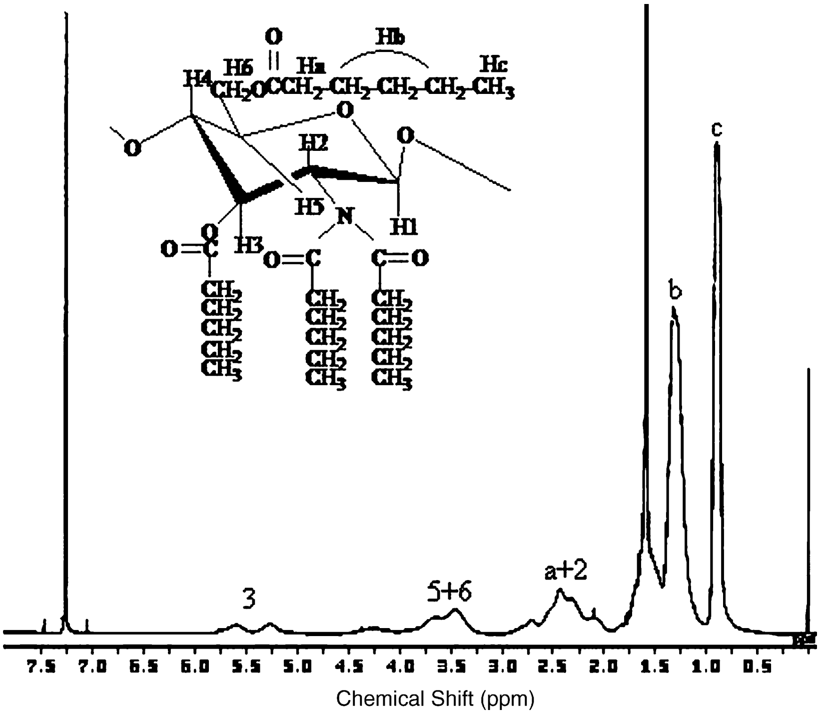


Fig. 2. ^1H NMR spectrum of H-chitosan in $CDCl_3$.

0.50–0.80 for θ solvents. A higher k_H value implies that the interactions between different molecules become stronger. k_H assumes very high values when intermolecular association exists (Bohdanecky & Kovar, 1982). The k_H values for the H-chitosan in chloroform, dichloromethane and tetrahydrofuran solutions are 0.376, 0.496, and 0.508, respectively, suggesting that the three H-chitosan solutions possess the same orders of magnitude for polymer–polymer interactions. The k_H values for these systems fall between good solvents and θ solvents.

Finally, we show the Utracki–Simha plot (Utracki & Simha, 1963), η_{sp} versus $c \cdot [\eta]$, in Fig. 4. In dilute regime, the polymer chains are far apart from each other and the intermolecular interactions are weak, the collapse of the data confirms that the solutions were truly dilute and they obeyed the Huggin's equation in the limit of zero concentration.

3.3.2. Dynamic light scattering

The dynamic light scattering experiment was carried out on solutions of the H-chitosan in the three chosen solvents (chloroform, dichloromethane and tetrahydrofuran). Measurements were taken from polarized scattered light at the wavelength of 514.5 nm and at 30 °C. The results are shown in Fig. 5. Values of D_0, k_D, the normalized second cumulant, μ_2/Γ^2 as well as the hydrodynamic radius, R_H from the Stokes-Einstein relationship are listed in Table 4. R_H values are 50.1, 38.5, and 39.9 nm for chloroform, dichloromethane and tetrahydrofuran, respectively. This suggests that the H-chitosan chain expands the most in chloroform.

Table 2
Molar volume and attraction constants (Painter & Colerman, 1997)

Group	Molar volume constant, V_i^* ($cm^3\ mole^{-1}$)	Molar attraction constant, V_i^* ((cal $cm^3)^{0.5}$ mole
–CH3	318	218
–CH2	16.5	132
>CH–	1.9	23
–OCO–	19.6	298
–CO–	10.7	262
–O–	5.1	95
>N–	−0.5	−3

Table 3
Intrinsic viscosity, $[\eta]$ and Huggins coefficient, k_H for H-chitosan solutions dissolved in different organic solvents at 30 °C

Solvent	$[\eta]$ (dl/g)	k_H
Chloroform	1.427±0.008	0.376±0.012
Dichloromethane	1.402±0.003	0.496±0.005
Tetrahydrofuran	1.385±0.003	0.508±0.003

k_D is the constant describing the concentration dependence of the diffusion coefficient. It is well known that (Teraoka, 2002) in a sufficiently good solvent the diffusion coefficient increases with polymer concentration. As the solvent quality becomes poorer, k_D becomes eventually negative. From Table 4, for all our samples k_D values are positive, indicating that the solvents investigated are good solvents for the H-chitosan. k_D values also support the result of k_H as determined by viscometry

The normalized second cumulant, μ_2/Γ^2, indicating size polydispersity, is tabulated in Table 4 (Patterson & Jamieson, 1985). For the chloroform solution, the normalized variance, μ_2/Γ^2, is 0.61, The normalized second cumalant values for dichloromethane and tetrahydrofuran are 0.40 and 0.38, respectively. The normalized second cumulant for

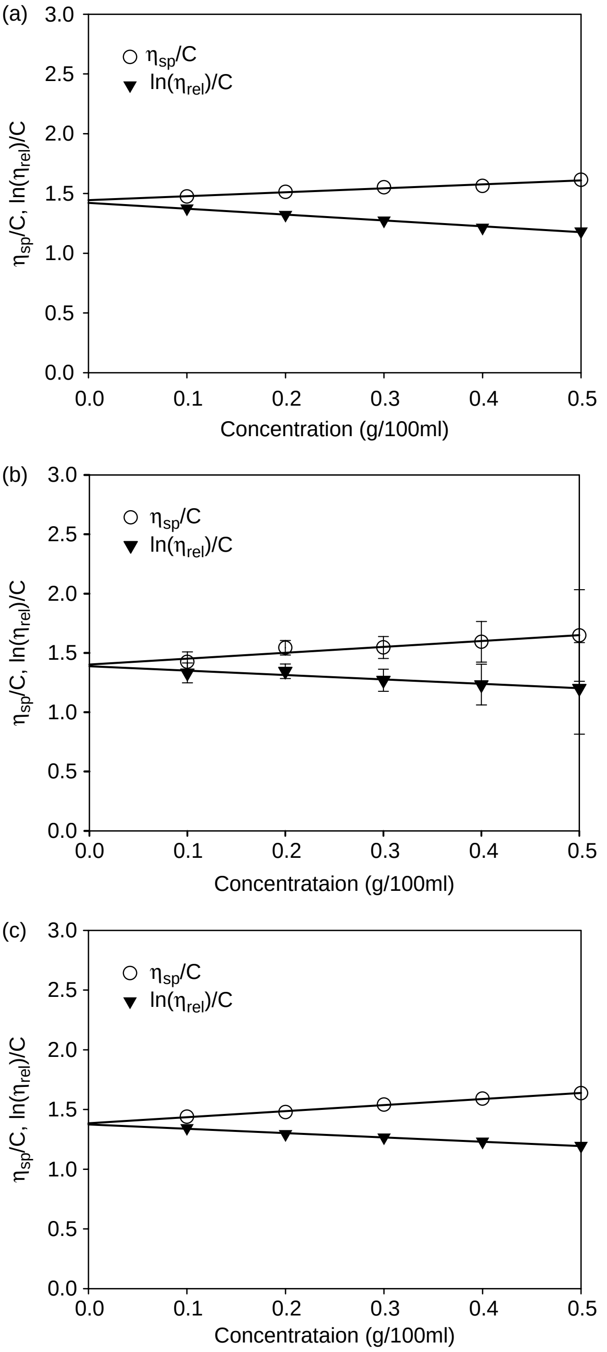


Fig. 3. The intrinsic viscosity of H-chitosan dissolved in (a) chloroform, (b) dichloromethane, and (c) tetrahydrofuran at 30 °C.

the chloroform solution is higher than those of the other two solutions, suggesting that the degree of polydispersity of H-chitosan molecules in chloroform is higher than those in dichloromethane or tetrahydrofuran solution (Patterson & Jamieson, 1985).

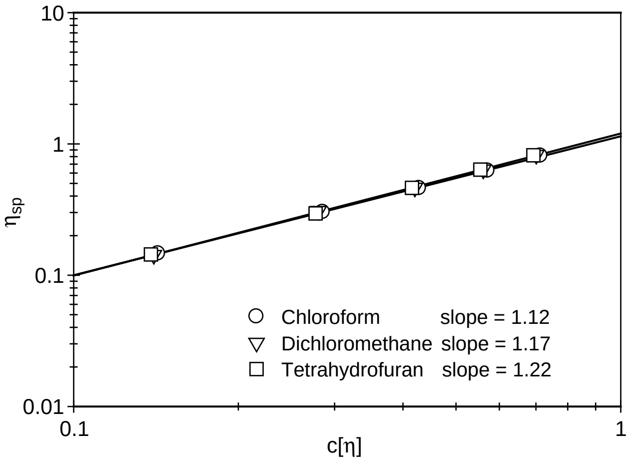


Fig. 4. Specific viscosity dependence of the product concentration-intrinsic viscosity for H-chitosan in three solvent investigated.

R_H values are 50.1, 38.5, and 39.9 nm for chloroform, dichloromethane and tetrahydrofuran, respectively. This suggests that the H-chitosan chain expands the most in chloroform. This can be correlated with the solubility parameters of H-chitosan and chloroform. Our results are in good agreement with those of the earlier experiment on dynamic light scattering of poly(*p*-methoxy)phenyl acetylene in chloroform (Cametti, Codastefano, D'Amato, Furlani & Russo, 2000; Cametti, D'Amato, Furlani & Russo, 2003). It should be noted, as pointed out by Lee and coworker (Lee, Pearce & Kwai, 1996), that the hydrodynamic radius is not solely a function of the chain size or contour length, but it depends on the chain flexibility. The chain flexibility may vary with solvent, resulting in a more compact structure with a lower hydrodynamic radius.

Finally, Fig. 6 shows that D_0 is inversely proportional to solvent viscosity, as would be expected from the Stokes-Einstein relationship.

3.4. Surface tension

Another interesting feature, which has rarely been investigated, concerns the surface and interfacial activities of the hydrophobically modified chitosan, H-chitosan. The surface tension of H-chitosan solutions in the three different organic solvents was measured by the pendant drop method. Geometry of a drop was analyzed optically (Fig. 7). The surface tension of a system is governed by the usual thermodynamic variables and primarily by the chemical nature of the components present in the surface phase. The surface activity phenomenon can be used to explain its molecular structure (i.e. the nature of its monomeric units, its orientation, and overall distribution in solvent medium as well as interaction with the solvent molecule).

Fig. 8 shows surface tension vs. concentration for the three H-chitosan solutions. Surface tensions of H-chitosan dissolved in chloroform and tetrahydrofuran generally decrease with increasing concentration, and no maxima or minima can be observed. The decease in surface tension could be attributed to the increase in adsorption of the various H-chitosan molecules at the air-solution interface as the polymer concentration increases leading to the interfacial excess of the polymer. At low H-chitosan concentrations, H-chitosan molecules absorb at the interface but they may escape into the air phase as insufficient number of the H-chitosan molecules are available

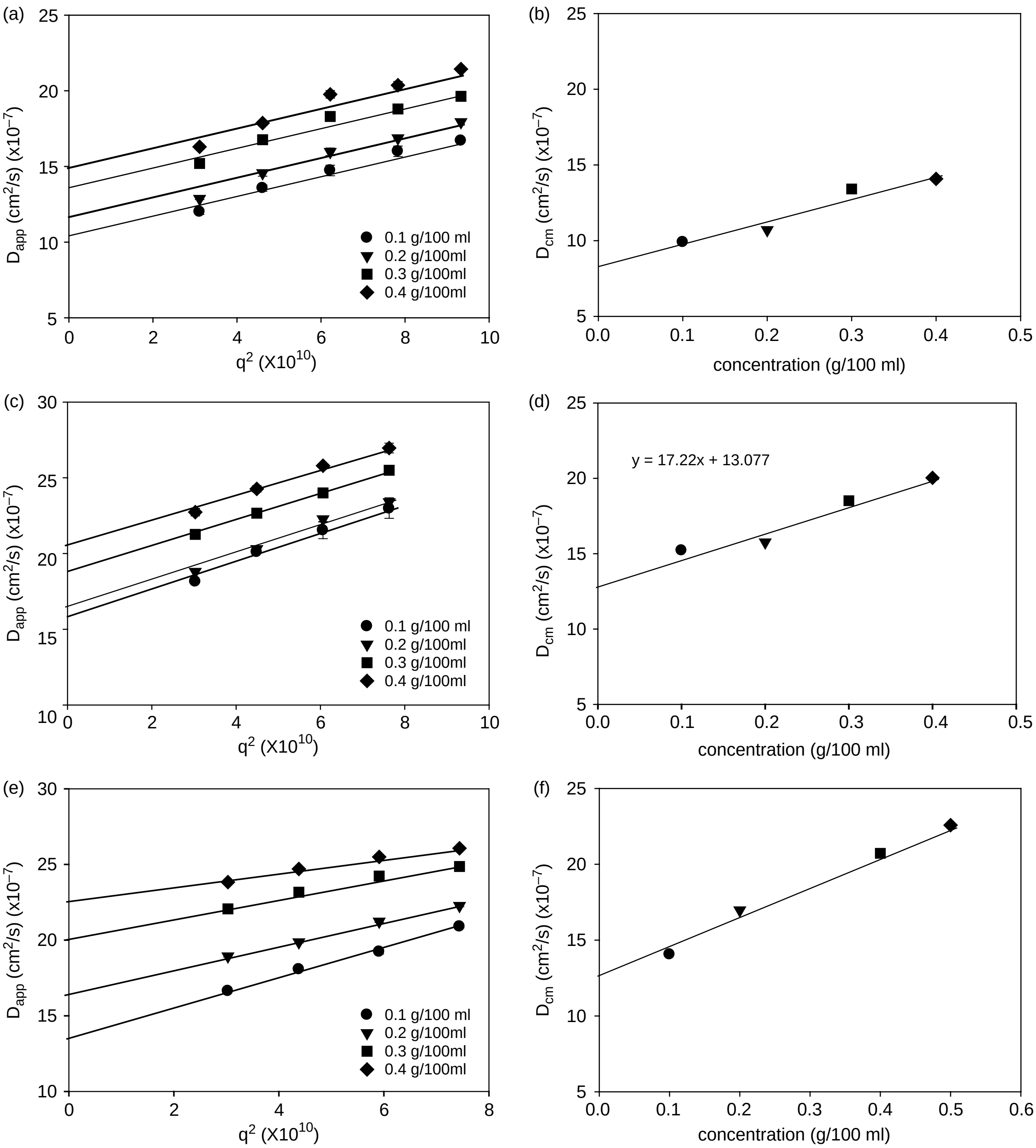


Fig. 5. The apparent diffusion coefficient and diffusion coefficient of H-chitosan in the three solvents investigated at different concentrations in (a–b) chloroform, (c–d) dichloromethane, and (e–f) tetrahydrofuran in dilute regime at 30 °C.

to form intermolecular aggregates. As a result, a sharp decrease in surface tension is observed in the lower polymer concentration limit. In the higher H-chitosan concentration range, the interface becomes saturated with H-chitosan molecules and the intermolecular aggregates start to provide a favorable environment for the hydrophobes. Consequently, a less pronounced decrease in surface tension can be observed in the higher H-chitosan concentration range. On the other hand, the surface tension of H-chitosan dissolved in dichloromethane increases with increasing concentration. In this solvent, it is

Table 4
D_o, k_D, u_2/Γ^2 and R_H data obtained from dynamic light scattering measurement for H-chitosan solutions in different organic solvents at 30 °C

Solvent	$D_o \times 10^7$ (m^2/sec)	R_H (nm)	k_D	u_2/Γ^2
Chloroform	8.21 ± 0.0	50.12 ± 0.2	15.24 ± 0.6	0.61 ± 0.03
Dichloromethane	13.11 ± 0.4	38.51 ± 1.2	16.73 ± 1.3	0.40 ± 0.07
Tetrahydrofuran	12.09 ± 0.1	39.92 ± 0.2	20.78 ± 0.2	0.38 ± 0.02

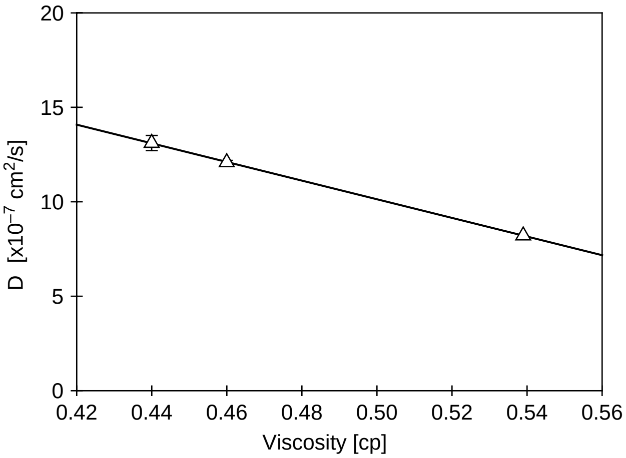


Fig. 6. The diffusion coefficient as the function of the viscosity of the solvent for H-chitosan in the three solvents investigated.

Fig. 7. Optical drop shape of H-chitosan solution dissolved in chloroform and variation of surface tension on concentration for H-chitosan in the three solvents investigated.

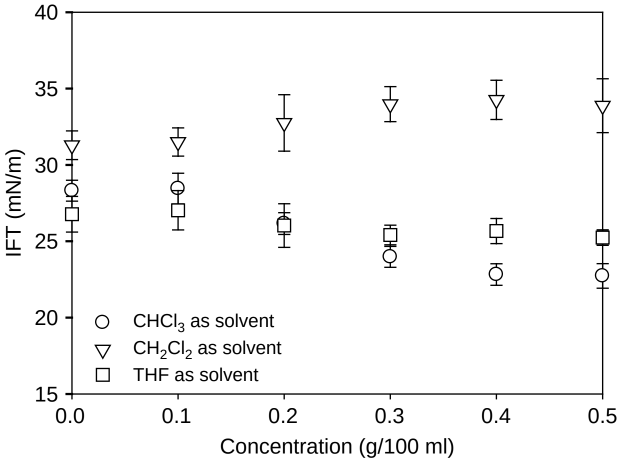


Fig. 8. Surface tension for H-chitosan in three solvents investigated.

likely that intermolecular aggregates may have been well formed starting even at a low polymer concentration.

4. Conclusions

Hexanoyl chitosan with DS of 3.92 was prepared and dissolved in various organic solvents such as chloroform, dichloromethane and tetrahydrofuran in order to study the effect of solvent on its solution properties. Dilute solution properties of H-chitosan in three organic solvents, chloroform, dichloromethane or tetrahydrofuran were measured to investigate the relationship between polymer–solvent interaction: the solution viscosity, the hydrodynamic radius, and the air–liquid interfacial activities The k_H values for the H-chitosan in the three solvents indicate that the three H-chitosan solutions possess comparable polymer–solvent interactions. The R_H value determined in chloroform appears to be larger than those in dichloromethane and tetrahydrofuran, suggesting that a more favorable unwinding of the polymer chain occurs in chloroform. This is directly related to the comparable values between the solubility parameters of the H-chitosan and chloroform. Surface tension of H-chitosan dissolved in chloroform and tetrahydrofuran decreases with increasing concentration, whereas the surface tension of the H-chitosan dissolved in dichloromethane increases with increasing concentration.

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