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Dilute solution properties of four natural chitin in NaOH/urea aqueous system

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ABSTRACT

Four kinds of natural chitin originating from crab (C1), shrimp (C2), silkworm chrysalis (C3) and flies shell (C4) were dissolved in 8 wt.% NaOH/4 wt.% urea aqueous solution. Dilute solution behavior of chitin was examined by laser light scattering and viscometry. The Mark–Houwink equation and the relationship between the *z*-average radius of gyration (R_g) and the average-weight molecular (M_w) for C1 in the solvent at 25 °C were determined to be $[\eta] = 0.26M_w^{0.56\pm0.02}$ (mL g^{-1}) and $R_g = 0.15M_w^{0.47\pm0.03}$ (nm), respectively. On the basis of the polymer solution theory, the conformation parameters of C1 to C4 samples were calculated to be in the range of 25–18 nm for the length of the Kuhn statistical segment (Q_k), and 43–32 for the characteristic ratio (C_∞), respectively. It indicated that chitin molecules existed in a random-coil chain conformation, and chain flexibility increases from C1 to C4 in NaOH/urea aqueous system.
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1. Introduction

Chitin is one of the most abundant natural polysaccharide with an estimated production after cellulose. It is believed that at least 100,000 million tons of chitin are synthesized and degraded, but only over 150,000 tons of chitin is made available for commercial use every year (Pillai, Paul, & Sharma, 2009). Chitin has unique structures, multi-dimensional properties and highly sophisticated functions. Moreover, excellent biocompatibility, admirable biodegradability with ecological safety, and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity, have provided ample opportunities for further development of chitin (Jayakumar, Nwe, Tokura, & Tamura, 2007; Mourya & Inamdar, 2008; Rinaudo, 2008). It has become of great interest not only as an under-utilized resource but also as a new functional biomaterial of high potential in various fields (Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004; Wang et al., 2009; Zheng, Zhou, Du, & Zhang, 2002), including biomedicine, food, environmental protection, agriculture, ecology, etc.

Chitin is a linear polysaccharide composed of β-(1–4)-linked 2-acetamido-2-deoxy-D-glucose units. The high crystallinity of chitin was supported by hydrogen bonds mainly through the acetamido group, which has limited the further utilization of this natural biopolymer to a small area (Kurita, 2006; Rinaudo, 2006; Yi et al., 2005). It is difficult to break the inter- and intra-molecular hydrogen bonds by using of common inorganic solvents or organic solvents. Therefore, research and development of new chitin solvents is significant to exploit a renewable resource and alleviate pollution problems.

Chitin can be dissolved in few solvents that have been reported including *N*,*N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) 5% (w/w) (Poirier & Charlet, 2002; Terbojevich, Carraro, & Cosani, 1988), an alkaline–ice mixture (Einbu, Naess, Elgsaeter, & Vårum, 2004), ionic liquids (Wu, Sasaki, Irie, & Sakurai, 2008), calcium chloride–MeOH (Tamura, Nagahama, & Tokura, 2006; Tamura et al., 2004), some strong acids, and fluorinated solvents (Pillai et al., 2009). Some Mark–Houwink equations for chitin in the solvents such as DMAc/LiCl and alkaline-ice mixture were established (Einbu et al., 2004; Poirier & Charlet, 2002; Terbojevich et al., 1988). However, these solvents are generally corrosive, toxic, volatile, or high cost, and the resulting chitin solutions are not stable due to possible degradation. Thus, the search for solvents that are capable of dissolving chitin directly is still closely associated with the development of new applications.

Recently, Cai et al. (2008), Zhou and Zhang (2000), Zhou, Zhang, and Cai (2004) have reported that cellulose can be dissolved in NaOH/urea aqueous system. NaOH/urea/water is one of the cheapest cellulose solvents, and has a low environmental impact compared to other solvent systems. Chitin and cellulose possess similar skeletal conformation (Kumar, 2000). Both cellulose and chitin are highly crystalline, which is typical for polysaccharides with extensive hydrogen bonding. This makes it possible to dissolve chitin in NaOH/urea aqueous system to impart functionality. In our previous work, we tried to dissolve chitin in the NaOH/urea system, and the dissolution and rheological behaviors

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of chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution have been studied (Hu et al., 2007). In this work, the dilute solution properties of chitin, originating from crab, shrimp, silkworm chrysalis and flies shell, in 8 wt.% NaOH/4 wt.% urea aqueous solution were investigated and compared. We hope to provide a convenient way for the measurements of the average molecular weight from the intrinsic viscosity of chitin on the basis of the Mark–Houwink equation.

2. Experimental

2.1. Materials

Four kinds of chitin originating from crab(C1), shrimp(C2), silkworm chrysalis(C3) and flies shell(C4) were supplied by Shangdong Jinhu Chitin Co. Ltd. They were powered, and sifted to select the particles with the diameter of less than 0.635 mm diameter particles. The crab samples were heterogeneously hydrolyzed to different molecular weights according to the previous literature method (Einbu, Grasdalen, & Vårum, 2007) by treatment in 3 M HCl at 25 °C for 3, 12, 24, 48 and 60 h, respectively. The treated chitin samples were denoted as C1–1, C1–2, C1–3, C1–4 and C1–5. The chemical agents used were of analytical grade, and were used without further purification.

2.2. Preparation of chitin solution

Chitin solution was prepared according to the previous method (Hu et al., 2007) . An adequate amount of NaOH, urea and distilled water (8:4:88 by weight) were added into a 250 mL beaker, and the resulting mixture aqueous solution was stored in a refrigerator. Chitin powder (4 g lots) was dispersed in NaOH/urea aqueous solutions (200 g each). The suspensions were kept at -20 °C and stirred vigorously twice over 36 h. The chitin solution was subjected to centrifugation at 4500 rpm for 20 min at 5–10 °C to exclude the slightly remaining undissolved part. The original concentration of the chitin samples for viscosity and light scattering measurements varied from 0.10 to 1.14 mg.mL^{-1}. The relatively lower concentrations of chitin solution were used to measure the dilute solution propertis to prevent aggregation behavior of the chitin samples.

2.3. Viscosity measurement

Intrinsic viscosities ($[\eta]$) of the chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution were measured at 25 ± 0.1 °C using an Ubbelohde capillary viscometer. The chitin solution was filtered by a G3 sand filter before measurement. The kinetic energy correction was always negligible. Huggins and Kraemer equation were used to estimate the $[\eta]$ value by extrapolation to concentration (c) to be zero as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (1)$$

$$(\ln \eta)/c = [\eta] - \beta[\eta]^2 c \quad (2)$$

where k' and β are constant for a given polymer at a given temperature in a given solvent, and η_{sp}/c is the reduced specific viscosity; $(\ln \eta)/c$ is inherent viscosity.

2.4. Light scattering

The light scattering measurements were performed using an ALV/DLS/SLS-5000E light scattering goniometer system (ALV/CGS-8F, ALV, Germany). The light source was a 22-mW vertically polarized He–Ne laser equipped with an ALV/LSE-5003 light scattering electronics and multiple tau digital correlator. The wavelength of light source was 632.8 nm. The scattering angles used in the static light scattering measurements ranged from 30° to 150°. Zimm plots were obtained by plotting K_c/R_θ versus $q^2 + kc$

$$\frac{Kc}{R_\theta} = \frac{1}{M_w}\left[1 + \frac{(qR_\theta)^2}{3}\right][1 + 2A_2 M_w c] \quad (3)$$

where R_θ is the Rayleigh ratio, A_2 is the second virial coefficient, and K is an instrument constant defined by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \quad (4)$$

Here, N_A is Avogadro number.

A scattering angle of 90° was used for measurements of dynamic light scattering. Dynamic light scattering measures a time profile of the normalized autocorrelation function of the light intensity, $g^{(2)}(t)$, which is related to the electric field normalized correlation function, $g^{(1)}(t)$, through the Siegert relation:

$$g^{(2)}(t) = [1 + \beta|g^{(1)}(t)|^2] \quad (5)$$

where β is the correlation factor ($0 < \beta < 1$). $g^{(1)}(t)$ can be written as the inverse Laplace transform of the distribution of the relaxation rates, $G(\Gamma)$

$$g^{(1)}(t) = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \quad (6)$$

where $G(\Gamma)$ denotes the Γ distribution function, for relaxation times, τ, $g^{(1)}(t)$ will be expressed as

$$g^{(1)}(t) = \int_0^\infty G(\tau) e^{-t/\tau} d\tau \quad (7)$$

where $\tau G(\tau) = \Gamma G(\Gamma)$, and Γ is the decay rate given by $\Gamma = 1/\tau$.

The apparent hydrodynamic radius was calculated using the Stokes–Einstein equation

$$R_h = \frac{\kappa T q^2 \tau_c}{6\pi\eta} \quad (8)$$

where k is the Boltzmann constant, T the absolute temperature, q the scattering vector ($q = 4\pi n_s \sin(\theta/2)/\lambda$, where n_s is the refractive index of the solvent, θ the scattering angle, and λ the wavelength of the incident laser light in vacuum), η is the solvent viscosity, and τ_c the characteristic decay time.

The samples were carefully filtered with 0.22 μm filters (NYL, 13 mm Syringe filter, Whatman, Inc., USA) directly into the light scattering cuvettes, unless otherwise specified. The value of the refractive index increment (dn/dc) was measured with a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co., Tokushima, Japan) at a wavelength of 632.8 nm. The dn/dc value of chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution was 0.181 cm^3 g^{-1}.

3. Results and discussion

3.1. Stability of chitin in NaOH/urea aqueous solution

FT-IR was employed to characterize the structures of C1, C2, C3 and C4. Fig. 1 shows the FT-IR spectra of four kinds of chitin. In these spectra, a clear double-peak was displayed in amide I band from 1620 to 1660 cm^{-1}, indicating that C1, C2, C3 and C4 are α-chitin. Molecular weight and the degree of acetylation (DA) are important structure parameters for chitin. The relative viscosity (η_{rel}) of a polymer is relative to the molecular weight. To investigate the stability of chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution, the relative viscosity of C1 was measured after storing it for different time at 25 °C. Fig. 2 shows the relative viscosity of chitin solution as a function of time. During this period, the relative

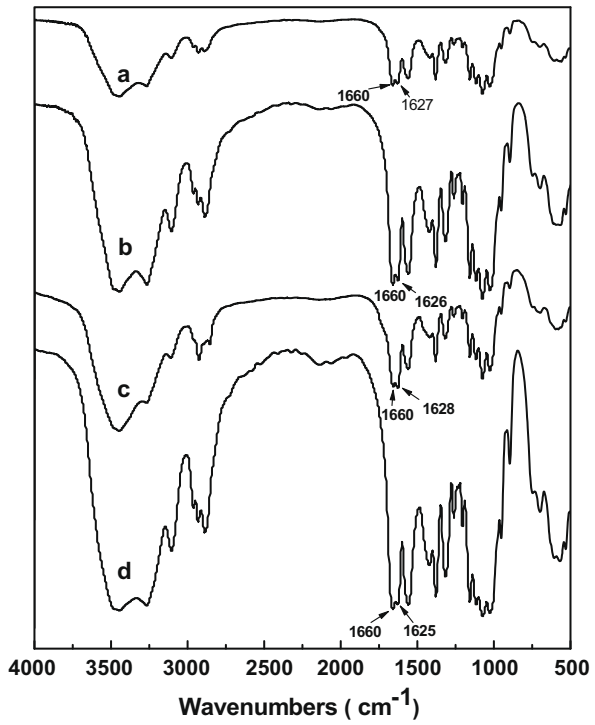

Fig. 1. The FT-IR spectra of C1(a), C2(b), C3(c) and C4(d).

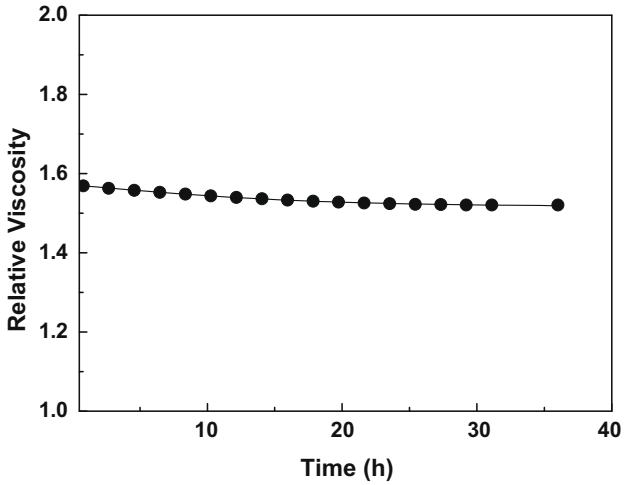

Fig. 2. Relative viscosity (η_{rel}) versus time of the C1 chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C (c = 1.0 mg/mL).

viscosity decreased only from 1.57 to 1.52, which indicated no significant degradation for chitin in this solvent system for at least 36 h. Furthermore, the *DA* value of chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution, was determined with elemental analysis by the method described by Hu et al. (2007). The value of *DA* for C1 decreased from 0.97 to 0.93, aftering storing for 36 h. About 4.1 % loss in the *DA* value has been observed. The results show that chitin solution is relatively stable in 8 wt.% NaOH/4 wt.% urea aqueous, and this solution is more stable than that in alkali (Einbu et al., 2004).

3.2. Determination of intrinsic viscosity

For each chitin sample, the relative viscosities of several solutions with different concentrations were measured in a capillary viscosimeter. The intrinsic viscosity was determined by plotting reduced viscosity and inherent viscosity versus concentration. Table 1 shows the intrinsic viscosity results of the chitin samples. The values of the intrinsic viscosity decreased from C1 to C4, which implied that chitin with different weight molecular could be produced from different sources. Moreover, good linear relationship of η_{sp}/c and $(\ln \eta_{rel})/c$ versus concentration for the chitin fractions have been obtained (not shown). This indicates that chitin is completely dissolved in 8 wt.% NaOH/4 wt.% urea aqueous solution, and exhibits the normal solution behavior.

3.3. Static light scattering of chitin solution

Static light scattering was used to determine the average-weight molecular (M_w), radius of gyration (R_g), and the second virial coefficient (A_2). For each Zimm plot, four to five different concentrations of chitin were used. Fig. 3 illustrates the typical Zimm plot of C3 and C4 chitin samples in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C. In this solvent system, the Zimm plot did not dis-

Table 1
Molecular parameters for the four natural chitin(C1-C4) and five degradated chitin.

Sample	$M_w \times 10^{-3}$	R_g (nm)	A_2 (mL mol g^{-2})	[η] (mL/g)	R_h (nm)
C1	2156	153	9.15×10^{-5}	1021	98
C2	922	94	9.39×10^{-5}	557	72
C3	847	88	1.49×10^{-5}	487	60
C4	673	72	5.51×10^{-4}	443	52
C1–1	1463	126	1.36×10^{-4}	846	81
C1–2	836	113	2.05×10^{-4}	658	67
C1–3	583	75	1.22×10^{-4}	416	45
C1–4	312	64	2.36×10^{-4}	351	37
C1–5	188	48	2.41×10^{-4}	265	33

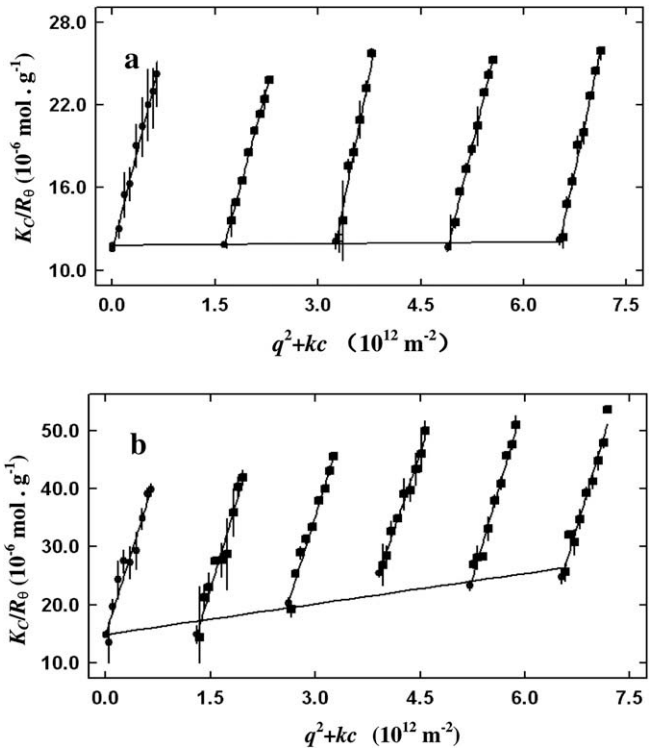

Fig. 3. Zimm plots for chitin solutions made from sample C3 (a) and C4 (b). The experimental data are denoted ■, and the extrapolated values are denoted ●.

play any significant distortion, indicating a normal solution behavior of polymer. Extrapolation to zero angle against c and to zero concentration against q^2 gave linear plots. From these straight lines, M_w, R_g, and A_2 were calculated in the customary manner. The molecular parameters obtained from the associated Zimm plots are given in Table 1.

In general, the R_g values are related to the actual space of the polymer chain in the solution, and the M_w also plays an important role. The values of M_w and R_g decrease from C1 to C4, respectively. The relatively high values of R_g for C1 has a relatively large molecular weight in 8 wt.% NaOH/4 wt.% urea aqueous solution. And the values of M_w and R_g decrease with the increase of the degradation time for the C1 chitin sample. The second virial coefficient is a thermodynamic parameter indicative of solvent–polymer interactions. The A_2 values range from 0.9×10^{-4} to 5.5×10^{-4} mL mol.g^{-2} for four natural chitin samples. The relatively large and positive values suggest that 8 wt.% NaOH/4 wt.% urea aqueous solution is a good solvent for chitin.

3.4. Dynamic light scattering of chitin solution

The distribution function $G(\Gamma)$ were analyzed using the CONTIN program though the inverse Laplace transformation technique. The distribution functions for the four natural chitin samples versus the hydrodynamic radius (R_h) are shown in Fig. 4. All the chitin samples present a single peak, indicating that no obvious aggregates takes place for the used range of concentrations. This further shows that 8 wt.% NaOH/4 wt.% urea aqueous solution is a good solvent for chitin. The R_h results are summarized in Table 1. The values of R_h were found to shift to lower values for the samples from C1 to C4. In a given polymer solution, the ratio of geometric to hydrodynamic radius ($\rho = R_g/R_h$) describes to what extent a particle/polymer is drained by the solvent, and depends on its chain architecture and conformation. Fig. 5 shows that the plots of ρ versus different molecular weights. It is obvious that the ρ values is independent of M_w and has average value of 1.51. The previous experimental results have verified that the value of 1.52 was close to the predicted value for a flexible coil in a good solvent (Wu & Zhou, 1995). It is noted that the mean value of ρ is very similar to that of 1.52, implying that the chitin molecules have a random coil structure in 8 wt.% NaOH/4 wt.% urea aqueous solution.

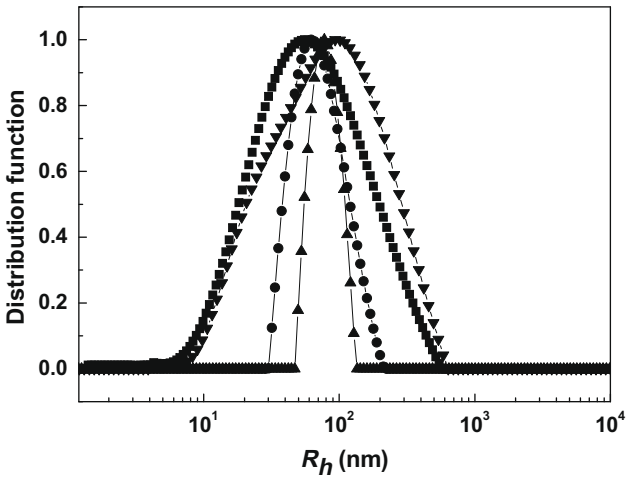

Fig. 4. The probability density of the equivalent hydrodynamic radius was obtained from dynamic light scattering data. The chitin solutions are prepared from C1 (▼), C2 (▲), C3 (●), C4 (■).

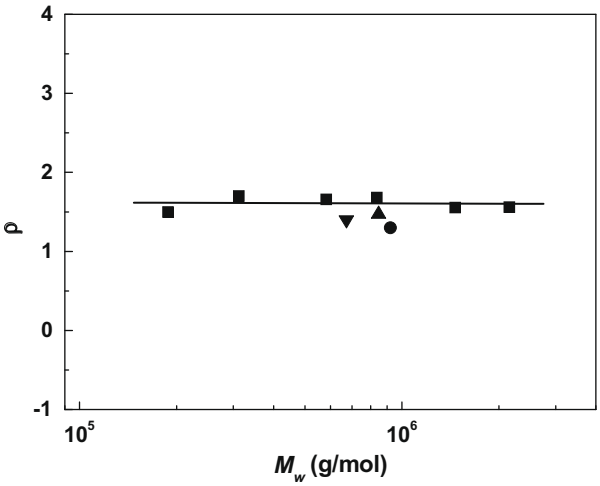

Fig. 5. ρ as a function of M_w for the C1 (■) chitin fractions, C2 (●), C3 (▲) and C4 (▼) in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C.

3.5. Relation between intrinsic viscosity and molecular weight

The intrinsic viscosity of a polymer in solution is related to M_w by the Mark–Houwink equation.

$$[\eta] = KM^{\alpha} \tag{9}$$

The M_w dependence of $[\eta]$ for chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C is shown in Fig. 6a. By plotting log($[\eta]$) versus log(M_w) for the C1 chitin fractions, the Mark–Houwink equations for the C1 chitin in the M_w range from 1.88×10^5 to 2.156×10^6 was established as

$$[\eta] = 0.26M_w^{0.56\pm0.02} \text{ (mL/g)} \tag{10}$$

The values of the parameters K and α depend on both the polymer–solvent system and the temperature. Generally, α with a rough value of 0.5 suggests that the polymer molecules behave as a dense sphere, and the value from 0.6 to 0.8 indicates the existence of a flexible chain and a greater value than one for an elongated rod. If the structure of the polymer chain is a perfect hard sphere, the exponent will be 0 (Park & Choi, 1996). Our experimental value of 0.56 for chitin was ascribed to a random coil structure. Therefore, we have established a new Mark–Houwink equation for chitin in NaOH/urea aqueous solution, which is colorless and nontoxic solvent system. It is convenient to measure the M_w of chitin from the $[\eta]$ data on the basis of the new equation.

3.6. Relation between radius of gyration and molecular weight

The radius of gyration of a polymer is related to the molecular weight by the equation

$$R_g = CM_w^b \tag{11}$$

where C and b for a given sample are empirical constants. The plot of R_g versus M_w for the C1 chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C is shown in Fig. 6b. The resulting relation is expressed as

$$R_g = 0.15M_w^{0.47\pm0.03} \text{ (nm)} \tag{12}$$

In view of the polymer solutions theory, the b values of 0.33, 0.50–0.60, and 1.0 reflect the chain shape in adapting for a sphere, a random coil, or a rigid rod, respectively (Tao, Zhang, & Cheung, 2006). The b value of 0.47 suggests that chitin molecules are more inclined to random coil.

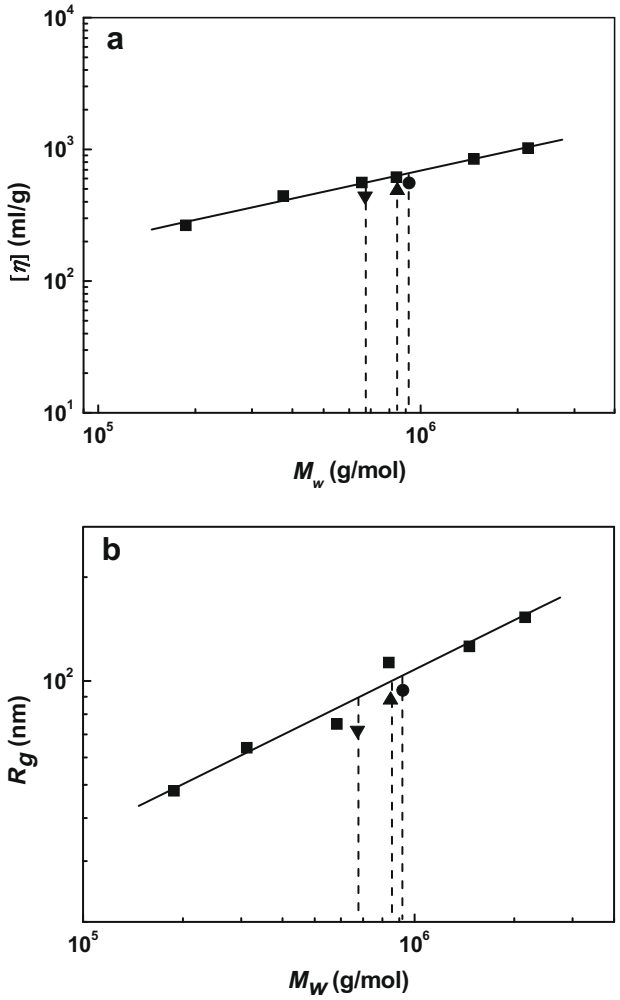

Fig. 6. Plot of $[\eta]$ versus M_w (a) and plot of R_g versus M_w (b) for the C1 (■) chitin fractions in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C, in comparison with the C2 (●), C3 (▲) and C4 (▼) chitin samples.

The fractal dimension (d_f) of monodisperse polymers can be determined from the M_w dependence of R_g by Eqs. (11) and (13) (Gelade et al., 2001; Tao, Zhang, Yan, & Wu, 2007).

$$d_f = 1/b \tag{13}$$

The value of d_f was calculated to be 2.12 for chitin. The d_f value of 2.12 is characteristic for a particle that has an internal structure between a hard sphere (d_f = 3.0) and a fully swollen randomly branched macromolecule in a thermodynamically good solvent (d_f = 2.0) (Hanselmann, Burchard, Ehrat, & Widmer, 1996).

From the Mark–Houwink equation, the d_f value of the polymers can also be derived by using the following relation (Burchard, 1999)

$$d_f = 3/(1+\alpha) \tag{14}$$

where α is the exponent of the Mark–Houwink equation. Thus, the value of the d_f was calculated to be 1.92 for chitin, which is similar to that from Eq. (13). Since the fractal dimension is a measure of the compactness of a polymer chain, the larger the fractal dimension, the more compact the structure. In view of the result from the d_f value for chitin, we may further confirm that the C1 chitin has a random coil structure in 8 wt.% NaOH/4 wt.% urea aqueous solution.

3.7. Chain dimensions of four natural chitin in NaOH/urea aqueous solution

Based on the results mentioned above, the worm-like cylinder model can be used for the characterization of the chain conformation of the C1 chitin samples. Bushin, Tsvetkov, Lysenko, and Emelyanov (1981) and Bohdanecky (1983) independently showed that the Yomakawa–Fujii–Yoshizaki theory (Yamakawa & Fujii, 1974; Yamakawa & Yoshizaki, 1980) for $[\eta]$ of unperturbed worm-like cylinder can be replaced approximately by

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2} \tag{15}$$

$$A_\eta = A_0 M_L \Phi_{0,\infty}^{-1/3} \ (\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}) \tag{16}$$

$$B_\eta = B_0 \Phi_{0,\infty}^{-1/3} (2q/M_L)^{-1/2} \ (\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}) \tag{17}$$

where q and M_L are the persistence length and the molar mass per unit contour length, respectively. A_0 and B_0 are tabulated in Bohdanecky's article (Bohdanecky, 1983), and $\Phi_{0,\infty}$ is 2.87×10^{23}. The $(M_w{}^2/[\eta])^{1/3}$ versus $M_w{}^{1/2}$ is plotted in Fig. 7. Substitution of the intercept and slope of this plot into Eqs. ()()()(15)–(17) yields 402 nm^{-1} for M_L and 4 nm for q, indicating a flexible chain characteristic for the C1 chitin.

The characteristic ratio (C_∞) can represent how much the chain is extended by steric hindrance. The C_∞ is defined as follows (Zhang et al., 2001):

$$C_\infty = M_0/(\lambda M_L l^2) \tag{18}$$

where M_0 is the average molecular weight of the repeating unit in chitin, λ^{-1} is the Kuhn's segment length ($\lambda^{-1} = 2q$), and l is the bond length of the anhydroglucose unit in chitin. With the l value of 0.514 nm for chitin, the C_∞ of the chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution was calculated to be 15. The C_∞ value of chitin is lower than 20.9 for cellulose in NaOH/urea aqueous solution at 25 °C (Zhou et al., 2004), which has been described as semistiff chain conformation. Usually, the C_∞ of polymers is affected by bone angle and steric hindrance including backbone chain and side chain, etc. The acetyl groups of chitin interfere with the formation of intermolecular hydrogen bond partially. This results in the relatively lower C_∞ value for chitin than that for cellulose. Therefore, the chitin exists as a random coils in NaOH/urea aqueous solution with a low Mark–Houwink exponent of 0.56, and small values of M_L, q, and C_∞.

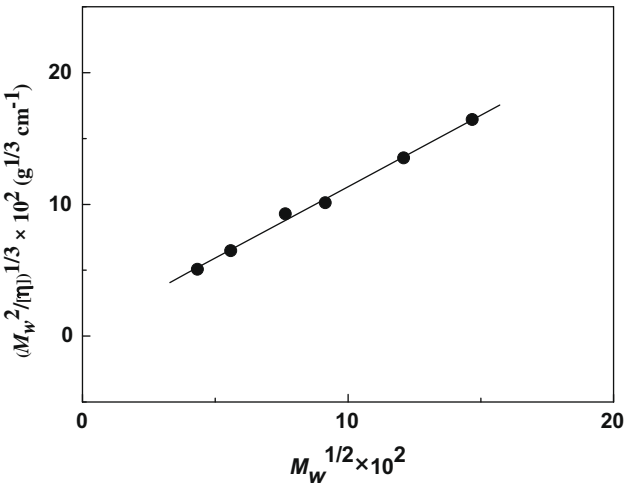

Fig. 7. Plot of $(M_w{}^2/[\eta])^{1/3}$ versus $M_w{}^{1/2}$ for the C1 chitin in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C.

In addition, according to the method described by Einbu et al. (2004), the number of Kuhn statistical segments (N_k), the length of the Kuhn statistical segment (Q_k) and the contour length (L_c) of the chitin molecules are determined by the equations, respectively.

$$N_k Q_k^2 = \langle r_{e-e}^2 \rangle \tag{19}$$

$$N_k Q_k = L_c \tag{20}$$

$$L_c = \frac{M_w}{M_{mon}} L_{mon} \tag{21}$$

$$R_g^2 = \frac{N_k + 2}{6(N_k + 1)} \langle r_{e-e}^2 \rangle \tag{22}$$

where $< r_{e\text{-}e}{}^2 >$ is the mean square end-to-end distance, L_{mon} is the length of a projection of the repeating unit on the chitin chain axis and M_{mon} is the molecular weight of the repeating unit in chitin. With the L_{mon} value of 0.514 nm for chitin, the M_{mon} is 203 g/mol (Einbu et al., 2004; Terbojevich et al., 1988). The radius of gyration and the weight-average molecular weight obtained from light scattering experiments and Eqs. (19)–(22) yield N_k, Q_k, and L_c. The length of the Kuhn statistical segment describes the local chain stiffness. Provided that the physical properties are the same along the chain, this length should rise with the M_w increasing for the polymers the same structure. The values of Q_k are calculated to be 25, 22, 21, and 18 nm for the C1, C2, C3, and C4, respectively. Furthermore, the C_∞ is determined by

$$C_\infty = \frac{\langle r_{e-e}^2 \rangle_0}{n L_{mon}} \tag{23}$$

$$\langle r_{e-e}^2 \rangle_0 = \frac{\langle r_{e-e}^2 \rangle}{\alpha_s} \tag{24}$$

where $\langle r_{e-e}^2 \rangle_0$ is the unperturbed mean square end-to-end distance, n ($=M_w/M_{mon}$) is the number of main-chain bonds. The linear expansion factor, α_s, is calculated according to the previous literature method (McMormick, Callais, & Hutchinson, 1985). The values of characteristic ratio for four natural chitin samples are calculated to be 43, 38, 36, and 32, respectively. This reflects that the chain flexibility increases from C1 to C4. Moreover, C_∞ values obtained for chitin in NaOH/urea aqueous are similar to that of chitin in alkali at 20 °C (Einbu et al., 2004), which has been described as random coils conformation. The values of C_∞ values for chitin in NaOH/urea aqueous are lower than that of chitin in DMAc–LiCl solvent (Terbojevich et al., 1988). It may be that chitin exists as more extended chain conformation in DMAc–LiCl than in NaOH/urea aqueous system.

The data of intrinsic viscosity and molecular weight for C2, C3 and C4 are also shown and compared in Fig. 6a. The values of intrinsic viscosity for C2, C3 and C4 are slightly lower than these of C1 with the corresponding M_w. It means that the other three chitin chains are slightly contraction compared with that of the C1 chain. Furthermore, the M_w values of the other three chitin samples were calculated by the data of the intrinsic viscosity in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C on the basis of Mark–Houwink equation. The M_w values for C2, C3 and C4 are 900, 800, and 650 kg mol^{-1}, respectively. The calculated values are in good agreement with the results from laser light scattering (shown in Table 1). According to previously similar manner, the data of R_g and M_w for C2, C3 and C4 are also shown and compared in Fig. 6b. The values of R_g for C2, C3 and C4 are a little small than these of C1 with the corresponding M_w. It further indicates that the C1 chains are slightly extended than those of the other three chitin. Therefore, in view of the results mentioned above, the flexibility for four kinds of natural chitin molecular chain is the order of C4 > C3 > C2 > C1 in 8 wt.% NaOH/4 wt.% urea aqueous solution at 25 °C.

4. Conclusions

Four kinds of natural chitin were dissolved directly into 8 wt.% NaOH/4 wt.% urea aqueous solution to form a transparent solution. Dilute solution properties of chitin in NaOH/ urea aqueous solution have been determined. The Mark–Houwink equation and the relationship between the z-average radius of gyration and the weight-average molecular weight for the C1 chitin were determined in the solvents at 25 °C, respectively. The molecular parameters and chain dimensions for four natural chitin were given. The results showed that 8 wt.% NaOH/4 wt.% urea aqueous solution was a good solvent to chitin, and the chitin molecules behaved as random coils. Moreover, chain flexibility slightly increases from C1 to C4. A novel, simple, and nontoxic solvent for chitin was provided to examine the molecular weight and solution properties. This solvent system was an attractive one that could be applied to the further exploitation of chitin.

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