Available online at www.sciencedirect.com

Carbohydrate Polymers 64 (2006) 190–196

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Laser-light-scattering study of structure and dynamics of waxy corn amylopectin in dilute aqueous solution

Cheng Yang [a,*], Bo Meng [a], Mingqing Chen [a], Xiaoya Liu [a], Yufei Hua [b], Zhongbin Ni [a]

[a] *School of Chemical and Material Engineering, Southern Yangtze University, Hui He Road 170, Wuxi, Jiangsu 214036, P.R. China*
[b] *School of Food Science and Engineering, Southern Yangtze University, Wuxi, 214036, P.R. China*

Received 26 July 2005; received in revised form 6 September 2005; accepted 8 November 2005
Available online 20 December 2005

Abstract

The average molecular weight ($\bar{M}_w$), gyration radius ($<R_g>$), second virial coefficient (A_2) and fractal dimension (d_f) of waxy corn amylopectin in aqueous solution were characterized by static light scattering. The results indicated that the single waxy corn amylopectin molecule had a compact structure compared with the linear polymer and was like a swollen branched cluster. The associated waxy corn amylopectin molecule was like a non-swollen branched cluster. The dynamics of waxy corn amylopectin in dilute aqueous solution were investigated by dynamic light scattering. When $qR_g \leq 2$ (where q is the scattering vector and R_g is the gyration radius of amylopectin), the single line-width distribution was found, which was caused by the translational diffusion of waxy corn amylopectin in dilute aqueous solution. The average hydrodynamic radius $<R_h>$ could be obtained through Stokes-Einstein equation. When $qR_g > 2$, the dynamics of waxy corn amylopectin were dominated by the internal motion of waxy corn amylopectin branching sections, and the first cumulant line-width ($<\Gamma>$) could be scaled to the scattering vector (q) as $<\Gamma> \sim q^n$ ($n = 2.73 \pm 0.06$). It was found that some internal motions were not found at certain observation length by dynamic laser light scattering and some internal motions were suppressed due to the hyperbranched structure of amylopectin. The reduced cumulant $\Gamma^* = <\Gamma>/(q^3 k_B T/\eta_0)$ could not approach a plateau value with increase of the qR_g, and the $<\Gamma>/(q^3 k_B T/\eta_0)$ value of waxy corn amylopectin was much lower than the value of the linear polymer due to the branched structure and rigid chain of waxy corn amylopectin.

Keywords: Laser light scattering; Amylopectin; Structure; Dynamics; Dilute solution

1. Introduction

Starch is the second most abundant natural polysaccharide, and is widely used in food industry, paper industry and degrading plastic industry. Amylopectin is one of the two main components of starch and is a highly and nonrandom branching polysaccharide. Amylopectin consists of D-glucopyranose monomers and connected by either α-(1,4) or α-(1,6)-glucosidic bonds. Sequence of α-(1,4) connected monomers produces a linear stretch of chain, whereas α-(1,6) bonds act as branching point for further linear stretch. The fine structure of amyplopectin was described as 'cluster' model and non-random branching macromolecule (Bertoft, 2004; Nikuni, 1978; Robin, Mercier, Duprat, Charbonnière, & Guilbot, 1975; Thompson, 2000).

The molecular weight, gyration radius and hydrodynamic radius of amyplopectin were extensively investigated by laser light scattering and size exclusion chromatography (Bello-Pérez, Roger, Colonna, & Paredes-López, 1998; Durrani & Donald, 2000; Galinsky & Burchard, 1995; Hanselmann, Burchard, Ehrat, & Widmer, 1996; Millard, Wolf, Dintzis, & Willett, 1999; Roger, Bello-Pérez, & Colonna, 1999; Yoo & Jane, 2002). However, the results obtained by these authors were very different from each other partly due to the different origin of sample and partly due to the samples preparation method. The molecular weight of non-degraded amylopectin was reported to range from 1.70×10^8 g/mol to 5.60×10^8 g/mol, and the gyration radius of non-degraded amylopectin was reported to vary from 170 to 342 nm.

The dynamics of amylopectin in dilute solution were less considered than its static properties. Only a few paper dwelled on the dynamics of amylopectin. The dynamics of degraded potato starch (Galinsky & Burchard, 1996, 1997), corn amylopectin and high amylose content starch (Bello-Pérez, Roger, Colonna, & Paredes-López, 1998; Roger, Bello-Pérez, & Colonna, 1999) in dilute aqueous solution had been

---

[*] Corresponding author. Tel.: +86 510 5865915; fax: +86 510 5865424.
E-mail address: cyang@sytu.edu.cn (C. Yang).

0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.11.017

investigated by dynamic light scattering. In dynamic light scattering, the diffusion coefficient and hydrodynamic radius of amylopectin can be evaluated from the intensity-intensity correlation function when the relaxation motion is attributed to the pure translational diffusion motion. In the case of large qR_g (where q is the scattering vector and R_g is the gyration radius of amylopectin), the internal motion of amylopectin would be found and the dynamic behaviors of starch in aqueous solution were determined by their structure and composition. However, the influence of polydispersity and branched structure on the internal motion of amylopectin was still an open question.

The dynamics of polymer chain in dilute solution is a fundamental problem in polymer physics and was extensively studied by experiment and theory (de Gennes, 1967; Han & Akcasu, 1981; Teraoka, 2002; Wu, Chan, & Xia, 1995; Wu & Zhou, 1996). The dynamics of individual long chain polymer include the diffusion motion and internal motion of segment. When $qR_g \gg 1$, the intensity-intensity correlation function was dominated by the internal motion of linear chain. In this case, the first cumulant line-width $<\Gamma>$ could be scaled to q as $<\Gamma> \sim q^3$ (Teraoka, 2002). With the increase of the qR_g, the reduced cumulant $\Gamma^* = <\Gamma>/(q^3 k_B T/\eta_0)$ could approach the plateau value 0.071 and 0.079 predicated by theory with or without a preaverage Onseen tensor, where $<\Gamma>$, q, k_B, T and η_0 are the first cumulant line-width, scattering vector, Boltzmann constant, absolute temperature and solvent viscosity (Han & Akcasu, 1981). On the other hand, there is yet no theory that deals with the dynamics of branched polymer in dilute solution. Furthermore, the difficulty of synthesizing the branched polymer with high molecular weight and narrow molecular weight distribution limited the study of their dynamics in experiment (Trappe, Bauer, Weissmüller, & Burchard, 1997).

The high branching density and large size with relatively narrow distribution of waxy corn amylopectin make it a good model to investigate the dynamics of branched polymer. In present study, the waxy corn amylopectin was chosen to study the dynamics of amylopectin in aqueous solution. This amylose-free amylopectin could avoid the influence of the translation diffusion of the small weight amylose on the internal motion of the amylopectin. Here we focused on the effect of the structure, temperature and the kind of the solvent on the internal motion of waxy corn amylopectin.

2. Experiment Section

2.1. Materials

Amylopectin from waxy corn was purchased from Tokyo Kasei Kogyo Co., Ltd, Japan. The amylopectin was dissolved in 0.5 M NaOH solution or DMSO/H_2O (90% wt/wt) with magnetic stirring for 18 h at room temperature (10 ± 2 °C). After centrifuging with 5000 r/min for 20 min, the dilute NaOH aqueous solutions or DMSO/H2O (90% wt/wt) solutions of amylopectin were passed through the 0.45 μm Millipore filter into a dust-free cell to remove the dust for light scattering experiment. The final concentration of amylopectin in aqueous solution was $6\times10^{-5} - 2\times10^{-4}$ g/mL.

2.2. Laser light scattering

A modified commercial laser light scattering spectrometer (ALV/DLS/SLS-5022F) was used, which was equipped with an ALV-5000 multi-τ digital time correlator and a He–Ne laser (Uniphase, output power ≈20 mW at $\lambda = 632.8$ nm). In static LLS, angular dependence of the excess absolute time-average scattered intensity, i.e. Rayleigh ratio $R_{vv}(q)$, of dilute solution can lead to the weight-average molar mass $\bar{M}_w$, the second virial coefficient A_2, and the root-mean-square z-average radius $<R_g^2>_z^{1/2}$ (or simply as $<R_g>$). The specific refractive index increments dn/dc of amylopectin in 0.5 M NaOH solution and DMSO/H_2O (90 %wt/wt) were used as 0.142 and 0.074 mL/g, respectively. In dynamic LLS, the intensity-intensity time correlation function $G^2(t,q)$ in the self-beating mode was measured, where t is the delay time. $G^{(2)}(t,q)$ can be related to the normalized first-order electric field-electric field time correlation function $|g^{(1)}(\tau,\theta)| = [<E(0,q)E^*(t,q)>]$ as (Chu, 1991; Berne & Pecora, 1976)

$$G^2(t,q) = \langle I(0,q)I(t,q)\rangle A[1+\beta|g^{(1)}(t,q)|^2] \qquad (1)$$

where A[$\equiv <I(0)>^2$] is the measured baseline and β is the coherent factor, depending on the detection optics. For broadly distributed relaxation, $|g^{(1)}(t,q)|$ is related to a characteristic line-width distribution $G(\Gamma)$ as

$$|g^{(1)}(t,q)| = \int_0^\infty G(\Gamma)e^{-\Gamma t}\mathrm{d}\Gamma \qquad (2)$$

$G(\Gamma)$ can be calculated from the Laplace inversion of the measured $G^{(2)}(t,q)$ on the basis of Eqs. (1) and (2). $|g^{(1)}(t,q)|$ was analyzed by a Cumulant analysis to obtain the relative line-width distribution width $\mu_2/<\Gamma>^2$, where average line-width $<\Gamma> = \int_0^\infty \Gamma G(\Gamma)\mathrm{d}\Gamma$ and $\mu_2 = \int_0^\infty G(\Gamma)(\Gamma - <\Gamma>)^2\mathrm{d}\Gamma$. The polydispersity index (M_w/M_n) of macromolecule is related to the relative line-width distribution width $\mu_2/<\Gamma>^2$ as (Teraoka, 2002)

$$M_w/M_n = \exp\left(\left(\mu_2/<\Gamma>^2\right)\left(1/\nu^2\right)\right) \qquad (3)$$

where ν is the Flory exponent for the macromolecule. The Flory exponent ν for amylopectin in NaOH solution was used as 0.48 in this study (Galinsky & Burchard, 1995). For a pure diffusive relaxation, $(\Gamma/q^2)_{q\to0,c\to0}$ leads to the translational diffusion coefficient D, which is further related to the hydrodynamic radius R_h by the Stokes-Einstein equation: $R_h = k_B T/(6\pi\eta D)$, with k_B, T, and η being the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. The laser light scattering experiments were carried out at 10 ± 0.1, 17 ± 0.1 and 25 ± 0.1 °C. The concentrations of amylopectin for static light scattering experiment were 6×10^{-5}, 1×10^{-4} and 2×10^{-4} g/mL and the concentration of amylopectin for dynamic light scattering experiment was 2×10^{-4} g/mL. The concentrations of amylopectin for light scattering experiment were the same at different temperatures.

3. Results and discussion

The molecular weight and the gyration radius of amylopectin are so large that interpretation of the scattering data is different from that of the linear polymer. For linear polymer, the molecular weight, gyration radius and second virial coefficient can be evaluated from Zimm-Plots of dependence of scattering light strength on scattering angle and concentration. For amylopectin, however, the angular envelope is not a line in a Zimm-Plots but shows a curvature at small scattering vector (q) that can cause difficulties in the required extrapolation. In these cases, the molecular weight, gyration radius and second virial coefficient can be evaluated from the Berry plot (Bello-Pérez, Roger, Colonna, & Paredes-López, 1998; Galinsky & Burchard, 1995). Fig. 1 shows the Berry plot of the scattered light from waxy corn amylopectin in NaOH aqueous solution at 10±0.1 °C. The average molecular weight $\bar{M}_w$, the z-average gyration radius $<R_g>$ and the second virial coefficient A_2 of waxy corn amylopectin obtained from the Berry plot were listed in Table 1. The $\bar{M}_w$, $<R_g>$ and A_2 of waxy corn amylopectin in NaOH solution at 10 °C were similar with those at 17 °C. However, at 25 °C, $\bar{M}_w$ and $<R_g>$ of waxy corn amylopectin in NaOH solution increased to 5.3×10^8 g/mol and 276 nm, respectively, and A_2 decreased to 2.16×10^{-8} mol mL/g^2. The larger $\bar{M}_w$ and $<R_g>$ of amylopectin at 25 °C could be attributed to the association of amylopectin at higher temperature. The lower A_2 of amylopectin at 25 °C indicated that the hydrogen bond interaction between the amylopectin and water decreased and the polymer–polymer interaction increased with the rise in temperature. This caused the amylopectin association in aqueous solutions. Even in dilute solution, the amylopectin could associate and re-crysatllize from the aqueous solution with the increase of the store time (Putaux, Buléon, & Chanzy, 2000). The association and recrysatllization of starch in the solution is so-called retrogradation of the starch in food industry (Kohyama, Matsuki, Yasui, & Sasaki, 2004; Silverio, Fredriksson, Andersson, Eliasson, & Åman, 2000). The retrogradation of the starch is related directly to the store period and quality of starch-based food. In present study, the molecular weight of amylopectin at 25 °C was 4 times that at 10 °C, i.e. the associated number was about 4 at 25 °C. The associated waxy corn amylopectin was found to be capable of dispersing stably in NaOH solution at 25 °C for a long time without increase of the associated number.

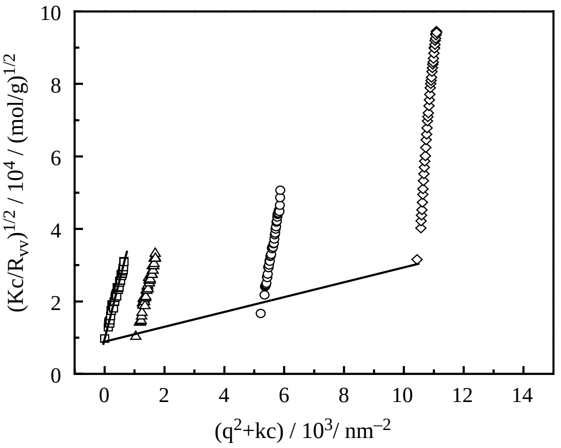

Fig. 1. Typical Berry plot of waxy amylopectin in 0.5 M NaOH solution at $T=10$ °C.

Table 1
Molecular characteristics of waxy corn amylopectin in aqueous solutions

Solvent	Temperature (°C)	$\bar{M}_w$ (g/mol)	A_2 (mol mL/g^2)	$\langle R_g\rangle$ (nm)	$\langle R_h\rangle$ (nm)
0.5 M NaOH solution	10	1.29×10^8	9.4×10^{-8}	223	172
0.5 M NaOH solution	17	1.42×10^8	8.8×10^{-8}	228	175
0.5 M NaOH solution	25	5.3×10^8	2.2×10^{-8}	276	282
DMSO/H$_2$O (90 %wt/wt)	25	1.5×10^8	5.5×10^{-8}	238	190

Amylopectin separated from different starch have different molecular weights and sizes. Yoo & Jane (2002) reported that the $\bar{M}_w$ and $<R_g>$ of amylopectin separated from different starch varied from 7.0×10^7 to 5.7×10^9 g/mol and 191 to 782 nm, respectively. They found amylopectins of waxy starches had substantially larger $\bar{M}_w$ than did those of normal starch counterparts. The degradation or association of amylopectin induced by samples preparation methods have significant effect on the $\bar{M}_w$ and $<R_g>$ of amylopectin. It was found the $\bar{M}_w$ of waxy maize varied from 2.5×10^8 to 7.5×10^8 g/mol depending on the starch dispersion preparation methods, such as direct dispersion-solubilization into solvent, extrusion followed by dispersion-solubilization into solvent, and jet-cooking of an aqueous starch slurry followed by transfer into solvent, and so on (Millard et al., 1997). Hanselmann et al. (1996) reported that with the heating time at 175 °C increasing from 20 to 40 min, the $\bar{M}_w$ and $<R_g>$ of waxy corn starch decreased from 3.6×10^8 to 3.75×10^7 g/mol and from 320 to 121 nm, respectively. Roger et al. (1999) found that the $\bar{M}_w$ and $<R_g>$ of corn amylopectin decreased from 2.7×10^8 to 1.1×10^8 g/mol and from 259 to 190 nm, respectively, when the microwave heating time increased from 35 to 70 s. The $\bar{M}_w$ and $<R_g>$ of waxy corn amylopectin in this study were of the same order of magnitude as those of corn amylopectin reported by Hanselmann et al. (1996) and Roger et al. (1999). However, the $\bar{M}_w$ and $<R_g>$ of the single waxy corn amylopectin chain in present study were smaller than those of non-degraded amylopectin reported by Hanselmann et al. (1996) and Roger et al. (1999).

Fig. 2 shows the lg$P(q)$ plot with lg(qR_g) for waxy corn amylopectin in NaOH aqueous solution at 10 °C. At the asymptote regime, the lgP(q)–lg(qR_g) was a line with the slope -2.11 ± 0.01, i.e. the waxy corn amylopectin in NaOH aqueous solution was self-similar with fractal dimension $d_f=2.11$. At the 25 °C, the d_f of associated waxy corn amylopectin increased to 2.5. For linear polymer chain in good solvent and theta solvent, the fractal dimension is 1.67 and 2.00, respectively. For fully swollen cluster and non-swollen cluster,

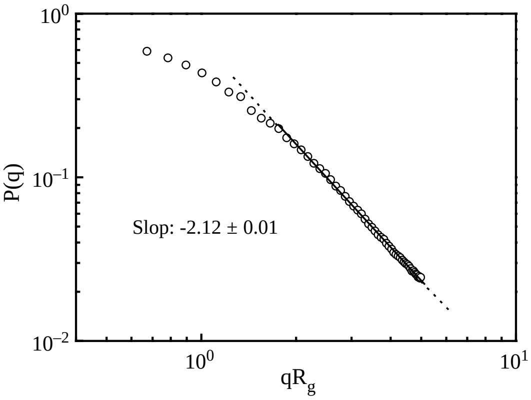

Fig. 2. Typical plot of $P(q)$ vs qR_g for waxy amylopectin in 0.5 M NaOH solution at $T=10$ °C.

the fractal dimension d_f predicated by percolation theory was 2.0 and 2.5, respectively (Stauffer, 1985). Obviously, waxy amylopectin chain has the compact structure compared with the linear polymer chain. The single waxy corn amylopectin molecule was like a fully swollen cluster and the associated waxy corn amylopectin was like a non-swollen cluster.

Fig. 3 shows the first cumulant line-width $<\Gamma>$ plot with q^2 at the small scattering angle ($qR_g \leq 2$). The plot of $<\Gamma>$ with q^2 is a line passing through the origin. This indicated that what we observed was the translational diffusion motion of amylopectin at the small scattering angle. According to Stokes-Einstein equation, the hydrodynamic radius ($<R_h>$) could be evaluated. By evaluating the exact hydrodynamic radius ($<R_h>$) and combining it with the gyration radius ($<R_g>$), we could give the shape of amylopectin. $\rho = <R_g>/<R_h>$ was 1.3 and 0.98 for a single waxy corn amylopectin chain in NaOH solution at 10 °C and associated waxy corn amylopectin in NaOH solution at 25 °C, respectively. The typical ρ of a flexible chain in the good solvent is ~ 1.7 and deceases with the branching of chain. The typical ρ of a star polymer with 4 arms is 1.33 and typical ρ of a star polymer with arms $\gg 1$ is ~ 1.079 (Brown, 1996). Because the associated waxy corn amylopectin was composed of four single amylopectin molecules, it was not difficult to understand why the ρ of the associated waxy corn amylopectin was lower than that of a single waxy corn molecule. With ρ combined with d_f of the waxy amylopectin in NaOH solution, the single waxy corn amylopectin and associated waxy corn amylopectin in aqueous solution were speculated as swollen and non-swollen branched cluster, respectively.

Although the $\bar{M}_w$ and $<R_g>$ of the single waxy corn amylopectin chain in present study were smaller than those of non-degraded corn amylopectin reported by Roger et al. (1999), the ρ of the single waxy corn amylopectin chain was similar to the ρ of corn amylopectin investigated by Roger et al. (1999). They reported that the ρ of corn amylopectin deceased from 1.3 to 1.1 with increase of microwave heating time or store time. This indicated that the degradation or association of amylopectin induced by different samples preparation methods might have more significant effect on the molecular weight and size than the internal structure of amylopectin.

When $qR_g > 2$, the first cumulant line-width $<\Gamma>$ was not a dependence of the q^2. Fig. 4 shows that $<\Gamma>$ could be scaled to q as $<\Gamma> \sim q^n$, where $n = 2.73 \pm 0.06$, 2.72 ± 0.02 and 2.70 ± 0.05 for amylopectin in NaOH solution at 10, 17 and 25 °C, respectively and $n = 2.70 \pm 0.02$ for amyliopectin in DMSO/H_2O. Considering the acceptable experimental error, the n value could be taken as a universal value 2.73 ± 0.06 for amylopectin in NaOH solution and DMSO/H_2O. The first cumulant $<\Gamma>$ dependence of $q^{2.73 \pm 0.06}$ indicated that relaxation motion measured by dynamic laser light scattering was not the pure translational diffusion motion. Instead it should be attributed to the internal motion of waxy corn amylopectin. For a flexible polymer chain, the theory predicted that the first cumulant line-width $<\Gamma>$ could be scaled to q as $q^n (n = 3.0)$ when $qR_g \gg 1$ and it was found the n value varied between 2.85–3.0 in experiments. No theory has been set up for the internal motion of branched polymer.

Roger et al. (1999) found that the n values for low and high amylose content starch were changed from 2.8–2.89 at short sample treatment time and n value could change with the increase of the sample treatment time. Trappe et al. (1997)

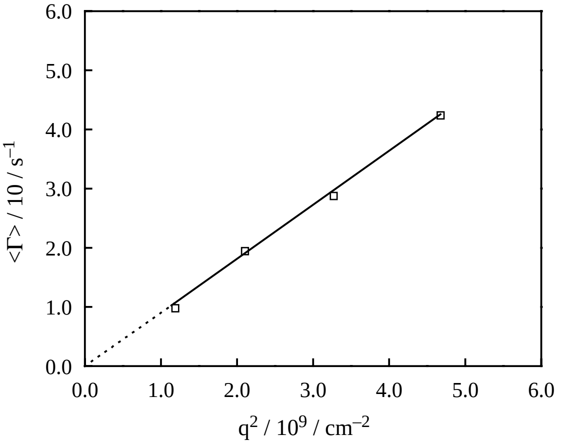

Fig. 3. The first cumulant average line-width ($<\Gamma>$) dependence of scattering vector (q) for waxy amylopectin in 0.5 M NaOH solution at small scattering angle ($qR_g \leq 2$) at $T=10$ °C.

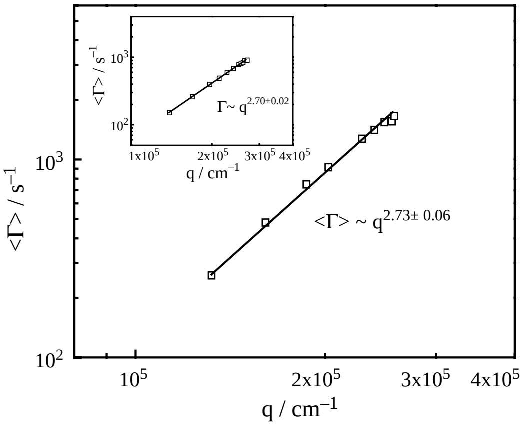

Fig. 4. The first cumulant average line-width ($<\Gamma>$) dependence of scattering vector (q) for waxy amylopectin in 0.5 M NaOH solution at large scattering angle ($qR_g > 2$) at $T=10$ °C. The insert is the first cumulant average line-width ($<\Gamma>$) dependence of scattering vector (q) for waxy amylopectin in DMSO/H2O at large scattering angle ($qR_g > 2$) at $T=25$ °C.

found the n value varied between 2.8 and 2.85 for the randomly branched polyester. In present study, the $n=2.73$ for waxy corn amylopectin was smaller than the n value for the randomly branched polyester (Trappe, Bauer, Weissmüller, & Burchard, 1997) and the n value for some starch with high amylose content (Roger, Bello-Pérez, & Colonna, 1999). One possible reason for lower n value could be the polydispersity of polymer. For polydispersity system, the translational diffusion motion of small size molecules will couple with the internal motion of the large size amylopectin, because $<\Gamma>$ of the pure translational diffusion could be scaled to the q as $<\Gamma> \sim q^2$, it will make the n decrease. However, although the size distribution of random branched polyester ($M_w/M_n \sim 370$, as reported by Trappe (1997)) and high amylose content starch was much broader than that of the waxy corn amylopectin in present study ($M_w/M_n = 1.9$), the n value for random branched polymer and the n value for high amylose content starch were higher than the n value for waxy corn amylopectin in present study. This indicated that the reason for lower n value for waxy corn amylopectin was not dominated by its polydispersity. Another possible reason for the lower n value could be some internal motion modes were not able to find due to the observation length ($1/q$). The internal motions are composed of many orders motion and have a distribution spectrum. Wu & Zhou (1996) found that some internal motions were not observable due to the observation length scale ($1/q$). For detail discussion of the influence of the polydispersity and the observation length on the internal motion of the waxy corn amylopectin, the CONTIN FIT for the correlation function of amylopectin was carried out to obtain the line-width distribution of amylopectin. Fig. 5 shows the scattering vector normalized line-width distribution of amylopectin in DMSO/H_2O. When $qR_g \leq 2$, there existed only one single peak and the position of the peak remained nearly unchanged in spite of the change of the scattering angle, and the single peak was attributed to the pure translational diffusion. When $qR_g > 2$, however, the second peak at larger Γ/q^2 appeared, and the first peak broadened and shifted to larger Γ/q^2 due to mixing with larger Γ resulted from internal motion of amylopectin. Fig. 6 shows the line-width $<\Gamma>_{\text{peak2}}$ of second peak plot with q. The fact that the line-width of second peak was not a dependence of q^2 indicated that the second peak was caused by the internal motion of amylopectin rather than originated from the translational diffusion motion of small size amylopectin due to the polydispersity. This also indicated that influence of the polydispersity of amylopectin on its internal motion was small. Fig. 5 also showed that when $qR_g < 4$ and $qR_g > 5.7$ the line-width distribution broadened and shifted to larger Γ/q^2 with the increase of the qR_g.

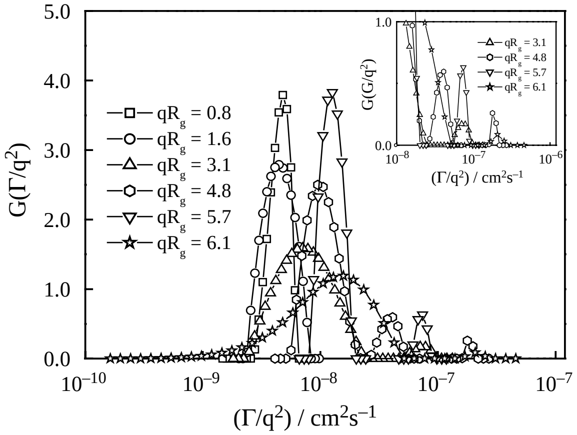

Fig. 5. Typical line-width distribution $G(\Gamma/q^2)$ of waxy corn amylopectin in DMSO/H_2O at $T=25$ °C. The insert shows a fivefold enlargement of the second peak in the range of the $1\times10^{-8} < \Gamma/q^2 < 1\times10^{-6}$ cm^2/s.

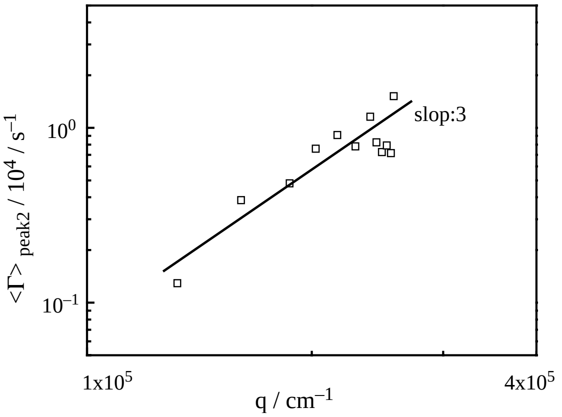

Fig. 6. The average line-width of second peak ($<\Gamma>_{\text{peak2}}$) dependence of scattering vector (q) for waxy corn amylopectin in DMSO/H_2O at $T=25$ °C. The line (slope is 3) is just to guide the eye.

However, when $4 < qR_g < 5.7$ the line-width distribution narrowed and shifted to larger Γ/q^2. This indicated indeed that some internal motions were not found at certain observation length ($1/q$) of dynamic light scattering. Our experimental result was in agreement with the discussion by Wu & Zhou (1996). According to their calculation, they found that some energetically favorable internal motions were not ‘seen’ in dynamic light scattering in a certain range of qR_g.

For a flexible polymer chain, when $qR_g \sim 1$, the internal motion of polymer chain would be found, while the internal motion of microgels which was strongly suppressed due to the cross-linking could only be found when $qR_g > 13$ (Wu & Zhou 1996). In present study, we observed the internal motion of amylopectin when $qR_g > 2$, this was because amylopectin has branched structure which suppressed the internal motions of amylopectin. Fig. 7 shows the ‘cluster’ model of amylopectin. It could be divided into many local motion units for amylopectin according to its branched structure. With the decreasing of the observed length ($1/q$), we could ‘see’ more motion mode originating from the small motion units. Thus, the line-width distribution gradually shifted to the larger Γ/q^2 (as shown in Fig. 5). However, the minimum observed length ($1/q$) was 39 nm for our dynamic laser light scattering. Some internal motions originating from the motion units smaller than 39 nm could not be found by dynamic laser light scattering. Note also that the amylopectin was a hyperbranched macromolecule with 4–4.5% branching density (Thompson, 2000; Galinsky & Burchard, 1995). As this density of amylopectin was higher

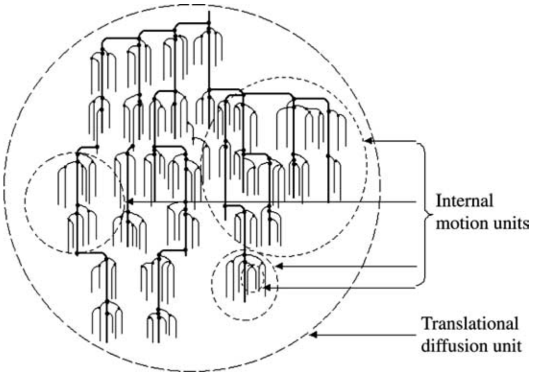

Fig. 7. The schematic of the translational diffusion unit and internal motion units of waxy corn amylopectin according to the cluster model of amylopection depicted by Robin et al. (1975).

than that of branched polyester and high amylose content starch, more internal motions of amylopectin were suppressed and ignored than that of the branched polyester and high amylose content starch. This could possibly be the dominated reason for the lower *n* value of waxy corn amylopectin.

For a linear flexible polymer chain, with the increase of qR_g, $<\Gamma>/(q^3k_BT/\eta_0)$ could approach to the plateau values 0.071 and 0.079 theoretically predicted with or without a preaverage Onseen tensor. It was found in experiment that for linear flexible polymer the plateau value was about 0.05–0.06 (Wu, Chan, & Xia, 1995; Wu &Zhou, 1996). Fig. 8 indicated that $<\Gamma>/(q^3k_BT/\eta_0)$ for amylopectin could not approach the plateau value with the increase of the qR_g. As discussed above, this could be explained by some internal motions of amylopectin being ignored. The apparent average hydrodynamic radius increased due to the association of waxy corn amylopectin at 25 °C. This made $<\Gamma>/(q_3k_BT/\eta_0)$ at 25 °C lower than at 10 °C at the small qR_g. However, at large qR_g, the $<\Gamma>/(q^3k_BT/\eta_0)$ values at fixed *q* were similar at different temperature. On the other hand, Fig. 8 indicated that the $<\Gamma>/(q^3k_BT/\eta_0)$ values at fixed *q* for waxy corn amylopectin in DMSO/H_2O were in agreement with that for waxy corn amylopectin in NaOH solution at large qR_g. Note that the DMSO/H_2O and NaOH solutions were all the good solvent for waxy corn amylopectin (second virial coefficient $A_2>0$). These indicated that $<\Gamma>/(q^3k_BT/\eta_0)$ at large qR_g had the universal value for waxy corn amylopectin in good solvent. The $<\Gamma>/(q^3k_BT/\eta_0)$ values at fixed *q* for waxy corn amylopectin were much smaller than that of linear flexible polymer. Note also that $<\Gamma>$ has the meaning of a reciprocal time. It was reasonable that the $<\Gamma>/(q^3k_BT/\eta_0)$ values at fixed *q* were lower than that of linear polymer chain due to the rigid chain and hyperbranched structure of amylopectin, which constrain the relaxation of the segment of the amylopectin, increasing the relaxation time of amylopectin segment.

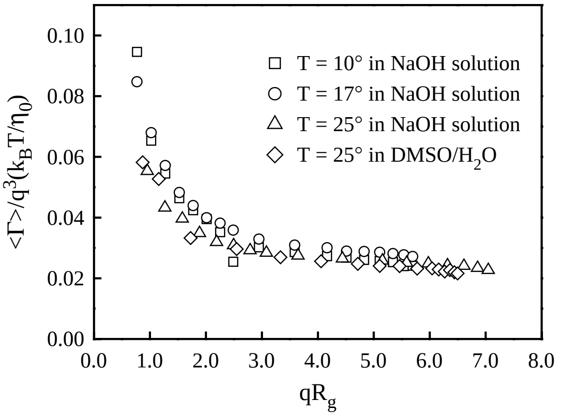

Fig. 8. Plots of $<\Gamma>/(q^3k_BT/\eta_0)$ vs qR_g for waxy amylopectin in aqueous solution.

4. Conclusion

Waxy amylopectin had a compact structure compared with the linear polymer. The fractal dimension d_f and $\rho=<R_g>/<R_h>$ for single waxy corn amylopectin in NaOH solution were 2.11 and 1.3, respectively. With the increasing of the temperature, waxy corn amylopectin could associate. The d_f and $\rho=<R_g>/<R_h>$ of associated waxy corn amylopectin in NaOH solution were 2.5 and 0.98, respectively. At small scattering angle ($qR_g<2$), only the translational diffusion motion of amylopectin was found. When $qR_g>2$, the internal motion dominated the dynamics of amylopectin, the first cumulant line-width ($<\Gamma>$) could be scaled to the scattering vector (q) as $<\Gamma>\sim q^{2.73\pm0.06}$. Some internal motions were not observed by dynamic laser light scattering due to the observation length. The $<\Gamma>/(q^3k_BT/\eta_0)$ did not approach a plateau value with the increase of the qR_g and had much lower value than that of linear flexible polymer.

Acknowledgements

The financial support of the National Natural Science Foundation (20506008, 20476040, 20374025) is gratefully acknowledged.

References

Bello-Pérez, L. A., Roger, P., Colonna, P., & Paredes-López, O. (1998). Laser light scattering of high amylose and high amylopectin materials, stability in water after microwave dispersion. *Carbohydrate Polymers*, *37*, 383–394.

Berne, B., & Pecora, R. (1976). *Dynamic light scattering*. New York: Plenum Press.

Bertoft, E. (2004). On the nature of categories of chains in amylopectin and their connection to the super helix model. *Carbohydrate Polymers*, *57*, 211–224.

Brown, W. (1996). *Light scattering (principles and development)*. Oxford: Clarendon Press.

Chu, B. (1991). *Laser light scattering* (2nd ed.). New York: Academic Press.

de Gennes, P.-G. (1967). Quasi-elastic scattering of neutrons by dilute polymer solutions. I: Free draining limit. *Physics*, *3*, 37–45.

Durrani, C. M., & Donald, A. M. (2000). Shape, molecular weight distribution and viscosity of amylopectin in dilute solution. *Carbohydrate Polymers*, *41*, 207–217.

Galinsky, G., & Burchard, W. (1995). Starch fractions as examples for nonrandomly branched macromolecules. 1. Dimensional properties. *Macromolecules*, *28*, 2363–2370.

Galinsky, G., & Burchard, W. (1996). Starch fractions as examples for nonrandomly branched macromolecules. 2. Behavior in the semidilute region. *Macromolecules*, *29*, 1498–1506.

Galinsky, G., & Burchard, W. (1997). Starch fractions as examples for nonrandomly branched macromolecules. 4. Angular dependence in dynamic light scattering. *Macromolecules*, *30*, 6966–6973.

Han, C. C., & Akcasu, A. Z. (1981). Dynamic light scattering of dilute polymer solutions in the non-asympotic q-region. *Macromolecules*, *14*, 1080–1084.

Hanselmann, R., Burchard, W., Ehrat, M., & Widmer, H. M. (1996). Structure properties of fractionated starch polymer and their dependence on the dissolution process. *Macromolecules*, *29*, 3277–3282.

Kohyama, K., Matsuki, J., Yasui, T., & Sasaki, T. (2004). A differential thermal analysis of the gelatinization and retrogradation of wheat starches with different amylopectin chain lengths. *Carbohydrate Polymers*, *58*, 71–77.

Millard, M. M., Dintzis, F. R., Willett, J. L., & Klavons, J. A. (1997). Light-scattering molecular weights, intrinsic viscosities of processed waxy maize starches in 90% DMSO and H_2O. *Cereal Chemistry*, *74*, 687–691.

Millard, M. M., Wolf, W. J., Dintzis, F. R., & Willett, J. L. (1999). The hydrodynamic characterization of waxy maize amylopectin in 90% dimethyl sulfoxide–water by analytical ultracentrifugation, dynamic, and static light scattering. *Carbohydrate Polymers*, *39*, 315–320.

Nikuni, Z. (1978). Studies on starch granules. *Stärke/Starch*, *30*(4), 105–111.

Putaux, J. L., Buléon, A., & Chanzy, H. (2000). Network formation in dilute amylose and amylopectin studied by TEM. *Macromolecules*, *33*, 6416–6422.

Robin, J. P., Mercier, C., Duprat, F., Charbonnière, R., & Guilbot, A. (1975). Lintnerized starches. Chromatographic and enzymatic studies of insoluble residues from acid hydrolysis of various cereals, particularly waxy maize starch. *Starch/Stäke*, *7*, 36–45.

Roger, P., Bello-Pérez, L. A., & Colonna, P. (1999). Contribution of amylose and amylopectin to the light scattering behavior of starches in aqueous solution. *Polymer*, *40*, 6879–6909.

Silverio, J., Fredriksson, H., Andersson, R., Eliasson, A. C., & Åman, P. (2000). The effect of temperature cycling on the amylopectin retrogradation of starches with different amylopectin unit-chain length distribution. *Carbohydrate Polymers*, *42*, 175–184.

Stauffer, D. (1985). *Introduction to percolation theory*. London: Taylor & Francis.

Teraoka, I. (2002). *Polymer solution*. New York: Wiley.

Thompson, D. B. (2000). On the non-random nature of amylopectin branching. *Carbohydrate Polymers*, *43*, 223–239.

Trappe, V., Bauer, J., Weissmüller, M., & Burchard, W. (1997). Angular dependence in static and dynamic light scattering from randomly branched systems. *Macromolecules*, *30*, 2365–2372.

Wu, C., Chan, K. K., & Xia, K. Q. (1995). Experimental study of the spectral distribution of the light scattered from flexible macromolecules in very dilute solution. *Macromolecules*, *28*, 1032–1039.

Wu, C., & Zhou, S. (1996). Internal motions of both poly(*N*-isopropylacrylamide) linear chains and spherical microgel particles in water. *Macromolecules*, *29*, 1574–1578.

Yoo, S. H., & Jane, J. L. (2002). Molecular weights and gyration radii of amylopectins determined by high-performance size-exclusion chromatography equipped with multi-angle laser-light scattering and refractive index detectors. *Carbohydrate Polymers*, *49*, 307–314.