Available online at www.sciencedirect.com

ScienceDirect

Polymer 47 (2006) 8044–8052

polymer

www.elsevier.com/locate/polymer

Dynamics of amylopectin in semidilute aqueous solution

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

[a] *School of Chemical and Material Engineering, Southern Yangtze University, Hui He Road 170, Wuxi, Jiang Su 214036, PR China*
[b] *School of Food Science and Engineering, Southern Yangtze University, Hui He Road 170, Wuxi, Jiang Su 214036, PR China*

Received 4 March 2006; received in revised form 20 June 2006; accepted 16 August 2006
Available online 22 September 2006

Abstract

The dynamic behaviors of potato amylopectin and waxy corn amylopectin in semidilute solution were investigated by laser light scattering and viscometer. For potato amylopectin with relatively smaller molecular weight, only pure diffusion motion of amylopectin was found by LLS in dilute regime. When the concentration was above the critical overlapping concentration (C^*), three relaxation modes were found. The line-width of fast mode (Γ_f) had a q^2 dependence, where q is the scattering vector, and the correlative length ($\langle\xi_h\rangle$) could be scaled to concentration (C) as $\langle\xi_h\rangle \sim C^{-0.79\pm0.1}$ when $C > 2\%$. This mode was attributed to the cooperative relaxation motion of the ‘‘blobs’’ in the transient network. The line-width of slow relaxation mode (Γ_s) could be scaled with q as $\Gamma_s \sim q^{\alpha_s}$, α_s varying from 2.0 to 2.66 as the concentration increased. The relaxation time of slow relaxation mode (τ_s) had a $C^{1.8\pm0.1}$ dependence. This mode was originated from the association of the amylopectin. The medium mode was found when $C > 4\%$. The line-width of medium relaxation mode (Γ_m) could be scaled to q as $\Gamma_m \sim q^{\alpha_m}$, α_m varying from 2.7 to 2.5 with the increasing concentration. The relaxation time of medium relaxation mode (τ_m) had $C^{0.7\pm0.1}$ dependence. The relative intensity contribution of the medium relaxation mode decreased with a rise in the concentration. This mode was attributed to the thermally agitated density fluctuation in semidilute solution induced by heterogeneities of the transient network. For waxy corn amylopectin with relatively huge molecular weight ($\sim 10^8$ g/mol), only the internal motion of the single amylopectin molecule was found in dilute regime when $qR_g \geq 2$, where R_g is the gyration radius of amylopectin. It was also found that there were three relaxation modes in semidilute solution of waxy corn amylopectin. The fast relaxation mode was found to be caused first by the internal motion of the single amylopectin molecule, and then, with the increasing concentration, by the cooperative motion of the transient network. The medium and slow relaxations for waxy corn amylopectin have the same physical origin as those for potato amylopectin. However, the C dependence and the q dependence of the medium and slow relaxation times for waxy corn amylopectin were different from those for potato amylopectin. This was attributed to the strong dynamic coupling effect in semidilute solution of the waxy corn amylopectin. The concentration dependence of the viscosity of amylopectin in semidilute solution indicated that the topological entanglement of amylopectin was weak due to the highly branching.

Keywords: Light scattering; Amylopectin; Dynamics

1. Introduction

The dynamics of polymer chains in semidilute solution are the fundamental problem in polymer physics. Based on the ‘‘blob’’ theory proposed by de Gennes, the dynamics of the linear non-association polymers in semidilute solution have been studied extensively in experiments by dynamic light scattering [1–9]. Two relaxation modes were normally found in the intensity–intensity time correlation function while the polymer concentration was above the overlapping concentration. The fast one was attributed to the cooperative diffusion motion of the ‘‘blobs’’ in the transient network. Most experimental results were in agreement with the ‘‘blobs’’ theory of de Gennes [1,10]. However, the physical origin of the slow relaxation mode of polymer chains in semidilute solution was still an open question. For example, Strobl et al. [5] interpreted the slow mode as originating from the diffusion of the ‘‘cluster’’, which was caused by physical association of the polymer chains in semidilute solution; Stepanek and Brown [6]

---

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

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.08.030

attributed the slow relaxation to the reptation of polymer chains in semidilute solution because they found its relaxation time to be independent of scattering angle and was a dependence of $M^{2.3}$, where M was the molecular weight of the polymer. Also, Maisano et al. [7] found that the slow mode was a dependence of the polymer structure and suggested that it originated from the coupling between the viscoelastic relaxation of the transient network and concentration fluctuation. Recently, Wu et al. [8] suggested that the slow relaxation found in semidilute solution stemmed from the thermally agitated density fluctuation of the transient network and attributed the varied q dependence of line-width of the slow mode to the relative length of $1/q$ to the correlation length (ξ) of the density fluctuation.

The dynamics of branched polymers in semidilute solution were interesting and complicated. Unlike linear polymers, branched polymers were not expected to be fully interpenetrating when they were overlapping. This makes the dynamics of branched polymers in semidilute solution very different from linear polymers in semidilute solution. However, there was still no theory as for the dynamic behavior of branched polymers in semidilute solution and only a few experiments were related to the dynamics of branched polymers in semidilute solution [11–13].

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 non-random branched macromolecule with 4–4.5% branching density [14,15]. Thus, amylopectin could be a good model molecule for the study of the behavior of branched polymers in semidilute solution. On the other hand, the dynamics of amylopectin in semidilute solution are important for understanding of the retrogradation of starch-based food. Galinsky and Burchard [11] have investigated the dynamic behavior of degraded potato starch in semidilute solution. At high concentration, three relaxation modes were found by dynamic light scattering. The fast relaxation mode was attributed to the cooperative diffusion of "blobs", which was similar to the case of linear polymers in semidilute solution. The slow relaxation mode had a strong scattering angle dependence and was attributed to the associated cluster of starch. The diffusion coefficient of medium relaxation mode (D_m) was independent of the scattering vector (q) and D_m could be scaled to concentration (C) as $D_m \sim C^{-1.85}$, thus, they interpreted it as the reptation of the single amylopectin chain in semidilute solution. However, the authors also argued that the diffusion motion of amylose mixed with amylopectin might be observed. Because the amylose content of degraded starch was as high as ~22%, the translational diffusion of these smaller molecular weight linear polymers and their associated clusters would strongly effect the dynamics of the amylopectin in semidilute solution. Therefore, more experiments still had to be carried out to clarify the dynamics of amylopectin in semidilute solution.

In the present study, we used two amylose free amylopectins (waxy corn amylopectin and potato amylopectin) to investigate the dynamics of amylopectin in semidilute solution. The molecular weight of waxy corn amylopectin was as large as $\sim 10^8$ g/mol, so that only the internal motion of amylopectin was found in dilute solution when the scattering angle was larger than 30°. The molecular weight of the potato amylopectin was relatively small ($\sim 10^6$ g/mol), so that only the pure translational diffusion of amylopectin was found in dilute solution. It was interesting to compare their dynamics in semidilute solution.

2. Experiment section

2.1. Materials

Waxy corn amylopectin was purchased from Tokyo Kasei Kogyo Co., Ltd., Japan. Potato amylopectin was purchased from Sigma–Aldrich Co., UK. Both amylopectins were separately dissolved in 0.5 M NaOH solution with magnetic stirring at 80 °C for 30 min and then the stirring continued for 2 days at room temperature (20 ± 3 °C). Then the NaOH aqueous solutions of amylopectin were passed through the 0.45 μm or 0.8 μm Millipore filter into a dust-free cell to remove the dust for light scattering experiment.

2.2. Laser light scattering experiments

A commercial laser light scattering spectrometer (ALV/DLS/SLS-5022F, Germany) was used, which was equipped with an ALV-5000/EPP multi-τ digital time correlator covering 125 ns to 37 h in delay time and a He–Ne laser (Uniphase, output power ≈ 20 mW at $\lambda = 632.8$ nm). The specific refractive index increments dn/dc of amylopectin in 0.5 M NaOH solution was 0.142 mL/g. The concentrations of amylopectin for static light scattering experiment were 6×10^{-5}–2×10^{-4} g/mL. The laser light scattering experiments were carried out at 25 ± 0.1 °C. We performed all measurements within 1 day after sample preparation and no ageing effect was found.

2.3. Viscosity measurements

The viscosity of amylopectin solution was measured by using a coaxial viscometer (Brookfield RVDV-3+ model, England). The viscosity measurements were carried out at 25 ± 0.1 °C with the shear rates in the range of 100–1875 s^{-1}.

3. Results

3.1. Analysis of the laser light scattering data

In static LLS, the 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 $\overline{M_w}$, the second virial coefficient A_2, and the root-mean-square z-average radius $\langle R_g^2 \rangle_z^{1/2}$ (or simply as $\langle R_g \rangle$).

Fig. 1 is the Berry plot of the potato amylopectin in dilute solution. The average molecular weight ($\overline{M_w}$), average

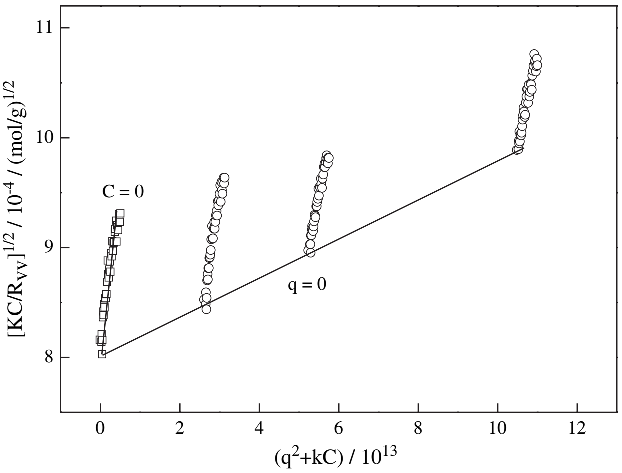

Fig. 1. The Berry plot of potato amylopectin in dilute solution at 25 ± 0.1 °C.

gyration radius ($\langle R_g \rangle$) and the second virial coefficient of potato amylopectin obtained from the Berry plot were 1.5×10^6 g/mol, 42 nm and 1.2×10^{-4} mol mL/g^2, respectively. The dilute solution behavior of waxy corn amylopectin was reported in our previous paper [16]. The average molecular weight ($\overline{M_w}$), average gyration radius ($\langle R_g \rangle$) and second virial coefficient (A_2) of waxy corn amylopectin were 1.29×10^8 g/mol, 223 nm and 9.4×10^{-5} mol mL/g^2, respectively. The overlapping concentration (C^*) of amylopectin could be calculated as $C^* = 3\overline{M_w}/(4\pi R_g^3 N_A)$, where $\overline{M_w}$, R_g and N_A are the average molecular weight, gyration radius and Avogadro constant, respectively. The calculated $C_g^* = 0.76$ wt% for potato amylopectin and $C_g^* = 0.46$ wt% for waxy corn amylopectin.

In dynamic LLS, the intensity–intensity time correlation function $G^2(t,q)$ (where t is the delay time) in the self-beating mode was measured. $G^{(2)}(t,q)$ can be related to the normalized first-order electric field–electric field time correlation function $|g^{(1)}(\tau,\theta)| = [\langle E(0,q)E^*(t,q)\rangle]$ as [17,18]

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

where A $[\equiv \langle I(0)\rangle^2]$ is the measured baseline and b 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

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

$G(\Gamma)$ can be calculated from the Laplace inversion of the measured $G^{(2)}(t,q)$ on the basis of Eqs. (1) and (2). For a pure diffusive relaxation, $(\Gamma/q^2)_{q\to 0, c\to 0}$ 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. Figs. 2 and 3 show that the delay time of correlation function increased and the correlation function changed from only one relaxation mode to three relaxation modes with the amylopectin concentration increasing from a dilute to a semidilute solution. To qualitatively extract the information related to these relaxation modes, we analyzed the intensity–intensity function by using the KWW function, which was normally used for semidilute solution [7,8,11,19]. The KWW function with three relaxation modes can be written as:

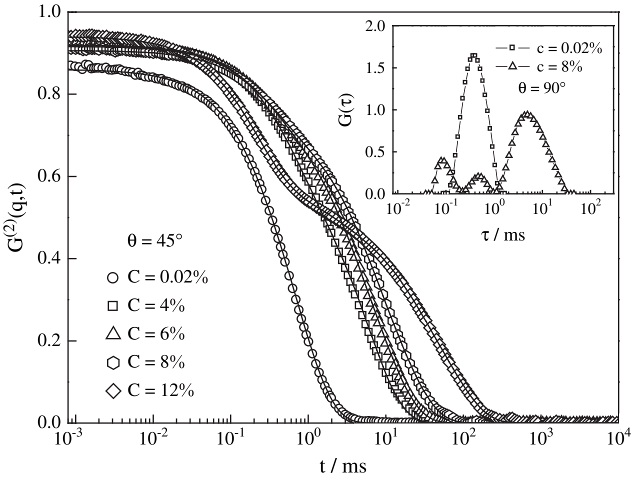

Fig. 2. The typical intensity–intensity correlation function for potato amylopectin in aqueous solution at different concentrations, the line was the fitted result by KWW equation. The inset shows the typical relaxation time distribution fitted by CONTIN method.

$$G^{(2)}(t,q) = B\Big(A_f \exp\left(-t/\tau_f\right) + A_m \exp\left((-t/\tau_m)^\beta\right) + A_s \exp\left((-t/\tau_s)^\gamma\right)\Big)^2 \tag{3}$$

where τ_f, τ_m and τ_s are the decay times for fast mode, medium mode and slow mode, respectively. A_f, A_m and A_s are the

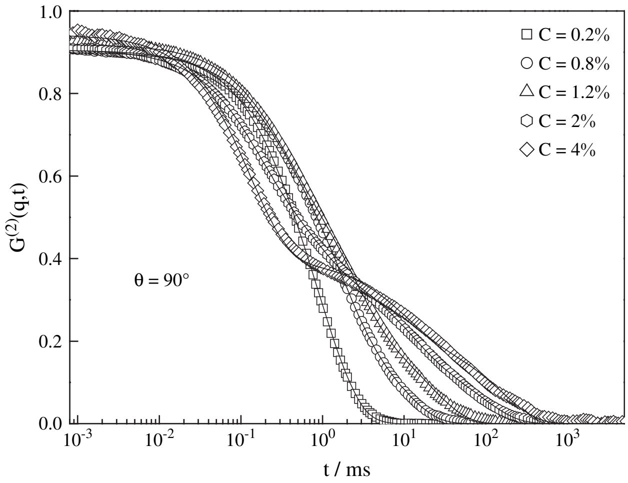

Fig. 3. The typical intensity–intensity correlation function for waxy corn amylopectin in aqueous solution at different concentrations, the line was the fitted result by KWW equation.

relative intensity contributions for fast mode, medium mode and slow mode, respectively, $0 < \beta \leq 1$ and $0 < \gamma \leq 1$, $A_\mathrm{f} + A_\mathrm{m} + A_\mathrm{s} = 1$.

The mean decay times for medium and slow modes are given by

$$\langle \tau_\mathrm{m} \rangle = \int_0^\infty \exp[-(t/\tau_\mathrm{m})^\beta]\mathrm{d}t = (\tau_\mathrm{m}/\beta)\Gamma(1/\beta) \quad (4a)$$

$$\langle \tau_\mathrm{s} \rangle = \int_0^\infty \exp[-(t/\tau_\mathrm{s})^\gamma]\mathrm{d}t = (\tau_\mathrm{s}/\gamma)\Gamma(1/\gamma) \quad (4b)$$

where Γ is the gamma function. A non-linear fitting was used to obtain the best-fit values of the decay times and their relative intensity contributions. All fit errors were smaller than 12%. β and γ were all ~0.9 and they varied slightly with varying the concentration. The experimental results are listed in Table 1.

3.2. Potato amylopectin

Fig. 4 shows that the line-width of fast relaxation mode (Γ_f) could be scaled to scattering vector (q) as $\Gamma_\mathrm{f} \sim q^{\alpha_\mathrm{f}}$, $\alpha_\mathrm{f} \approx 2.0 \pm 0.1$ and α_f being almost independent of the concentration. This fast relaxation was related to the cooperative motion of the "blob" in the semidilute solution of potato amylopectin. The correlation length of the "blob" ($\langle \xi_\mathrm{h} \rangle$) could be calculated according to Stokes–Einstein equation. Fig. 5 shows that when $C < 2\%$, the $\langle \xi_\mathrm{h} \rangle$ of potato amylopectin decreased with the increasing concentration and it could be scaled to C as $\langle \xi_\mathrm{h} \rangle \sim C^{-0.07 \pm 0.01}$. This indicated that the size of potato amylopectin shrunk slightly when it started overlapping. When C was higher than 2%, the size of the "blob" ($\langle \xi_\mathrm{h} \rangle$) could be scaled to C as $\langle \xi_\mathrm{h} \rangle \sim C^{-0.79 \pm 0.1}$.

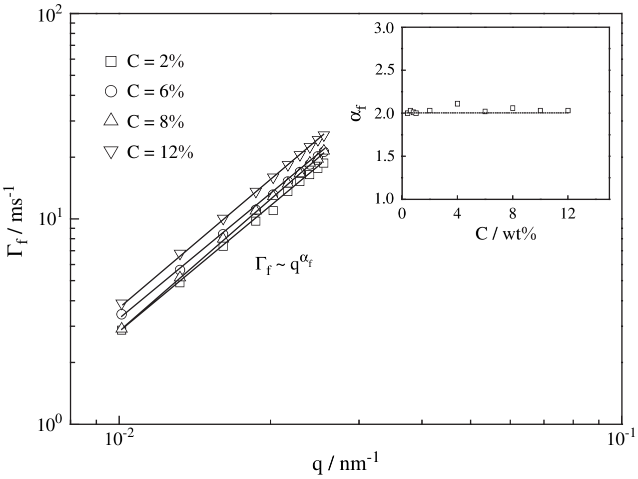

Fig. 4. The typical q dependence of the line-width of fast relaxation mode (Γ_f) for potato amylopectin. The inset shows the concentration dependence of the scaling exponent (α_f) in $\Gamma_\mathrm{f} \sim q^{\alpha_\mathrm{f}}$ for fast relaxation mode of potato amylopectin.

Fig. 6 shows that the line-width of slow relaxation mode (Γ_s) could be scaled to scattering vector (q) as $\Gamma_\mathrm{s} \sim q^{\alpha_\mathrm{s}}$, α_s increasing from 2.0 to 2.66 with increasing concentration. This relaxation mode could be attributed to the association of potato amylopectin in solution. At low concentration regime, the association behavior was so weak that the size of the associated cluster was smaller than the "observation length" ($1/q$), i.e., we could "see" the diffusion of the cluster. This explained why α_s was ~2.0 at low concentration. With the increasing concentration, the amylopectin became associated with large clusters, whose size was larger than the "observation length"

Table 1
DLS experimental results of the amylopectin solution ($\theta = 90°$)

Sample code[a]	C (wt%)	τ_f (ms)	$\langle \tau_\mathrm{m} \rangle$ (ms)	$\langle \tau_\mathrm{s} \rangle$ (ms)	A_f	A_m	A_s
P1	0.4	0.342 ± 0.007	–	–	–	–	–
P2	0.6	0.320 ± 0.006	–	–	–	–	–
P3	0.8	0.316 ± 0.006	–	–	–	–	–
P4	1	0.304 ± 0.005	–	–	–	–	–
P5	2	0.299 ± 0.004	–	0.668 ± 0.035	0.41 ± 0.01	–	0.59 ± 0.02
P6	4	0.147 ± 0.004	–	2.541 ± 0.102	0.15 ± 0.01	–	0.77 ± 0.02
P7	6	0.133 ± 0.004	0.898 ± 0.212	4.819 ± 0.380	0.12 ± 0.01	0.20 ± 0.01	0.67 ± 0.01
P8	8	0.091 ± 0.0004	1.014 ± 0.125	6.936 ± 0.361	0.15 ± 0.01	0.20 ± 0.02	0.66 ± 0.02
P9	10	0.088 ± 0.0022	1.304 ± 0.164	10.77 ± 0.551	0.22 ± 0.01	0.13 ± 0.01	0.66 ± 0.02
P10	12	0.073 ± 0.0014	1.379 ± 0.170	23.639 ± 1.344	0.35 ± 0.01	0.14 ± 0.01	0.51 ± 0.01
W1	0.4	0.153 ± 0.029	1.325 ± 0.173	7.200 ± 1.157	0.06 ± 0.005	0.45 ± 0.04	0.48 ± 0.06
W2	0.6	0.180 ± 0.028	1.531 ± 0.192	10.124 ± 1.118	0.07 ± 0.05	0.41 ± 0.04	0.51 ± 0.04
W3	0.8	0.218 ± 0.024	1.902 ± 0.167	18.001 ± 1.271	0.09 ± 0.06	0.38 ± 0.02	0.53 ± 0.02
W4	1	0.233 ± 0.018	1.943 ± 0.171	22.544 ± 1.377	0.11 ± 0.01	0.35 ± 0.01	0.54 ± 0.02
W5	1.2	0.285 ± 0.018	2.732 ± 0.201	42.970 ± 2.343	0.16 ± 0.01	0.33 ± 0.01	0.51 ± 0.01
W6	1.5	0.302 ± 0.012	4.013 ± 0.282	101.95 ± 4.756	0.22 ± 0.01	0.27 ± 0.01	0.51 ± 0.02
W7	1.8	0.285 ± 0.01	4.918 ± 0.375	149.72 ± 7.013	0.25 ± 0.02	0.23 ± 0.01	0.51 ± 0.02
W8	2	0.267 ± 0.02	7.185 ± 0.452	259.33 ± 12.91	0.27 ± 0.01	0.22 ± 0.01	0.51 ± 0.01
W9	3	0.196 ± 0.006	11.724 ± 1.084	253.30 ± 4.40	0.30 ± 0.01	0.17 ± 0.01	0.53 ± 0.02
W10	4	0.155 ± 0.002	10.833 ± 0.863	309.37 ± 15.52	0.35 ± 0.02	0.17 ± 0.01	0.47 ± 0.02

[a] P denotes the potato amylopectin and W denotes the waxy corn amylopectin.

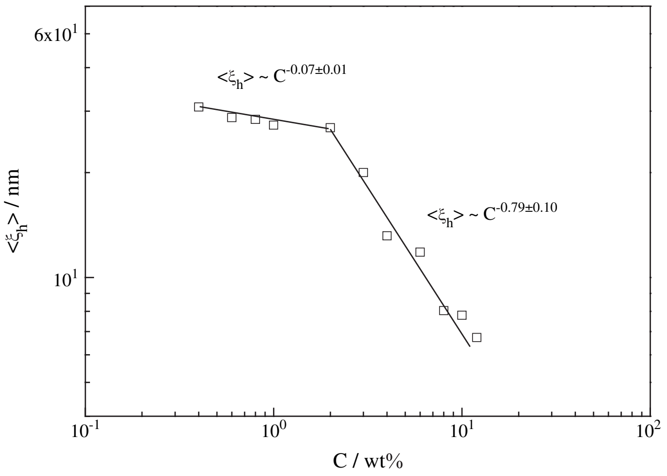

Fig. 5. The concentration dependence of cooperative correlation length ($\langle\xi_h\rangle$) for potato amylopectin in semidilute solution.

($1/q$). Therefore, the internal motion of these large clusters was observed. The character of the internal motion could be expressed as: $\alpha_s \sim 3.0$, however, as a result of the coupling of internal motion and diffusion motion of the large clusters α_s was $\sim$2.66. Fig. 6 also shows that the relaxation time of slow mode (τ_s) was dependent on $C^{1.8\pm0.1}$ in experimental concentration regime.

The medium relaxation mode was found when the concentration was higher than 4%, which was higher than the concentration in which association of amylopectin started. The $\langle\xi_h\rangle$ at this concentration (13 nm) was smaller than half the size of amylopectin (32 nm). In this case, the amylopectin was heavily overlapping. Fig. 7 shows that the line-width of medium relaxation mode (Γ_m) could be scaled to q as $\Gamma_m \sim q^{\alpha_m}$, α_m decreasing from 2.85 to 2.40 with the increasing concentration, and the τ_m had slight concentration dependence ($\tau_m \sim C^{0.7\pm0.1}$).

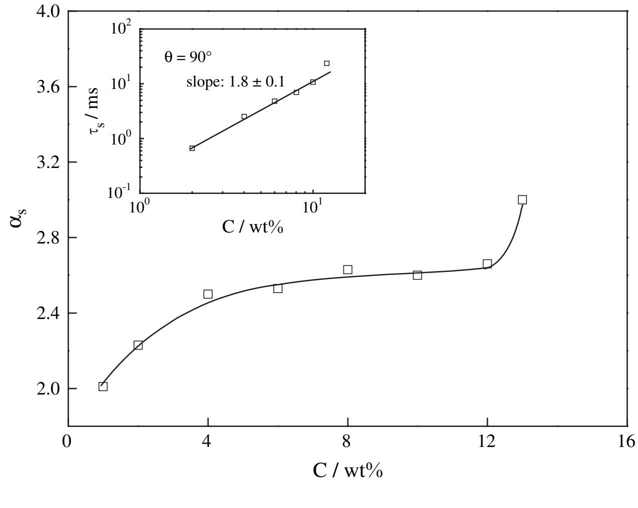

Fig. 6. The concentration dependence of the scaling exponent (α_s) in $\Gamma_s \sim q^{\alpha_s}$ for slow relaxation mode of potato amylopectin. The inset shows the concentration dependence of relaxation time of slow relaxation mode (τ_s) for potato amylopectin.

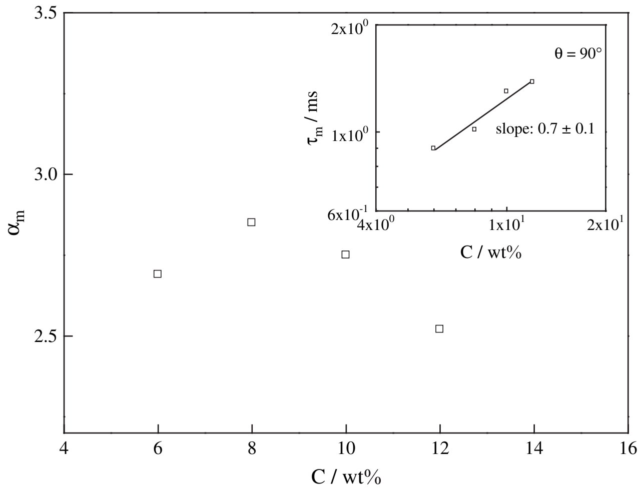

Fig. 7. The concentration dependence of the scaling exponent (α_m) in $\Gamma_m \sim q^{\alpha_m}$ for medium relaxation mode of potato amylopectin. The inset shows the concentration dependence of relaxation time of medium mode (τ_m) for potato amylopectin.

Fig. 8 shows the concentration dependence of the relative intensity contribution of the three relaxation modes. A_s increased and A_f decreased with the increasing concentration when $C < 4\%$. It was reasonable because the size of the associated clusters increased with increasing concentration, so that the scattering light intensity contributed from these clusters would become strong. This was similar to the case of the associative linear polymers [20–22]. However, it was surprising to find, when $C > 4\%$, A_s and A_m slightly decreased with the increasing concentration, A_f increased with a rise in the concentration. This was similar to the case of the gel system at postgel domain [19,22–24]. At the postgel stage the slow mode would be strongly constrained due to cross-linking so that the intensity–intensity function of gel is transformed from two relaxation modes to one relaxation mode. It is helpful to note that the amylopectin is a hyperbranching polymer

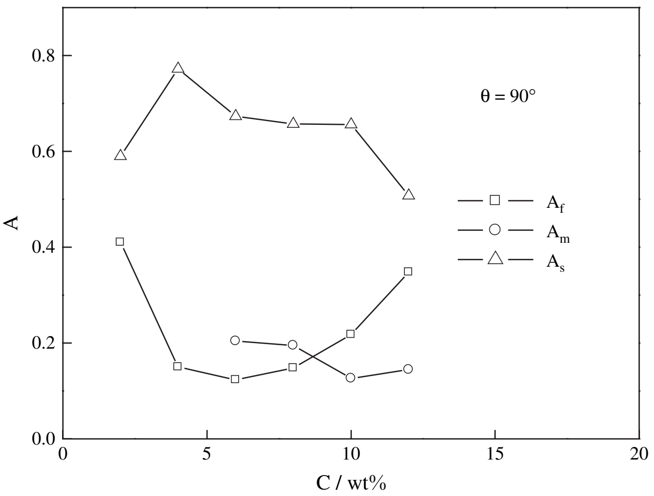

Fig. 8. The concentration dependence of relative intensity contribution (A) of three relaxation modes for potato amylopectin.

and can associate through H-bond interaction. When the amylopectin molecule overlapped, the strong physical cross-linking could occur through H-bond interaction. The strong physical cross-linking constrained the diffusion of the large associated cluster so that A_s decreased with a rise in the concentration.

3.3. Waxy corn amylopectin

The dynamics of waxy corn amylopectin in dilute solution were related to the translational diffusion motion and the internal motion of the amylopectin [16]. When $qR_g < 2$, the translational diffusion was found by DLS, and the line-width (Γ) could be scaled to scattering vector (q) as $\Gamma \sim q^2$. When $qR_g > 2$, only the internal motion was found by DLS, and the line-width (Γ) could be scaled to q as $\Gamma \sim q^{2.73\pm0.02}$.

Fig. 9 shows that α_f first increased with the increasing concentration, then decreased from 3.0 to 2.0 with the increasing concentration and the τ_f increased slightly with the increasing concentration and then also decreased with the increasing concentration. In dilute solution, only the internal motion of waxy corn amylopectin was observed due to the large size of waxy corn amylopectin. At semidilute regime, the dynamic correlation length ($\langle\xi_h\rangle$) decreased and the cooperative motion of amylopectin network could be observed with the increasing concentration. When the $\langle\xi_h\rangle$ became much smaller than the observation length ($1/q$), only the cooperative motion of amylopectin network could be observed. Because the line-width of internal motion of polymer chains was a dependence of q^3 and the line-width of cooperative motion was a dependence of q^2, α_f decreased from 3.0 to 2.0 with the rising concentration. Further, τ_f first increased then decreased with the increasing concentration because the internal motion relaxation time increased but cooperative motion relaxation time decreased with the increasing concentration. As it was difficult to prepare a homogeneous solution of the waxy corn amylopectin when $C > 4\%$, we did not continue investigating the case of higher concentration to examine the concentration dependence of cooperative motion of the waxy corn amylopectin.

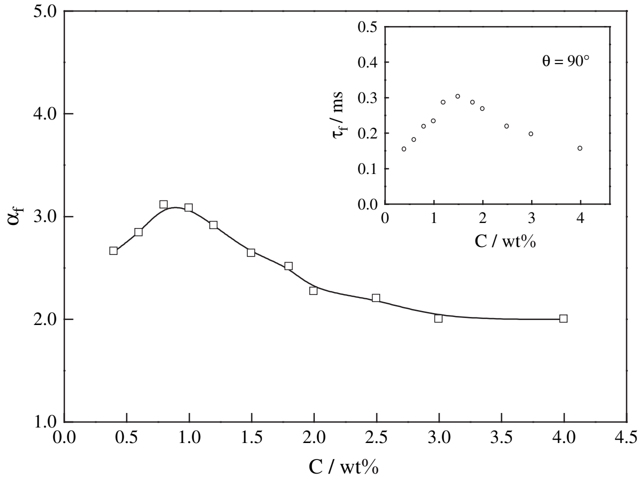

Fig. 9. The concentration dependence of the scaling exponent (α_f) in $\Gamma_f \sim q^{\alpha_f}$ for fast relaxation mode of waxy corn amylopectin. The inset shows the concentration dependence of relaxation time of fast relaxation mode (τ_f) for waxy corn amylopectin.

Fig. 10 shows that α_s and α_m for waxy corn amylopectin were all larger than 3 when $0.8\% < C < 3\%$. The concentration dependence of slow and medium relaxation times is shown in Fig. 11. Unlike the C dependence of τ_s and τ_m of potato amylopectin, the C dependence of τ_s and τ_m of waxy corn amylopectin could not be described by a single power law. The medium and slow relaxations of waxy corn amylopectin had stronger C dependence at higher concentration.

Fig. 12 shows that A_s increased with increasing concentration up to 1.0%, then it decreased slightly with the increasing concentration, whereas A_m decreased and A_f increased with the increasing concentration. This was similar to the case of the potato amylopectin.

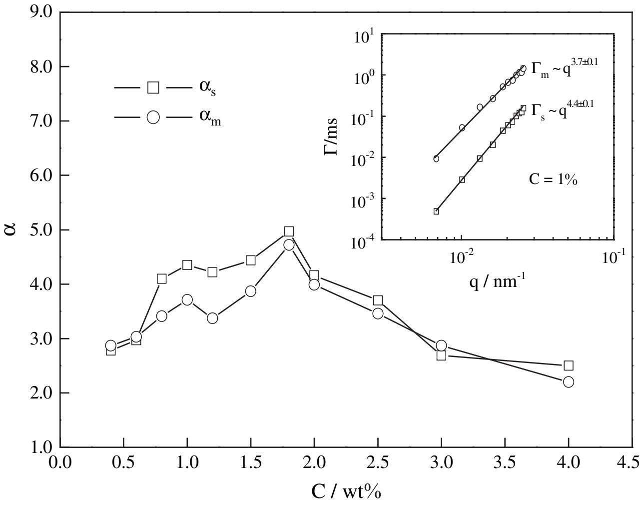

Fig. 10. The concentration dependence of the scaling exponent (α_s, α_m) in $\Gamma_s \sim q^{\alpha_s}$ and $\Gamma_m \sim q^{\alpha_m}$ for slow and medium relaxation modes of waxy corn amylopectin. The inset shows the typical q dependence of Γ for medium and slow relaxations at $C = 1\%$.

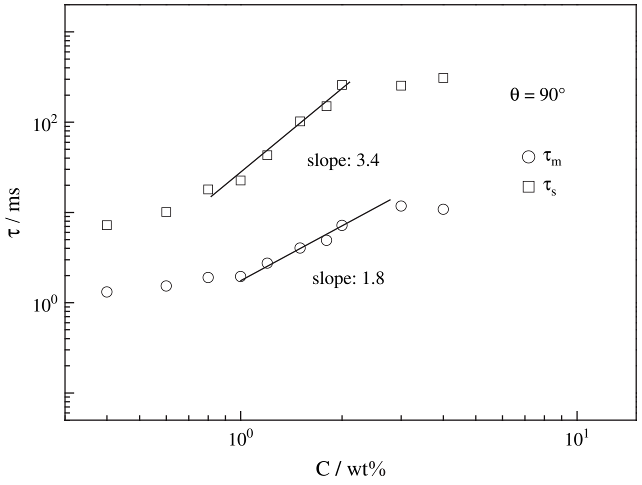

Fig. 11. The concentration dependence of relaxation time of slow and medium modes (τ_s,τ_m) for waxy corn amylopectin, the line is just to guide the eye.

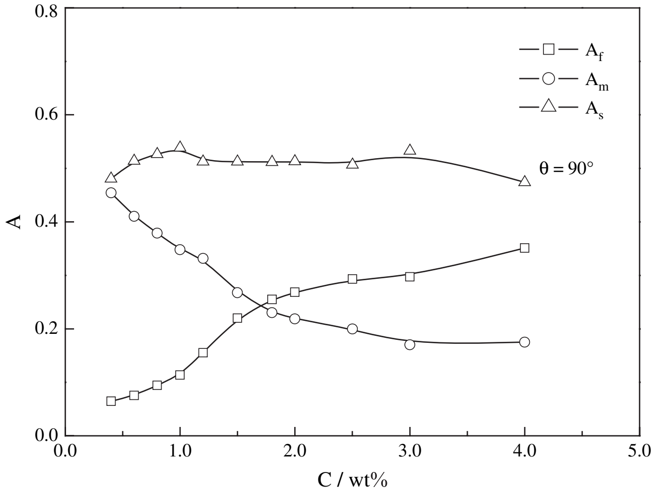

Fig. 12. The concentration dependence of relative intensity contribution (A) of three relaxation modes for waxy corn amylopectin.

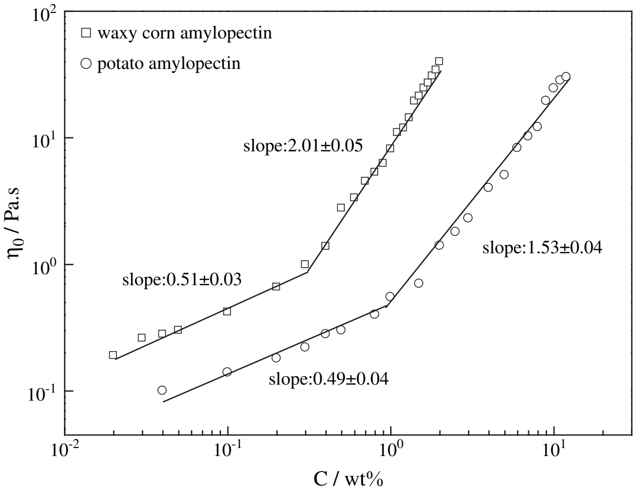

Fig. 13. The concentration dependence of the viscosity of amylopectin solution.

4. Discussion

4.1. Effect of branching on the dynamics of the amylopectin in semidilute solution

The overlapping and entanglement of linear polymer in semidilute solution were well known [1,10,25–27]. The dynamic correlation length of the linear polymer in semidilute solution can be scaled with the concentration as $\xi_h \sim C^{-0.75}$ [1,10]. In the unentangled regime, the concentration dependence of the solution viscosity is $\eta \sim C^{1.0}$, whereas in entangled regime, the concentration dependence of the solution viscosity is $\eta \sim C^{\alpha}$ with $\alpha = 3.4–3.7$ [27]. The dynamics of branched polymer are more complex than that of linear polymer. Both the branching chain length and branching density influence the dynamics of branched polymer [12,13,28]. With the increasing number of branched chains, the dynamic behavior of star polymer in semidilute solution was found to turn from linear polymer behavior to colloid behavior [13]. The dynamic behavior of hyperbranching polymer glycogen with branching density of 8% was reported to be similar to the dynamic behavior of colloid [12]. Amylopectin is a hyperbranching polymer with branching density of 4–4.5%, whose branching point was supposed to be able to prevent the interpenetration of polymers. However, the concentration dependence of the correlation length of the degraded potato starch in semidilute regime as reported by Galinsky and Burchard [11] ($\langle \xi_h \rangle \sim C^{-0.9}$) and shown in our present results ($\langle \xi_h \rangle \sim C^{-0.79}$) indicated that such branching structure of amylopectin could not prevent the interpenetration of molecules. Potato amylopectin solution showed a Newtonian liquid behavior when $C < 10\%$, however, the waxy corn amylopectin solution showed a non-Newtonian liquid behavior when $C > 0.8\%$. Fig. 13 shows the concentration dependence of the zero-shear viscosity of amylopectin solution. At the dilute concentration regime, the zero-shear viscosity of potato amylopectin solution had almost the same concentration dependence as that of waxy corn amylopectin. When the concentration was above the overlapping concentration, in the experimental concentration regime, the zero-shear viscosity of potato amylopectin could be scaled with C as $\eta_0 \sim C^{1.53\pm0.04}$ and the zero-shear viscosity of waxy corn amylopectin could be scaled with C as $\eta_0 \sim C^{2.01\pm0.05}$. The concentration dependence of zero-shear viscosity of amylopectin in semidilute solution was much weaker than that of linear polymer in entangled regime. This suggested that the topological entanglement of amylopectin was much weaker than that of the linear polymer due to the high branching. On the other hand, the rigidity of the amylopectin chain also might weaken the entanglement of amylopectin in semidilute solution. Compared with the case of potato amylopectin solution, the non-Newtonian behavior and concentration dependence of the zero-shear viscosity of waxy corn amylopectin solution were stronger. This indicated that the physical cross-link in semidilute solution of waxy corn amylopectin was stronger than that in semidilute solution of potato amylopectin.

4.2. Effect of association on the dynamics of amylopectin in semidilute solution

The dynamics of the associative polymer in semidilute solution were reported by many researchers [20–22,29–32]. The q dependence and the C dependence of the line-width of relaxation mode originating from the associated cluster were closely dependent on the study system. For example, Esquenet and Buhler [20] found that for large molecular weight hyaluronan, the line-width of slow relaxation originating from the associated cluster could be scaled to q^3, whereas for small molecular weight hyaluronan the q dependence of the line-width of slow relaxation was q^2 even at high concentration. Nemoto et al. [29] found that the line-width of slow relaxation caused by the associated large cluster was independent of q. However, Koňák et al. [21] found that the line-width of slow relaxation originating from the associated large cluster could be scaled to q^{α}, α varying from 2.0 to 5.0 with varying the concentration. The slow relaxation mode originating from the associated cluster was found in potato amylopectin solution when $C/C^* \sim 2.5$. Nevertheless, this slow relaxation mode was found in waxy corn amylopectin solution when $C/C^* \sim 1.0$. Furthermore, the q dependence and C dependence of the relaxation originating from associative cluster in waxy corn amylopectin solution were stronger than those of the relaxation originating from associative cluster in the potato amylopectin solution. The α_s and α_m for waxy corn amylopectin were all larger than 3 when $0.8\% < C < 3\%$. Koňák et al. [21] also found such strong q dependence of the relaxation originating from associative cluster. They explained their results by the dynamic coupling effect in semidilute solution predicted by Ngai et al. [26,27]. The dynamic coupling model predicted that if one primitive relaxation mode was modified by coupling with its environment through entanglement, this relaxation mode would become slower and the q dependence of the relaxation time would increase. If large α_s and α_m originated from the dynamic coupling effect, they would decrease with the disassociation of large clusters. This is because the disassociation of large clusters would weaken the physical cross-link in semidilute solution. Indeed, Table 2 shows that the α_s and α_m all decreased when the viscosity-corrected relaxation times of slow mode and medium mode decreased at higher temperature. Note that the decreasing of viscosity-corrected relaxation times of slow and medium modes indicated that the large clusters were partly disassociated. Thus, the decreasing of the α_s and α_m at higher temperature indirectly justified our attribution of the large α_s and α_m to the dynamic coupling effect in semidilute solution of waxy corn amylopectin. As the viscosity experiments indicated that the physical cross-link in potato amylopectin solution was weaker than that in waxy corn amylopectin solution, therefore, our attribution of the large α_s and α_m to the dynamic coupling effect could explain why the α_s and α_m for potato amylopectin were found smaller than those for waxy corn amylopectin.

4.3. The heterogeneity fluctuation of amylopectin in semidilute solution

The medium relaxation mode found in semidilute solution both of potato amylopectin and waxy corn amylopectin had a strong q dependence. The τ_m for potato amylopectin had slight concentration dependence ($\tau_m \sim C^{0.7\pm0.1}$), whereas the concentration dependence of τ_m for waxy corn amylopectin could not be scaled to a single power law. The relaxation mode which was different from the cooperative relaxation of transient network and the relaxation of the associative large cluster was also found by Galinsky and Burchard [11]. They investigated the dynamics of degraded potato starch in semidilute solution and found that the diffusion coefficient of medium relaxation mode (D_m) was independent of the scattering vector (q) and D_m could be scaled to concentration (C) as $D_m \sim C^{-1.85}$, thus, they interpreted it as the reptation of the single amylopectin chain in semidilute solution. Obviously, our results were not in agreement with the results of the Galinsky and Burchard [11]. The viscoelasitc relaxation was normally found in semidilute solution of linear polymer [2,6,7]. The dynamics of the linear polymer in semidilute solution were dealt with by Brochard and de Gennes [33] and developed by Adam and Delsanti [34] for the case of θ conditions. They predicted that there were two relaxation modes in semidilute solution of linear polymers. The fast relaxation mode was attributed to the cooperative motion of the "blobs" in the entangled network of polymers, while the slow relaxation mode was related to the viscoelastic nature of the transient network, in which case the chains can disentangle and the elastic stress relaxes with a decay time τ_s. They also predicted that $\tau_s \sim q^0M^3C^{1.5}$. The q dependence and C dependence of the medium relaxation found in semidilute solution of amylopectin were not in agreement with the theoretical prediction for viscoelastic relaxation of linear polymers in semidilute solution. Further, we could obtain some information on the molecular weight dependence of τ_m by comparing the τ_m of waxy corn amylopectin and the τ_m of potato amylopectin, although we could not examine the molecular weight dependence of τ_m because only two molecular weight samples were used. The molecular weight of waxy corn amylopectin is $\sim$70 times the molecular weight of the potato amylopectin. At $C = 4\%$, τ_m of potato amylopectin was $\sim$1 ms. If the medium relaxation originated from the elastic relaxation, the τ_m for waxy corn amylopectin would be $\sim 3 \times 10^5$ ms ($\tau \sim M^3$). However, it was found that the τ_m for waxy corn amylopectin was $\sim$10 ms at $C = 4\%$, which was far smaller than the predicted value if we attributed the medium relaxation to the elastic relaxation of the transient network.

Table 2
The viscosity-corrected relaxation times ($\theta = 90°$) and the scaling exponent (α) in $\Gamma \sim q^{\alpha}$ for waxy corn amylopectin in semidilute solution at 25 °C and 50 °C ($C = 1.8\%$)

T (°C)	$\tau_f T/\eta$ (Km^2/N)	$\tau_m T/\eta$ (Km^2/N)	$\tau_s T/\eta$ (Km^2/N)	α_f	α_m	α_s
25	81	970	25 637	2.54 ± 0.03	3.92 ± 0.19	4.16 ± 0.07
50	81	672	19 699	2.53 ± 0.08	3.45 ± 0.11	3.96 ± 0.12

It is to be noted that, first, the medium relaxation mode appeared after the association and strong overlapping of amylopectin; second, the relative intensity contribution of this medium relaxation (A_m) decreased with the increasing concentration. Therefore, this medium relaxation mode could be attributed to the density fluctuation in the semidilute solution, which was caused by heterogeneities in the transient network due to the association of the amylopectin. Similar results were found by Kjøniksen and Nyström [22] who surmised that the intermolecular association gave rise to large heterogeneities in the incipient semidilute regime and the solution structure was characterized by a collection of many clusters of various sizes which were slightly interconnected with each other. With the increasing concentration, the relative contribution of this density fluctuation decreased, i.e., more homogeneous network formed. Recently, Wu et al. [8] investigated this kind of density fluctuation in semidilute solution and sol–gel transition using a UV irradiation induced cross-linking system and found that the line-width of the density fluctuation (Γ_s) could be scaled to q as $\Gamma_s \sim q^{\alpha_s}$, α_s decreasing from 3.0 to 2.0 with the increasing of cross-linking density due to the decreasing of the correlation length of density fluctuation with the rising cross-linking density.

5. Conclusion

Three relaxation modes were found in semidilute solution of amylopectin. For potato amylopectin, the line-width of fast mode (Γ_f) had q^2 dependence, and the correlative length ($\langle \xi_h \rangle$) could be scaled with concentration (C) as $\langle \xi_h \rangle \sim C^{-0.79\pm0.1}$ when $C > 2\%$. This mode was attributed to the cooperative relaxation motion of the ''blobs'' in the transient network. For waxy corn amylopectin, the physical origin of the fast relaxation mode was transformed from the internal motion of the single amylopectin molecule to cooperative motion of the transient network with the increasing concentration. The slow relaxation mode found in semidilute solution of amylopectin was originated from the association of the amylopectin. It was found that the waxy corn amylopectin had stronger association behavior than potato amylopectin. The medium mode found in the semidilute solution of amylopectin was attributed to thermally agitated density fluctuation induced by heterogeneities of the transient network due to the association of amylopectin. The relative intensity contribution of medium relaxation mode decreased with increasing concentration. The C dependence and the q dependence of medium and slow relaxation times for waxy corn amylopectin were different from those for potato amylopectin, which was caused by the strong association effect in the semidilute solution of waxy corn amylopectin. The concentration dependence of the viscosity of amylopectin in semidilute solution was weaker than that of the linear polymer in entangled regime.

Acknowledgment

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

References

[1] de Gennes PG. Scaling concept in polymer physics. Ithaca, NY: Cornell University Press; 1979.
[2] Brown W, Stepanek P. Macromolecules 1988;21:1791; 1993;26:6884; Nicolai T, Brown W, Johnson RM, Stepanek P. Macromolecules 1999; 32:1128.
[3] Burchard W. Trends Polym Sci 1993;1:192.
[4] Koch T, Strobl G, Stuhn B. Polymer 1993;34:1988.
[5] Heckmeier M, Mix M, Strobl G. Macromolecules 1997;30:4454.
[6] Stepanek P, Brown B. Macromolecules 1998;31:1889.
[7] Faranone A, Magazu S, Maisano G, Ponterio R, Villari V. Macromolecules 1999;32:1128.
[8] Ngai T, Wu C. Macromolecules 2003;36:848; Ngai T, Wu C, Chen Y. Macromolecules 2004;37:987; J Phys Chem B 2004;108:5532; Wu C, Ngai T. Polymer 2004;45:1739.
[9] Fleischer G. Macromolecules 1999;32:2382.
[10] Teraoka I. Polymer solution. New York: Wiley; 2002.
[11] Galinsky G, Burchard W. Macromolecules 1996;29:1498; Macromolecules 1997;30:6966.
[12] Ioan CE, Aberle T, Burchard W. Macromolecules 1999;32:8655.
[13] Vlassopoulos D, Fytas G, Pakula T, Roovers J. J Phys Condens Matter 2001;13:855.
[14] Robin JP, Mercier C, Duprat F, Charbonnière R, Guilbot A. Starch/Stärke 1975;7:36.
[15] Thompson DB. Carbohydr Polym 2000;43:223.
[16] Yang C, Meng B, Chen MQ, Liu XY, Hua YF, Ni ZB. Carbohydr Polym 2006;64:190.
[17] Chu B. Laser light scattering. 2nd ed. New York: Academic Press; 1991.
[18] Berne B, Pecora R. Dynamic light scattering. New York: Plenum Press; 1976.
[19] Suzuki Y, Nozaki K, Yamamoto T, Itoh K, Nishio I. J Chem Phys 1992; 97:3808.
[20] Esquenet C, Buhler E. Macromolecules 2002;35:3708.
[21] Koňák Č, Helmstedt M, Bansil R. Macromolecules 1997;30:4342.
[22] Kjøniksen AL, Nyström B. Macromolecules 1996;29:7116.
[23] Horkay F, Buchard W, Geissler E, Hecht A-M. Macromolecules 1993;26: 1296.
[24] Horkay F, Buchard W, Hecht AM, Geissler E. Macromolecules 1993;26: 3375.
[25] Watanabe H. Prog Polym Sci 1999;24:1253.
[26] Ngai KL, Rajagopal AK, Teitler S. J Chem Phys 1988;88:5086.
[27] Rendell RW, Ngai KL, Mckenna GB. Macromolecules 1987;20:2250.
[28] Liu C, Li C, Chen P, He J, Fan Q. Polymer 2004;45:2803.
[29] Koike A, Nemoto N, Inoue T, Osaki K. Macromolecules 1995;28:2339; Nemoto N, Koike A, Osaki K. Macromolecules 1996;29:1445.
[30] Nyström B, Walderhaug H, Hansen FK. J Phys Chem 1993;97:7743.
[31] Nyström B, Thuresson K, Lindman B. Langmuir 1995;11:1994.
[32] Lin H, Liu Y, Yu TL, Liu W, Rwei S. Polymer 2005;46:5541.
[33] Brochard F, de Gennes PG. Macromolecules 1977;10:1157.
[34] Adam M, Delsanti M. Macromolecules 1985;18:1760.