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Laser light scattering of high amylose and high amylopectin materials, stability in water after microwave dispersion

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Abstract

Light scattering techniques were used for structural characterization of starches with diverse amylose and amylopectin level, dissolved in water by microwave heating in a high pressure vessel and stored during different times. In general, apparent molar mass ($\bar{M}_W$), gyration radius ($\bar{R}_G$) and hydrodynamic radius ($\bar{R}_H$) values decreased when storage time increased. This emphasised the depolymerization of the samples during the storage time. The fractal dimension obtained from the $\bar{R}_G$–$\bar{M}_W$ relationship showed that the samples presented, in general, a globular structure, with a higher level of branching when amylopectin level in the sample increased. The particle scattering factors and Kratky plots, well suited for studying the internal structure of a macromolecule, showed a depolymerization when storage time increased. The ν_{RH} values for Eurylon 5 (0.56) and Eurylon 7 (0.58) starches were close to the values reported for linear chains. For amylopectin (0.09) and normal corn starch (0.10) the ν_{RH} values were lower; these values would define a highly branched structure. The relaxation rate distribution of the samples showed that there are changes in the internal structure when storage time increases, and that these changes depend on amylose and amylopectin level present in the sample. The ρ values for the samples analyzed were between 0.88 and 1.3; these values are characteristic of branched structures.

Keywords: Light scattering; Amylose; Amylopectin; Storage time

1. Introduction

Starch, the major storage polysaccharide of higher plants, is a polymeric mixture of essentially linear (amylose) and branched (amylopectin) glucans. Starch owes much of its functionality to these macromolecules, as well as to their physical organization into the granular structure (French, 1984).

Starch is widely utilized in many industries where it must be dissolved or dispersed in aqueous media in nondegradative conditions (pH). However, the limited stability of solutions of starch components, linked to their solubility in neutral aqueous solution, present some problems; at present the physico-chemical behavior in solution is not yet sufficiently well understood.

Native starch is deposited in the form of partially crystalline granules. In order to dissolve this material in water, the granules have to be destructed under drastic conditions without degrading the macromolecule structure (Hanselmann et al., 1996). Recently, optimum conditions for sample solubilization without degrading the structure have been found by pre-treatment of samples with dimethylsulfoxide (DMSO) and dissolved by microwave heating in a high pressure vessel (MWHPV) (Bello-Pérez et al., 1998).

The ability of gelatinized starch chains to form ordered structures in pastes, gels, and baked foods during storage, a process often described by the term ‘retrogradation’, which is generally deleterious, greatly influences the texture and shelf-life of these products (Biliaderis and Prokopowich, 1994; Bello-Pérez and Paredes-López, 1995). Retrogradation studies have been realized using diverse techniques such as differential scanning calorimetry (Zelesnak and Hoseney, 1986; Gidley et al., 1995), X-ray diffraction (Gidley et al., 1995; Hoover and Senanayake, 1996), and compression–decompression tests (Inaba et al., 1994; Keetels et al., 1996). However, all those studies were performed using gels or concentrated solutions. Until now very few studies have been carried out to understand the stability of starch in dilute solutions and there are no results published on the behavior and stability in solution of starch

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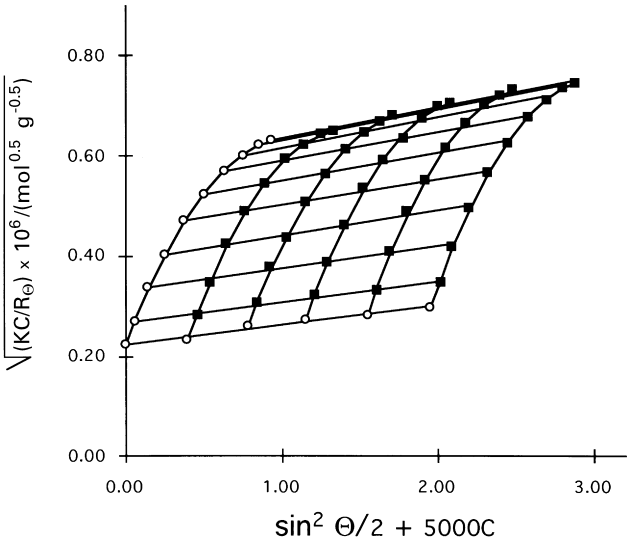

Fig. 1. Berry plot static obtained for Eurylon 5 starch in water at 25°C and stored for 48 h.

samples stored for periods of time and analyzed by light scattering techniques.

Thurn and Burchard (1985) postulated that the various structural elements of a macromolecule, such as polydispersity, overall molecular dimensions, hydrodynamic behavior and internal mobility, should exert a marked influence on its properties in solution. For this reason, they became interested in the structure and properties of native, nondegraded starch, which can be determined by light scattering (LS). There are two types of LS measurements, dynamic and static light-scattering (DLS and SLS, respectively). The foundation of DLS is based on the scattering of light by moving particles (Dalgleish and Hallett, 1995). In SLS, the intensity of scattered radiation is averaged over a fairly long time ($\approx$ 2 s), and this is in most cases long enough to smooth out all internal mobility (Burchard, 1992). SLS gives information about the weight average molecular weight, $\bar{M}_W$, the root-mean-square *z*-average radius of gyration, $\bar{R}_G$, and the light scattering second osmotic virial coefficient, A'_2 of macromolecules in dilute solution (Anthonsen et al., 1994). Measurements at different molar masses reveal an unexpected weak increase of the R_G, which is due to lateral (side-by-side) aggregation of chains. The conclusion could be confirmed by DLS according to which an increase in segment density occurs as the molar mass increases (Burchard, 1993). Recent developments of DLS technique allow a determination of the relaxation time distribution over a large time range. If different components of the system have characteristic relaxation times that are not too close, they can be determined individually in one measurement (Ousalem et al., 1993).

Aberle et al. (1994) reported M_W and R_G values of various species of starch using LS technique. Molar masses of 60×10^6 to 110×10^6 g mol^{-1} and radii around 220 nm were found for the amylopectins from the various starches. They mentioned that LS measurements allow probing internal structures of dimensions larger than 10 nm. Galinsky and Burchard (1995, 1996) studied starch fractions using SLS and DLS techniques. With these techniques they studied the dimensional properties and behavior in solution of amylopectin.

Recently, Hanselmann et al. (1996) reported that the presence of linear amylose and branched amylopectin molecules in solution and the resulting high polydispersity make it difficult to derive reliable information on the structural properties of each type of particle by common physical techniques of measurement. They reported (Hanselmann

Table 1
Macromolecular features of amylopectin and starch samples dissolved by microwave heating during 35 s and stored for different times

Sample	M_W (g mol^{-1})	R_G (nm)	R_H (nm)	ρ	d_f	C_i (mg ml^{-1})	C_f (mg ml^{-1})
Amylopectin 0 h	2.7×10^8	259	198	1.3	2.20	0.43	0.43
Amylopectin 24 h	1.4×10^8	224	203	1.1	1.88	0.34	0.32
Amylopectin 48 h	1.3×10^8	220	193	1.1	1.96	0.34	0.32
Amylopectin 72 h	1.1×10^8	200	183	1.1	2.00	0.38	0.37
Normal corn 0 h	2.5×10^8	267	198	1.3	2.28	0.38	0.38
Normal corn 24 h	1.1×10^8	223	206	1.1	1.90	0.31	0.31
Normal corn 48 h	1.1×10^8	214	205	1.0	1.94	0.34	0.32
Normal corn 72 h	5.2×10^7	188	170	1.1	2.10	0.34	0.34
Eurylon 5 0 h	3.1×10^7	172	180	0.95	1.69	0.45	0.45
Eurylon 5 24 h	2.0×10^7	150	160	0.94	1.40	0.4	0.40
Eurylon 5 48 h	2.0×10^7	143	146	0.98	1.33	0.42	0.40
Eurylon 5 72 h	1.6×10^7	135	127	0.98	1.28	0.41	0.35
Eurylon 7 0 h	2.3×10^7	187	210	0.89	1.55	0.42	0.42
Eurylon 7 24 h	8.8×10^6	133	152	0.88	1.25	0.44	0.42
Eurylon 7 48 h	8.8×10^6	125	137	0.91	1.20	0.38	0.38
Eurylon 7 72 h	7.9×10^6	110	92	1.2	1.05	0.43	0.36

M_W, molar mass; R_G, gyration radius; R_H, hydrodynamic radius; $\rho = R_G/R_H$.
d_f, fractal dimension (e.g. slopes of Figs. 3 and 4).
C_i, initial concentration (when the sample was prepared); C_f, final concentration (when the sample was analyzed after storage).

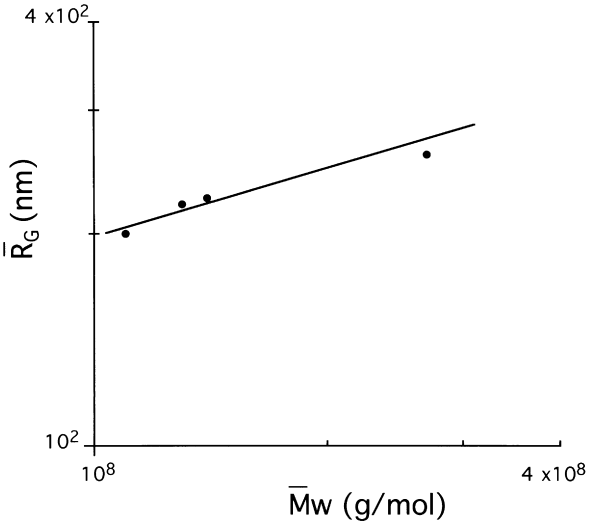

Fig. 2. Molecular weight dependence of the gyration radius of amylopectin samples stored for different times.

et al., 1995) on molar mass distributions which were obtained by sedimentation field flow fractionation (SdFFF). Waxy corn and potato starch can be fractionated by the SdFFF technique within a range of R_G between 50 and 500 nm. The analysis of the obtained particle scattering factors allowed extraction of information on the structural properties of amylopectin particles from one starch sample as a function of their molar mass.

The present study was undertaken to characterize the dimensions and structural properties of starch macromolecules without degradation after solubilization by microwave heating, and stored during different periods of time to know the behaviour of dilute starch solutions using light scattering techniques.

2. Materials and methods

2.1. Sample preparation

Corn commercial amylopectin was purchased from Sigma Chemical Co. (St. Louis, MO); normal starch, Eurylon 5 and Eurylon 7 starches, all from corn, were a gift from Roquette Frères (Lestrem, France). Samples were pre-treated by a procedure developed previously (Bello-Pérez et al., 1998). Amylose content was determined by amperometric titration at 4°C according to Planchot et al. (1996).

Table 2
Exponents of the scaling relationship for samples analyzed by laser light scattering

Sample	ν_{RG}	ν_{RH}	d_f
Amylopectin	0.27	0.09	3.70
Normal corn starch	0.23	0.10	4.34
Eurylon 5 starch	0.36	0.56	2.77
Eurylon 7 starch	0.45	0.58	2.22
Branched component [a]	0.39	0.48	2.56
Linear component [a]	0.61	0.61	1.64

ν_{RG} and ν_{RH} obtained from slope of M_W vs. R_G or R_H.
$d_f = 1/\nu$.
[a] Galinsky and Burchard (1995).

2.2. Sample solubilization

The solubilization procedure, detailed elsewhere (Bello-Pérez et al., 1998), consisted of weighing 10 mg of sample and adding 20 ml of water filtered previously through 0.1 μm (Anotop, Whatmann, Maidstone, UK) into a microwave bomb, heating during 35 s in the microwave, cooling, centrifuging and filtering. This treatment time was used because it does not produce sample degradation (Bello-Pérez et al., 1998). The samples were immediately analyzed (storage time, 0 h) and stored during 24, 48 and 72 h. After the storage time the samples were again centrifuged and filtered. Dilution series were made at room temperature yielding four lower concentrations. Carbohydrate concentration was measured by the sulfuric acid–orcinol colorimetric method (Planchot et al., 1996).

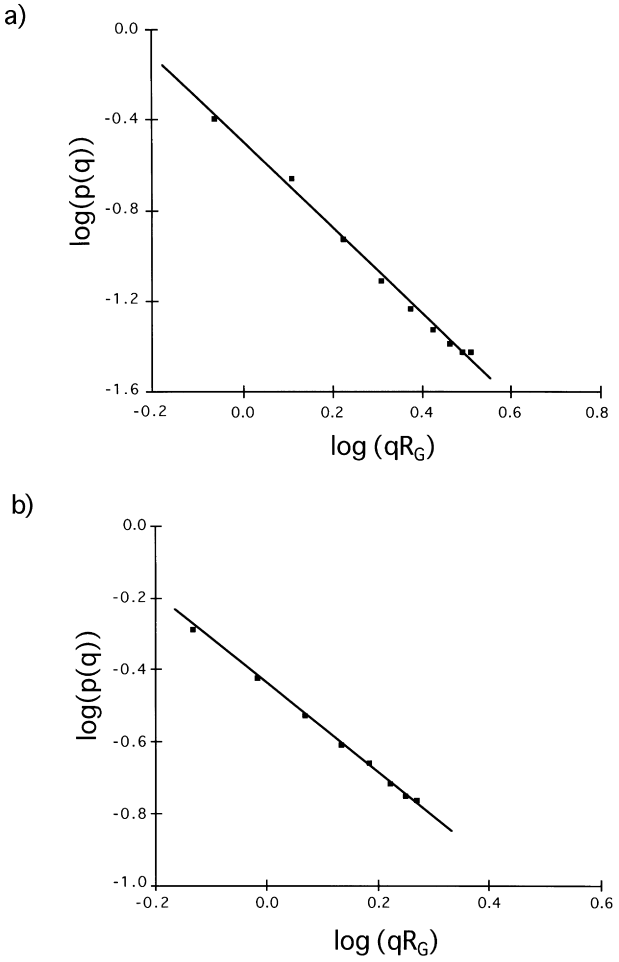

Fig. 3. Double logarithmic plot of particle scattering factor vs. the normalized scattering vector of samples stored for 48 h. (a) Amylopectin, (b) Eurylon 7 starch.

2.3. Static light scattering

Experiments were performed at 25°C in the angular range from 30 to 150° in steps of 15°, in the homo-dyne mode with full photon-counting detection and a 128-channel K7025 Malvern correlator. Incident radiation at 514.5 nm was obtained from a 3W Ar Ion Spectra-Physics laser vertically polarized. The refractive index increment (d*n*/d*c*) was 0.146 ml g^{-1}. Optical alignment was checked over the angular range described using filtered benzene. Monitoring programs were written in Basic and run on a HP9300 microcomputer. All fittings were performed using Berry plot with a home-made program.

2.4. Dynamic light scattering

DLS measurements were made with an ALV-5000 correlator (ALV-Laser, Vertriebsgesellschaft m.b.H. Lagen, Germany) in the angular range from 30 to 150° in steps of 30° using the previous equipment. Two different methods were used to treat the data: (i) a cumulant analysis (using ALV-5000 software, Version 5.0) to construct the dynamic Zimm plots and (ii) an inverse Laplace transformation (ILT) (where $g_1(t) = \int_0^\infty A(\tau)\exp(-t/\tau)d\tau$ and $A(\tau)$ is the distribution function of decay times τ) was performed to obtain the distribution of relaxation times from the measured autocorrelation functions by using the GENDIST® program written by Bob Johnsen (Uppsala University, Sweden). GENDIST® used a constrained regularization algorithm, denoted REPES, which gives results similar to the inversion routine CONTIN. However, REPES directly minimises the sum of the squared differences between the experimental and calculated $g_2(t)$ functions (Stepanek, 1993).

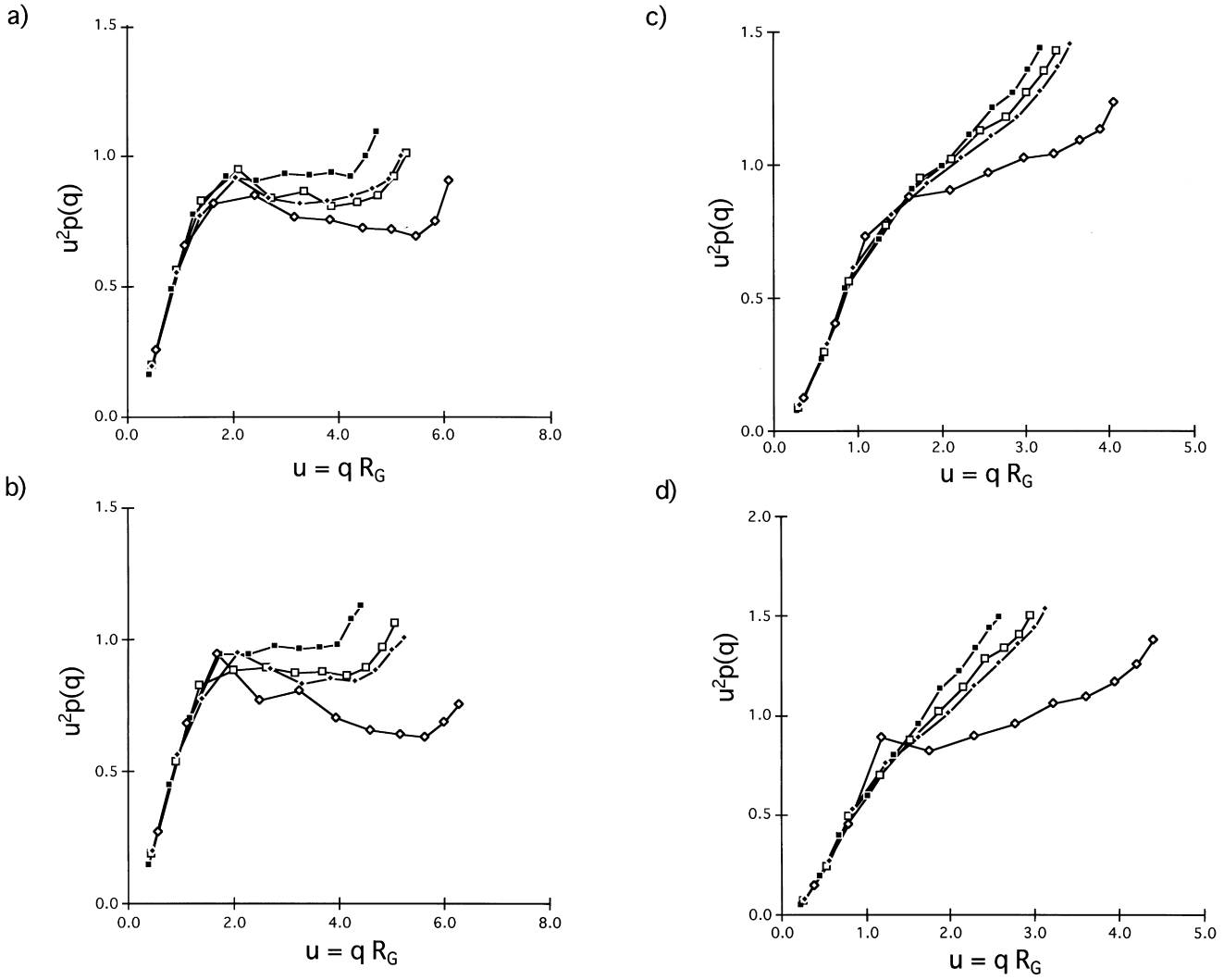

Fig. 4. Kratky plot of samples stored for different times. (a) Amylopectin, (b) normal corn starch, (c) Eurylon 5 starch, (d) Eurylon 7 starch. ◇, 0 h; ◆, 24 h; □, 48 h; ■ = 72 h.

3. Results and discussion

3.1. Static light scattering

Samples of amylopectin, normal starch (≈ 30% amylose), Eurylon 5 starch (≈ 50% amylose) and Eurylon 7 starch (≈ 70% amylose) were dissolved by microwave treatment and stored for different periods of time. Of these samples, the molar mass $\bar{M}_W$ and the radii of gyration $\bar{R}_G$ were measured by SLS and represented in a Berry plot (Fig. 1) rather than in the commonly applied Zimm plot (Aberle et al., 1994).

Measurements for the mentioned four materials to different storage times are shown in Table 1. The $\bar{M}_W$ was found to shift to lower values when the storage time increased. This behavior could be produced by depolymerization of starch components during storage, because in general, carbohydrate concentration (Table 1) did not change in all samples studied until 48 h of storage time. However, carbohydrate concentration of samples with high amylose level (Eurylon 5 and Eurylon 7) stored during 72 h decreased, this behaviour could be due to retrogradation. In this case, the low treatment time used for sample solubilization did not produce degradation as is shown elsewhere (Bello-Pérez et al., 1998) and with dilute solutions the retrogradation phenomenon is absent, except in samples with high amylose content stored during a long time. The $\bar{M}_W$ for the samples stored for 24 h decreased significantly in comparison with the samples immediately analyzed (e.g. normal corn at 0 h, 2.5×10^8 g mol^{-1} and 24 h, 1.1×10^8 g mol^{-1}); this behavior is due to the fact that a quickly depolymerization phenomenon is produced. The $\bar{M}_W$ for amylopectin samples stored during 24 and 48 h showed a slight difference, but the

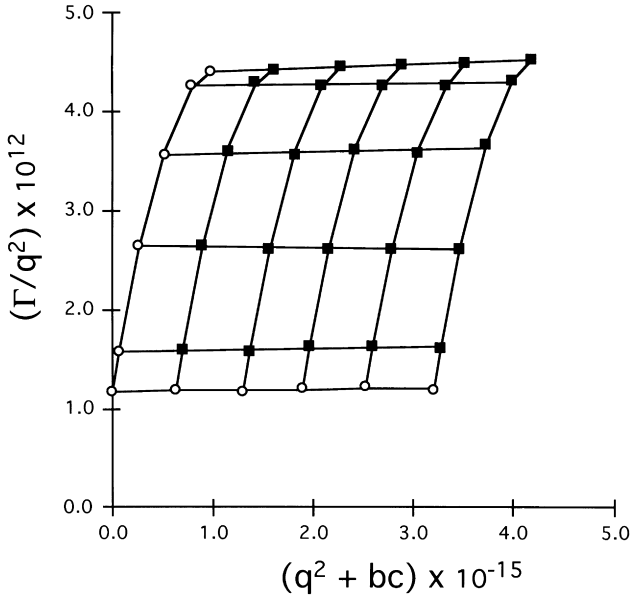

Fig. 5. Berry plot dynamic obtained for amylopectin in water at 25°C and stored for 48 h.

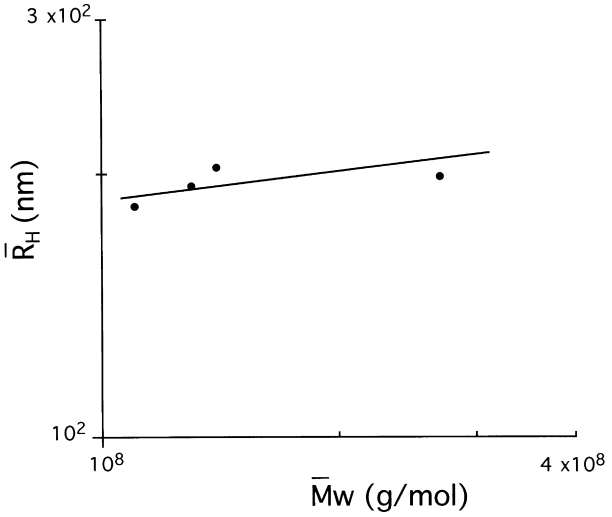

Fig. 6. Molecular weight dependence of the hydrodynamic radius of amylopectin samples stored for different times.

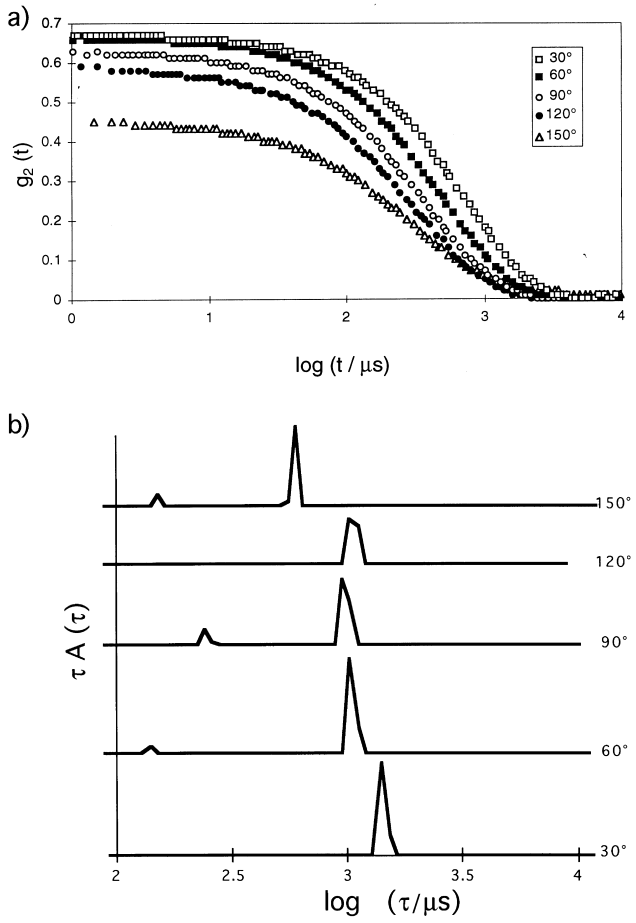

Fig. 7. Behavior of amylopectin sample at the highest concentration studied (0.37 mg ml^{-1}) and stored for 72 h. (a) Angular dependence of normalized time correlation function $g_2(t)$; (b) relaxation time distributions. ▲, 30°; ◇, 60°; ◆, 90°; □, 120°; ■, 150°.

$\bar{M}_W$ for normal corn, Eurylon 5 and Eurylon 7 starches stored at these times were identical. However, at 72 h of storage time the samples presented a diminished $\bar{M}_W$, but this diminishing is higher in the samples with high amylose level, retrogradation phenomenon play an important role in these samples. This behavior points out that amylose component plays an important role in the stability in solution of starch samples. The $\bar{R}_G$ values decreased when storage time increased (Table 1). These results indicate that the size of the molecules decreased due to the depolymerization of starch components.

Fig. 2 shows the $\bar{M}_W$ dependencies of $\bar{R}_G$ for an amylopectin sample. Within the limits of experimental error the $\bar{R}_G$–$\bar{M}_W$ relationship follows a common straight line in the double logarithmic plot and can be described by the power law behavior $\bar{R}_G = k\bar{M}^{\nu}$, as reported by Hanselmann et al. (1996). The curves of $\bar{R}_G$ for the different materials studied do not have the same slopes (ν_{RG} in Table 2); values between 0.23 and 0.45 were found. In general ν_{RG} values increased when amylose levels in the sample increased, except normal corn starch that presented a lower value than amylopectin. Additionally, the ν_{RG} values showed different global structures of the samples analyzed. The ν_{RG} values found for amylopectin and normal corn starch indicate high branched structures, and for Eurylon 5 and Eurylon 7 starches suggest more linear structures than the former samples. Values of 0.41 (waxy corn) and 0.42 (potato) of ν_{RG} were obtained by Hanselmann et al. (1996) using SdFFF. With the values of $\nu_{RG} = 0.41$ and 0.42, they rewrote the molar mass dependence of the radius of gyration as a power law of the molar mass (Hanselmann et al., 1996).

$$M = K' R_G^{1/\nu_{RG}} = K' R_G^{d_f} \quad (1)$$

They obtained $d_f = 2.44$ and 2.38, respectively, which are no longer integers but fractal dimensions. Such fractal dimensions are common for disordered objects and demonstrate self-similarity behavior. In this study, ν_{RG} values of 0.27 and 0.23 (Table 2), and d_f of 3.70 and 4.34, were found for amylopectin and normal corn starch, respectively. A fractal dimension higher than 3.0 would define a structure with a branching density higher than for a compact sphere. The formation of an aggregated structure such as microgel would better explain those values. For Eurylon 5 and Eurylon 7 starches with ν_{RG} of 0.36 and 0.45, a d_f of 2.77 and 2.22, respectively, is obtained which would define a structure between globular homogeneous ($d_f = 3.0$) and planar ($d_f = 2.0$). Galinsky and Burchard (1995), using SLS, reported ν_{RG} of 0.394 and d_f of 2.54 for the partially degraded potato starches.

In Fig. 3 the particle scattering factors ($p(q)$) from some samples studied at the different storage times are plotted against the dimensionless parameter $u(\equiv qR_G)$. Information about the structure of polymers can be obtained from $p(q)$, which describes the angular distribution of the scattered light. The asymptotic slope (the theory of fractals interprets this slope as being a fractal dimension) differs. These graphics showed dependence on the type of sample as well as on storage time. The d_f values for amylopectin and normal corn starch stored during 24 h were lower than those for the same sample immediately analyzed (0 h); but when the storage time increased (48 and 72 h) the d_f values increased. Eurylon 5 and Eurylon 7 starches showed a different behavior; the d_f values decreased with higher storage times. Additionally, in general, d_f decreased when amylose level increased. The d_f values, at all storage times, for amylopectin (between 1.88 and 2.20) and normal corn starch (between 1.90 and 2.28) are characteristic of a fully swollen randomly branched macromolecule in a thermodynamically good solvent ($d_f = 2.0$) (Hanselmann et al., 1996). We conclude that the amylopectin and normal corn starch dissolved at 35 s and immediately analyzed are swollen in water at 25°C, and the samples stored during 24, 48 and 72 h, can swell at a larger extent than those without storage (0 h). For Eurylon 5 and Eurylon 7 starches at all storage times, d_f was between 1.05 and 1.69 (Table 1). These values suggest an increase in linearity of the internal structure with the simultaneous depolymerization mentioned above as the storage time is increased. In this experiment d_f is found from the internal structure, in contrast to Eq. (1) which is related to the global structure (Hanselmann et al., 1996).

Additional information was obtained by applying a Kratky plot ($u^2p(q)$ vs. u). The four materials at the diverse storage times (Fig. 4) agree well at low $u = qR_G$ but differ in the asymptotic region. In this kind of diagram the asymptotic region at high u values is given increasing weight; therefore, even small changes in the particle scattering factor in this u domain can be detected and these are related to the internal structure (Burchard, 1983; Hanselmann et al., 1996). However, the value of u where the curves agree decreased when amylose level increased, which also suggests changes related to the internal structure.

Distinct differences are noticeable. For amylopectin (Fig. 4(a)) and normal corn starch (Fig. 4(b)) a plateau is reached for all storage times. The longer the storage time of these samples the stronger the function increased as u becomes larger; the increase is more evident in the sample with amylose (normal corn starch). This increase can be interpreted by a decrease in the branching density of the internal structure as the depolymerization progresses. That is corroborrated by HPSEC-MALLS results (Bello-Pérez et al., 1998) but it is strangely the inverse that Hanselmann et al. (1996) have observed.

For Eurylon 5 (Fig. 4(c)) and Eurylon 7 (Fig. 4(d)) starches a slight plateau is obtained only for samples immediately analyzed (0 h); when storage time increased a linear behavior was found, where the function ($u^2p(q)$) increased as u became larger. This linear behavior is reported for molecules with a rigid rod structure (Burchard, 1992).

4. Dynamic light scattering

The hydrodynamic radii values ($\bar{R}_H$) of the samples studied were obtained using dynamic Zimm plots (Fig. 5) and the corresponding values are shown in Table 1. In general, $\bar{R}_H$ values decreased when storage time increased, except for amylopectin and normal corn starch stored during 24 h where a slight increase was observed in comparison with the unstored samples (0 h). This diminution in $\bar{R}_H$ with higher storage time is due to sample depolymerization, as was observed with SLS. Eurylon 7 starch presented the highest $\bar{R}_H$ values; this behavior could be explained since higher amounts of linear chains generate experimental results that do not allow a good extrapolation of them.

In Table 2 ν_{RH} values (slope of the curve $\bar{M}_W$ vs. $\bar{R}_H$ (Fig. 6)) are shown; these ν_{RH} values increased when amylose level increased. However, amylopectin (0.09) and normal corn starch (0.10) showed very close values; a similar

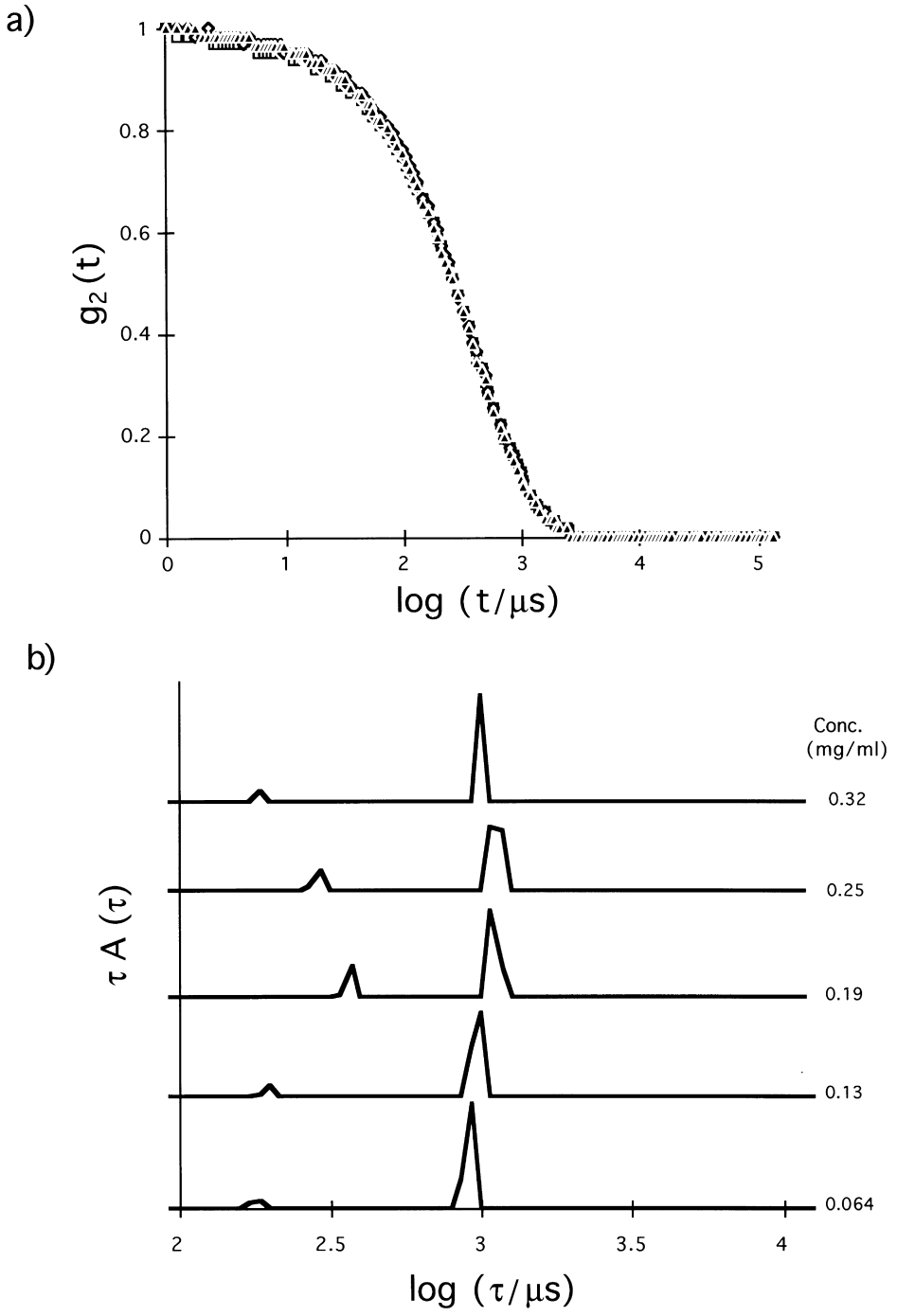

Fig. 8. Behavior of amylopectin sample stored for 48 h and measured at 90°. (a) Concentration dependence of normalized time correlation function $g_2(t)$; (b) relaxation time distributions. ▲, 0.32 mg ml^{-1}; ◇, 0.25 mg ml^{-1}; ◆, 0.19 mg ml^{-1}; □, 0.13 mg ml^{-1}; ■, 0.064 mg ml^{-1}.

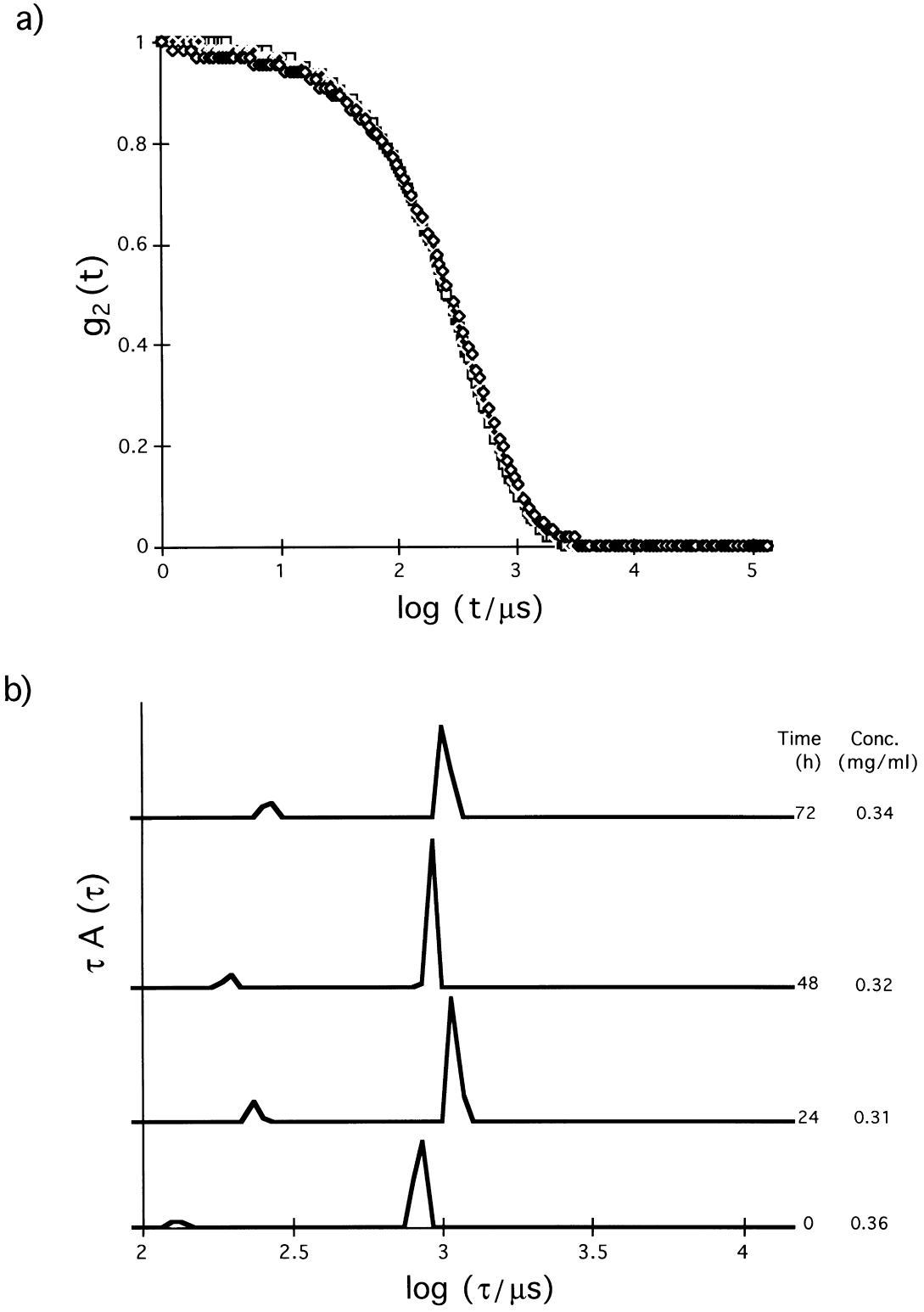

Fig. 9. Behavior of starches at the highest concentrations studied, stored for different times and measured at 90°. (a) Sample dependence of normalized time correlation function $g_2(t)$ for normal corn starch: ◇, 0.36 mg ml^{-1} and 0 h; ◆, 0.31 mg ml^{-1} and 24 h; □, 0.32 mg ml^{-1} and 48 h; ■, 0.34 mg ml^{-1} and 72 h; (b) relaxation time distributions for normal corn starch; (c) relaxation time distributions for Eurylon 5 starch; (d) relaxation time distributions for Eurylon 7 starch.

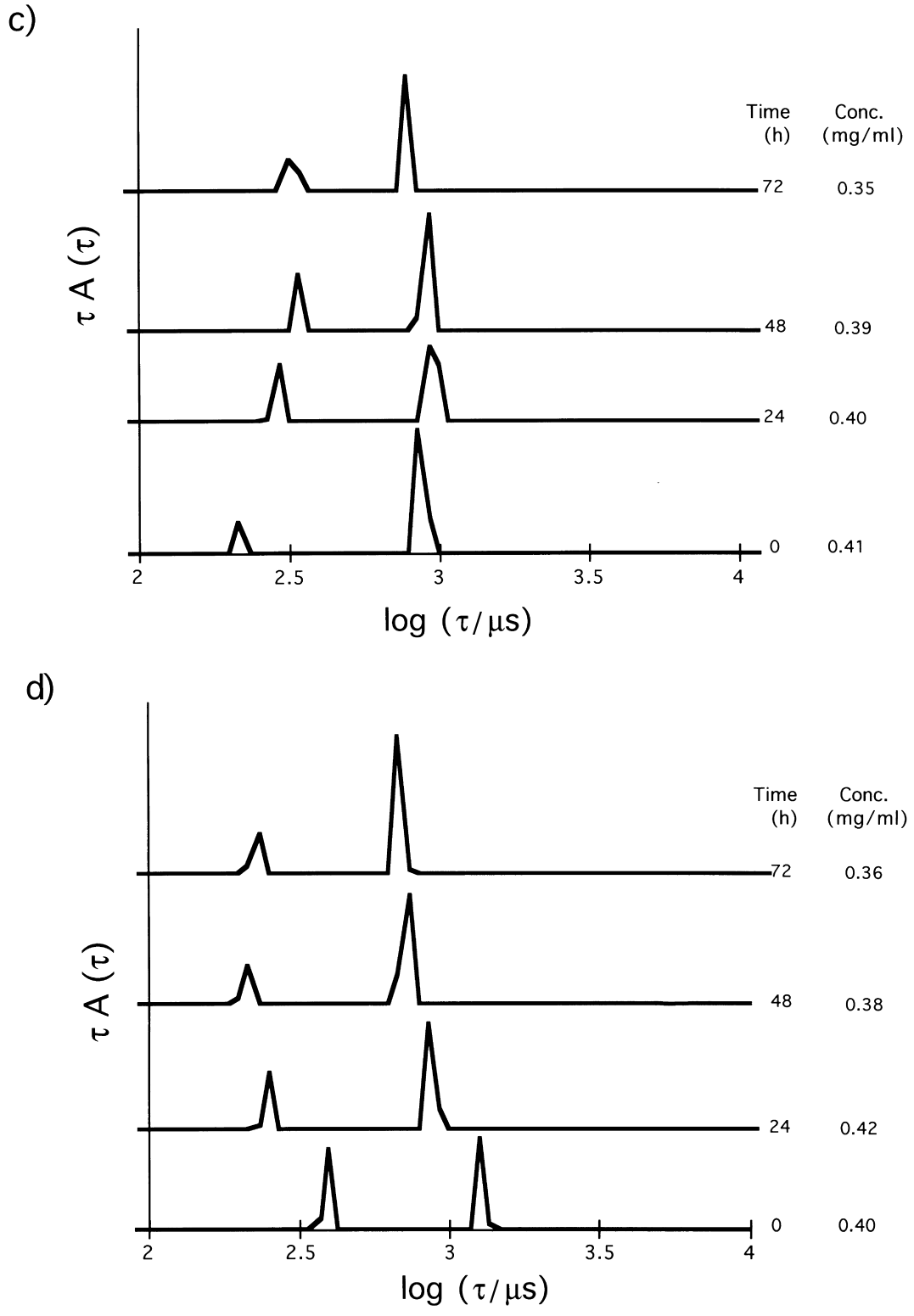

Fig. 9. Continued

behavior was found for Eurylon 5 (0.56) and Eurylon 7 (0.58) starches. ν_{RH} values for amylose in 0.1 M KCl (0.49) and amylose in 0.1 M KOH (0.57) were reported by Roger and Colonna (1992). There are different hydrodynamic behaviors depending on the solvent used. Values from the latter authors were close to theoretical values for linear chains (0.6 in good solvents and 0.5 in θ solvents). The ν_{RH} values found for Eurylon 5 (0.56) and Eurylon 7 (0.58) starches are close to the values reported for linear chains. To our knowledge only one ν_{RH} value of 0.48 has

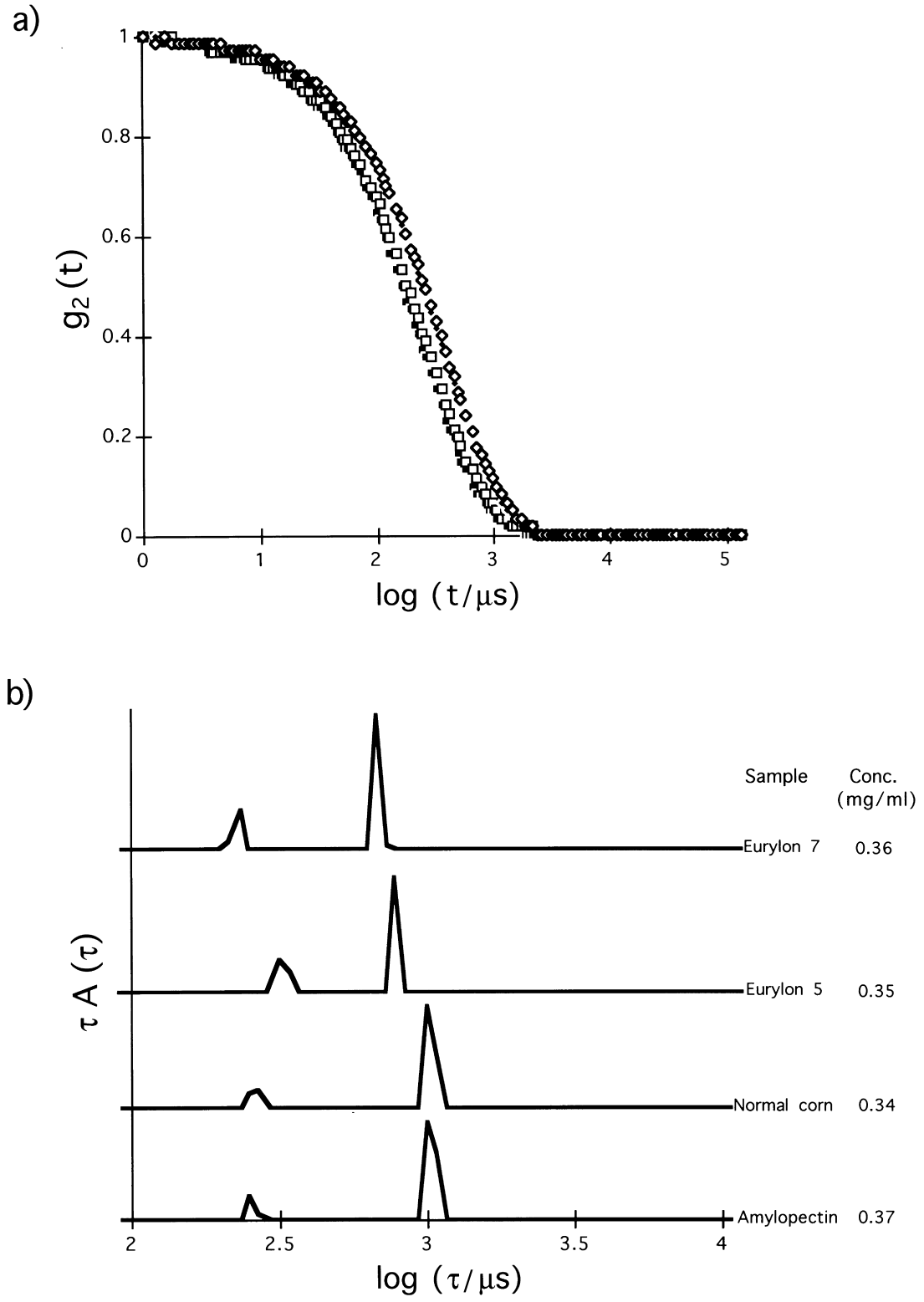

Fig. 10. Behavior of samples at the highest concentrations studied, stored for 72 h and measured at 90°C. (a) sample dependence of normalized time correlation function $g_2(t)$: ◇, amylopectin (0.37 mg ml^{-1}); ◆, normal corn starch (0.34 mg ml^{-1}); □, Eurylon 5 starch (0.35 mg ml^{-1}); ■, Eurylon 7 starch (0.36 mg ml^{-1}); (b) relaxation time distributions.

been reported up to now for such branched structures (Galinski and Burchard, 1995). It concerns normal potato starch fractions obtained by acid degradation. The ν_{RH} values determined for amylopectin and normal corn starch would define once again a very compact structure such as microgels.

Fig. 7(a) shows an example of the dependence angular $g_2(t)$ for amylopectin sample stored for 72 h and for the highest concentration studied (0.37 mg ml^{-1}). For all samples the relaxation times decreased with increasing scattering angle, following similar patterns as shown in Fig. 7(a). Fig. 7(b) depicts relaxation rate distributions at a series of angles for amylopectin. One principal population was observed with a slight change in the peak position when the angle increased. However, when the amount of amylose increased in the sample (results not shown) a bimodal distribution was observed.

The effect of concentration was analyzed for samples stored at different periods of time and measured at 90°. The intensity of time correlation function $g_2(t)$ for the different samples generally did not show changes at the different concentrations studied (Fig. 8(a)). For example, amylopectin (Fig. 8(b)) presents one population at approximately the same value of log τ. In the case of samples with higher amylose content (normal corn, Eurylon 5 and Eurylon 7 starches), a bimodal distribution was found, but also without differences in the peak positions when concentration decreased.

The intensity of time correlation function $g_2(t)$ for the samples studied (the highest concentration and 90°) did not present differences (Fig. 9(a)). The relaxation rate distribution of these samples (e.g. normal corn starch (Fig. 9(b))) shows that for samples with high amylopectin level (amylopectin and normal corn starch), the peak position of principal component slightly changed at higher log τ values and longer storage times. However, when amylose level in the sample increased (Eurylon 5 and Eurylon 7 (Fig. 9(c) and 9(d), respectively)), in general, the peak position of the principal component slightly changed at lower log τ values, this change being more notorious in the Eurylon 7 sample.

The different behavior found for the relaxation rate distribution of the samples studied show that there are changes in the internal structure when storage time increase; these changes depend on amylose and amylopectin level present in the sample.

When the different samples were compared at the same storage time (e.g. 72 h of storage time, the highest concentration and 90°) changes were found in the intensity of time correlation function $g_2(t)$ with respect to sample type. Amylopectin and normal corn starch presented similar and the highest intensities of time correlation function (Fig. 10(a)), Eurylon 5 starch showed a lower intensity of time correlation function than the former samples, and Eurylon 7 starch presented a slight difference with respect to Eurylon 5 in this correlation function. The behavior mentioned above between the samples can be seen in the distribution graph of Fig. 10(b). Amylopectin and normal corn starch did not show differences in the peak position of the principal component. However, when the amylose amount in the sample increased, the peak position of the principal component changed at lower log τ values, this change being higher in the Eurylon 7 sample. Again, these results show changes in the internal structure of the samples as a function of the amylose and amylopectin level.

The dimensionless ratio $\rho = (R_G/R_H)$ is a sensitive index of coil confirmation. The ρ values for the samples dissolved at different times are presented in Table 1. Amylopectin and normal corn starch gave ρ between 1.0 and 1.3 are characteristic of branched structures. It was also reported (Galinsky and Burchard, 1995) that for randomly branched systems the ρ parameter remains constant in the whole M_W region. Eurylon 5 showed ρ values slightly lower (between 0.94 and 0.98) than amylopectin and normal corn, but also these values can be considered for spheres or other globular structure. The ρ values for Eurylon 7 presented a different behavior; the ρ values increased when storage time increased, which shows a variation in the structure when the storage time increases. The ρ values for Eurylon 7 can be considered also for spheres or other globular structures.

In conclusion, the diminution in $\bar{M}_W$ and $\bar{R}_G$ values when storage time increased showed a depolymerization phenomenon in the samples. The fractal dimension obtained from $\bar{R}_G$–$\bar{M}_W$ relationship showed that amylopectin and normal corn starch presented a globular structure, with a high level of branching. Eurylon 5 and Euryon 7 starches also showed a globular homogeneous structure but with a lower amount of branching. Information about internal structure was obtained from the particle scattering factors and Kratky plots, which showed a depolymerization of the samples and variations in the internal structure when storage time increased.

The ν_{RH} values obtained from the $\bar{R}_H$–$\bar{M}_W$ relationship for Eurylon 5 and Eurylon 7 starches were close to the values reported for linear chains. For amylopectin and normal corn starch the ν_{RH} values were lower than those found for Eurylon samples; the former values would define a high branched structure.

The relaxation rate distribution of the samples showed that there are changes in the internal structure when storage time increased, these changes depending on the amylose and amylopectin level.

The ρ values for the samples analyzed were between 0.88 and 1.3; these values are characteristic to a sphere or globular structure. However, differences in the global structure when storage time increased were more notorious when the amylose level in the sample increased.

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